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The Drainage Exchange of Stormwater Potential in Flat Area Problems

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Abstract: Groundwater as an alternative source still does not contribute to the water supply in area of Parit Raja because of the limitation of water availability in the ground. This lacking of groundwater could be caused by the circumstance that the top layer of soil is dominated by compacted clay around 2 meters in which its permeability is small, so the water is difficult to infiltrate the ground. The recharge well technique was designed based on the flat area problems, layer of real condition, flow water table and low infiltration rate. Resistivity soundings were made at existing wells to assess the subsurface layers. Beside that, the past records on floods event, sub surface and surface studies were collected around study area as a preliminary studies. It was presented that the study area promised good prospects to increase the capability of groundwater and contribute to the drainage system by reducing the volume of rainfall runoff using the recharge well technique.

Key words: Groundwater, recharge well, water supply, drainage system.

1. Introduction

As we know that south Malaysia of Peninsular has been nature filled by peat soil and deep of clay layers. Low flows are often important ecologically. Some time, low flow movement to the rivers uncontrolled when the wet season out come. Then, flooding always occurred during rainy season caused by flat area and lacking of proper drainage system.

Recently, the development of Districts of Batu Pahat

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has caused the increasing number of inhabitant. More even in area of Parit Raja, the growing of population more than other areas since UTHM (Universiti Tun Hussein Onn Malaysia) is developed, which has been established as a big university. With the increase of buildings and pavement, the green area smaller causes too much stress on the remaining drainage area, which can cause several flooding in rural or urban especially Parit Raja area [1]. Besides, the drainage system in UTHM also had faced some terrible condition where in the end of year 2006, the flood happened and it caused partially sunk of UTHM old campus. This condition happened because of the poor drainage system around the campus. Thus, this research is then carried out to find out the best way to overcome that poor drainage system where the drilled well that is used to generate the source of water can be a part of drainage system during wet season to mitigate the flood.

This study examines the potential of artificial recharge, the water supplied to a surface infiltration or injection well recharge system. It is evaluated that the quantity of municipal storm-water runoff by the supporting drainage system may be suitable for ground water recharge, its potential use would be extremely site specific and a general evaluation is not useful. The well recharging process will be helpful in improving the groundwater quality because the groundwater that is observed contains a lot of iron [2]. The quality of groundwater can be diluted by the rainwater that can be recharged into the well. Thus, the rainwater itself is beneficial for the groundwater improvement. Wherefore, the potential source waters of impaired quality for artificial recharge consider treated storm-water runoff and potable water return flows.

2. Preliminary Studies

2.1 Top Soil Surface

A study on infiltration and particle size distribution has been done in the most area of UTHM campus. It was found that the rate of infiltration is in the range of 0.004-0.007 mm/s and the soil classification based on particle size is between silt to fine sand (Fig. 1). That mean, the top soil surface had low infiltration rate and high moisture content caused by the types of soil.

At the land occupied by clay soil at the top layers commonly has confined aquifer layer that can be used as groundwater recharge well. And hence, by providing a recharge well it is possible that the surface water runoff can be released by directing into the ground (confined aquifer) through recharge well.

2.2 Floods

Report from Department of Irrigation and Drainage, Malaysia was presented [3], at December 19, 2006 and January 12, 2007, Batu Pahat District was hit by a huge flood (Fig 2). More than 70% of the areas were flooded and it causes damage to property, business, or road. The flood caused by: (1) The rainfall intensity was too high, where 170 and 247 mm/day we recorded

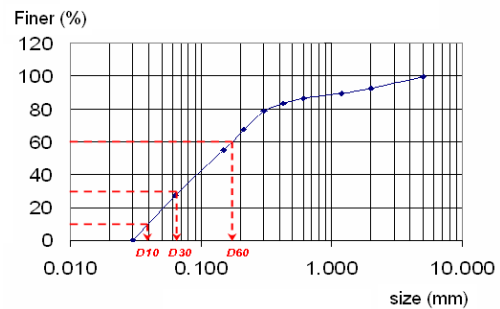


Fig. 1 Grain size distribution on related location.



Fig. 2 Flood problems in Batu Pahat district.

at Bekok Dam and 181 and 229 mm/day recorded at Sembrong Dam; (2) The capacity of the available reservoirs is insufficient to store rain runoff, where the occurred water levels were above the critical levels, 20.31 m over 17.5 m in Bekok Dam and 13.66 m over 12.0 m in Sembrong Dam; (3) The cross section of river is insufficient to flow the peak flow rate; (4) Most of areas of Batu Pahat are low infiltration rate and flat area (around 0.5 to 2 m above mean sea level) that causes the river is not capable to discharge storm water direct to the sea.

Hence, it is required to study on groundwater as an alternative source for water supply and to enhance the drainage system of flat area by using sub surface land as water storage [4]. This method will be designed based on the flat area problems such as soil type, layer of bedrock, flow water table in flat area, and low infiltration rate.

2.3 Subsurface Conditions

The research area in Fig. 3 selected by flooding problems and existing wells was shown by resistivity survey nearby RECESS (Research Centre of Soft Soil Malaysia), UTHM. The pseudo section of line survey was illustrated in Fig. 4 through the wells exist.

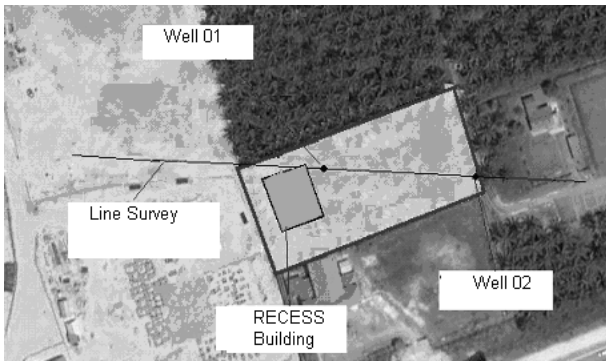


Fig. 3 The existing wells in RECESS area.

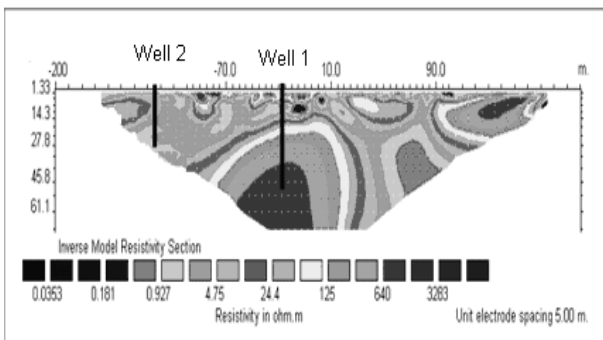


Fig. 4 Sub surface image through the wells.

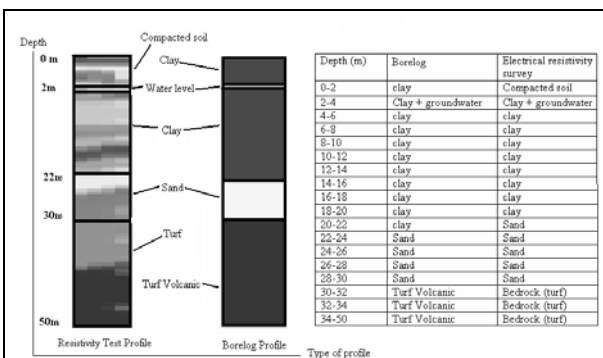


Fig. 5 Comparison of subsurface profile between borelog and resistivity result on Well 1.

The interpreted geological section on the basis of geo electrical resistivity survey is shown in Fig. 5 with two existing wells. This survey was tested at RECESS by using *Wenner_L* and *Wenner_S* Protocols. It was interpreted to 61.1 m deep with maximum length of survey tools. This method was conducted [5] and used in the resistivity soundings made at existing boreholes, both high and low yielding, to calibrate responses with geology. Application method had good records, it was concluded that this approach of looking for horizontal features was correct, because such features associated

with good borehole yields existed in the area.

The reliable and usable method was compared [6, 7] between borelog and resistivity image approximately. The Well 1 profile in Fig. 5 was being consistency almost 95% of strata profiles. The interpretation clearly shows that area contains the thickness of clay, sand and turf whichever water level around 2 m above mean sea level. Based on borelog profile, the top layer which contains clay and silty clay soil wherefore resistivity records is considered as a compacted soil cause the image of this layer mixed colours with others. The ground water saturated with maximum level around 2 m and had a little bit of salt water intrusion existed caused by the location of Pantai Rengit only 20 km nearly. Considering the yellow to brown colours as a sandy layer, a thickness of aquifer [6] approximately 10 m depth on that area was proved. The potential at another point to survey around it commonly does not dismay to carry out some of planning ground project effectively. This result is believable to find the reliable layer at real site condition without traditional and costly methods used.

It was assessed that top layer of clay was present, which varied in thickness from 1 m to 30 m, approximately. The layer of Tuff covered up to 30 m of the sub surface to hardrock of the layers. At all other locations, medium sand to coarse sand was present beneath the fine sand layer, which promised good prospects for the groundwater recharge [8]. Although, the deeper possible profile can be achieved by this method because the maximum length of cables was used until 400 m. The limitation of this survey should be provided another method by drilling as possible deep to find out the real profile and solve any water problems.

Based on Well 1 (Fig. 6), the drilling works by Maju Teknik Kota indicates (Well 1) at 1st crack zone in Tuff occur at the depth of 44 m to 46 m deep, spit well water approximately 0.91 m³/hr (200 gallons/hr). Similar recovery investigation work and test well records [9] at RISDA nursery, Kampung Panchor (MR



Fig. 6 Single well.

123/WL 568045) with diameter 203 mm and well depth 20 m found that the granite was friable and broken into fragments, the interstices between which could store groundwater. Other potential were considered in this area also in fractured rocks, which is water only moves through the fractures, even if the fractured matrix blocks are porous. It mean that the effective porosity of the rock mass is linked to the volume of these fractures.

According to records which were presented in Ref. [4], the real condition of deep soil is karsts, which is more potential as groundwater resources than granite and seal rocks in which the hydraulic conductivity is about $1 \times 10^{-1} - 1 \times 10^{-5}$ m/s. The presence of Karstification is important in areas of regionally important aquifers. It can indicate short groundwater travel time (high velocities), variability in well yields and vulnerability to pollution. For confined bedrock (usually sandstone) aquifers, the depth at which the top of aquifer is 150 m b.g.l, if possible, as this is the general practical limit for groundwater development [10]. Studies in Ref. [11] was found that capability of storativity of aquifer increase parallel to depth of well. Almost of the wells was drilled 100 m and above had a good capacity. Normally, drilling work should be deeper which is possible to get more capacity of the storativity of layers.

2.4 Water Level

A prior record for on existing well and borehole indicates that the water level available around 1-2 meters under mean sea level. It means that the layer under the ground had high water table. Based on

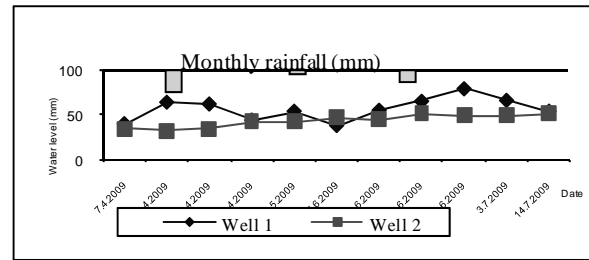


Fig. 7 Water level records.

the observation on water level (Fig. 7), the fluctuation on well 1 showed that the precipitation affects the water level in the well. But, the record from well 2 does not show a similar response in well 1. This situation indicates that relationship between these 2 well in the sub surface condition is not same in continuously layer. The different layer also affects the storage and capacity of the well. The weaknesses well in RECESS area are located in unsuitable point to find the good capacity storage. That mean is, the suitable point to identify the best mechanisms interaction of surface water and ground water was determined correctly.

2.5 Test Well

Before testing the wells for yield, the static water level was determined (Fig. 7). After initial water level of the wells had been determined, the wells were tested for yield by pumping at the maximum rate until the water level in the well stabilized. The depth of the water level was then noted. The difference is that the depth is the drawdown, and the discharge drawdown is an estimate of the specific capacity of the well [12]. The discharge of the well when the water level of water had been stabilized was measured. The yield capacity (m^3/day) of the well was determined by measuring the volume of water collected by the calibrated bucket per unit time. The equation is:

$$\text{Yield capacity} = \frac{\text{Discharge} \times 1000}{60 \times 60 \times 24} \quad (1)$$

Identification of aquifer parameters plays an important role in assessing and managing the groundwater resources. The constant flux pumping test is commonly applied to identify the aquifer parameters

from the measured drawdown data [13]. Analyses of the drawdown and recovery data Well 1 in Figs. 8 and 9 respectively indicated that water bearing layer has yield of $144.029 \text{ m}^3/\text{day}$ with coefficient of trasmissivity and storativity is $1.076 \text{ m}^2/\text{day}$ and 0.189 respectively. These records commonly tested to identify by estimating possible recharge and analyzing the real condition response to pumping. According this well test, half of pumping yield was loss by recovery in range 25-26 m in 50 minutes. This constructed well is not proper in determining the porous layer and have

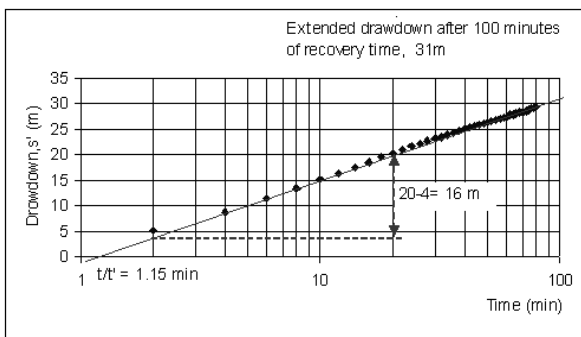


Fig. 8 Drawdown of pumping test.

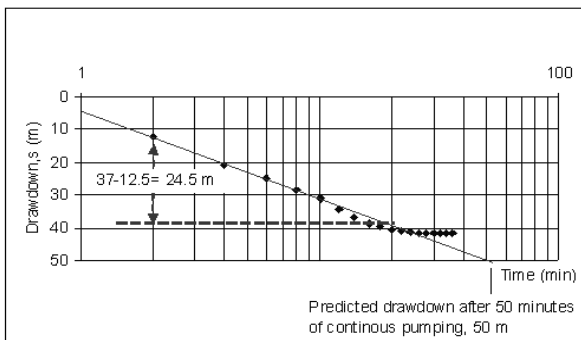


Fig. 9 Recovery test on single well.

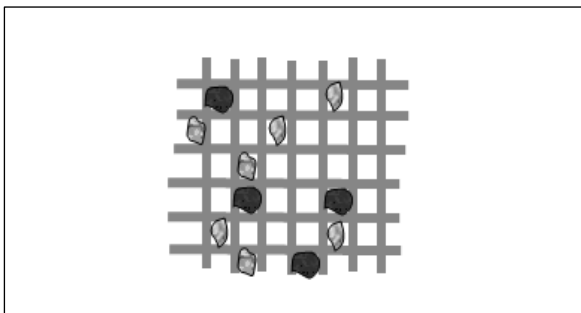


Fig. 10 Sand grains make opening screen blocked during pumping and recovery time.

small yield capacity and low static water levels. This may be due to the fact that the study area is occupied by varying clayey and sandy contents. It also depends on limitation and capability of water movements in the ground to recharge and discharge parts. Therefore, the ability to store the water at this point still lack and needs future studies on other points and area.

Some time, the shape of the louver openings is such that the shutter screen cannot be performed successfully used for naturally wells. The opening becomes blocked during the running procedure where the aquifer material contains any appreciable proportion of sand and fractures rock as shown in Fig. 10.

2.6 Sri Gading Records

An appraisal of geological logs from the exploratory drilling indicates that the subsurface is predominantly clayey in nature. The occurrences of sandy layers which are water bearing are rather limited both vertically and laterally. Some of the boreholes drilled penetrated an entirely clayey sequence [9]. This present investigation is aimed at studying the sub surface lithological and hydrogeological conditions in the area and to determine whether any useful amount of groundwater can be obtained for domestic and/or industrial/agriculture usage.

Generally, there is a top layer of brown, peaty clay which covers most of the area. Below the top covering is a layer of grey clay, which is frequently mottled and locally contains a lateritic hard pan. Greenish, shell bearing clay, probably of marine origin, is also extensive, particularly near the coast. The clay layers just above the bedrock are usually sandy in nature. Sand is limited in extent both vertically and laterally and often admixed with a little clay. In Sembrong area, sand occurs probably as a isolated lenses within the extensive clay layers and is there of limited capacity as aquifers. Also, elsewhere in the investigation area had sand layers only a few meters thick which do not appear to have extensive lateral continuity. This condition effects to this research needs to continue with

the proper investigation and perhaps that it can be refreshing some of suitable solution on these area problems.

Report on Soil Investigation for New Campus at UTHM-Phase I (January 2003) presented in Ref. [14] also found the same result with average 20 m depth of clay and silt. Only 2 point of bore hole shows a little bit of sandy layer at BH3 and BH10 (Table 1). The totals of 48 undisturbed soil samples were obtained from very soft clayey layer in BH-1, BH-3, BH-4, BH-5, BH-7, BH-8 and BH-9. Nevertheless, this study will be produced deeper recharge well more than 100 m deep and target to be found a good solution in this problems.

Therefore, meteorological and geo-hydrological/geophysical information about the recharge area, existing water table and its fluctuations, water demands, availability of run off water and socio economic condition are fundamental inputs for undertaking recharge projects [15]. This identification of recharge and discharge area is important for land use planning purposes.

Table 1 Types of soil for boreholes in new campus.

BH	BH depth	Clay	Silt	Sand
1	36.3	0-27	27-36.30	-
2	31.93	0-23	23-31.93	-
3	39.15	1.10-25	0-1.10, 28.2-39.15	25-28.2
4	34.8	0-23.6	23.6-34.8	-
5	34.62	0-22	22-34.62	-
6	34.62	0.8-24.8	0-0.8, 24.8-34.62	-
7	31.87	0-24.4	24.3 - 31.87	-
8	28.65	0-21.8	21.8- 28.65	-
9	37.77	0-23.2	23.2-37.7	-
10	45.3	0.8-11.2, 13-19	0-0.8 , 19-45.3	11.2 - 13

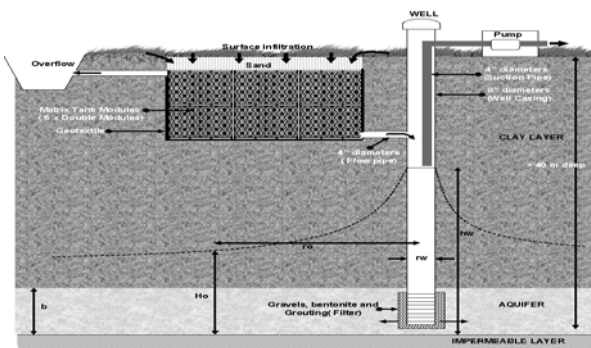


Fig. 11 Illustration of physical model.

3. Design of Concepts

The artificial recharge to groundwater aims at augmentation of its capacity by modifying the natural movement of surface water utilizing appropriate engineering structures. Artificial recharge techniques normally address to the following issues [15]: (a) Enhance the sustainable yield in areas where over development has depleted the aquifer. (b) Conservation and storage of excess surface water for future requirements, since these requirements often change within a season or a period and (c) Improve the quality of existing groundwater through dilution.

Artificial recharge well is a simple concept in which water is stored in subsurface permeable aquifers when water is plentiful and extracted during times of peak (Fig. 11). The recovery of confined aquifer is useful to us to modify the hydrology cycle in term as drain system solution. The basic equation for recharge well is:

$$Q = \frac{Kb(h_w - H_0)}{0.366 \log(r_0/r_w)} \quad (2)$$

Where,

Q = rate of injection (m^3/day);

K = hydraulic conductivity (m/day);

b = aquifer thickness (m);

h_w = head above the bottom of aquifer while recharging (m);

H_0 = ead above the bottom of aquifer;

when no pumping is taking place (m);

r_0 = radius of influence (m);

r_w = radius of injection well (m).

4. Discussion

Artificial groundwater recharge is possible in the depleting water table areas of Parit Raja plains using recharge tube wells. Estimation of availability of rechargeable water is very important before planning any groundwater recharge project [8]. The geo-electrical resistivity survey may be effectively used to search suitable sites for recharge.

However, resistivity tests were conducted at some locations in the study area using ABEM SAS 4000. One

of the resistivity test which was done through the existing wells showed that the almost 95% of comparison result with borelogs interpretation was accurate and usable [6]. The borelog records show that the layer of aquifer found at 30-40 m depth and some layer at 44- 46 m depth at the bedrock as fracture rock. Therefore, one area was decided as a potential area to build the recharge well model whether it aquifer or fracture rock thickness. The development of considerable amounts of groundwater through high capacity wells is possible.

Provision of silt basin and suitable filter can ensure long life for recharge tube well [8]. This study applied the bio ecology concept (MASMA-Urban Stormwater Management Manual for Malaysia) [16] as a surface infiltration filter by controlling the quality and quantity of recharge water. It also can be protected any debris from breaking a quiet of recharge system. The filter designed based on the area of catchments, level, amount and flow of runoff and ground water table records. With the capsule concept, the water will be collected through the capsule before passing away to the well. All water quantity and quality should be considered in evaluating the filter assessment.

The drainage system is affected by several small south flowing rivers. Due to the generally flat terrain, the flow in the rivers is usually sluggish, and even during rainy season is often inundated. Hence, it is required to enhance the availability of groundwater by recharging waste water into the ground using recharge well, especially in the area of UTHM with hope the result is significant. It can be implemented in the similar areas around Batu Pahat district. And, it is also expected that by using artificial recharge, the volume of water in the pond is reduced, so the pond is able to anticipate the storm water. This groundwater studies as an alternative source for water supply and to enhance the drainage system of flat area by using sub surface land as water storage.

5. Conclusion

According to the overview studies respectively, the potential area as adequate aquifer storage should be found by drilling as deep as possible in layers. Standard exploration techniques can be used to identify channel aquifers and resistivity methods proved useful to locate successful sites. By discharging filtered surface water into the ground could increase the potential of groundwater and also would reduce the volume of water in the channel and pond, then the groundwater will be able to contribute the water supply and the drainage system will be able to anticipate stormwater. At the vertical drainage in REWES applications able balancing the hydrologic cycle and control the environmental aspects via recharging and discharging useful water by rotating in the ground naturally.

References

- [1] W. Zhou, Drainage and flood in karts terranes, *Environ. Geology* 51 (2007) 963-973.
- [2] M.F. Mohd Yusof, D. Tjahjanto, Study on the quality of groundwater recharge well as alternative sources for water supply in the field Laboratory in RECESS, F.Y.P. Thesis, UTHM, 2009.
- [3] D. Tjahjanto, S. Musa, M.B. Ridzuan, A study on artificial recharge well as a part of drainage system and water supply in UTHM, in: *Proceeding of National Seminar on Sustainable Development: Ecological, Economical & Social Aspect*, 2007, pp. 106-111.
- [4] D. Tjahjanto, M.F. Tajul Baharuddin, N. I. Ahamt Nor, A.A. Abdul Latiff, A. Madun, Water availability and stormwater control using artificial recharge on groundwater, in: *Proceeding National Conferences on Water for Sustainable Towrds*, 2006, p. 5.
- [5] D.K. Buckley, P. Zeil, The character of fractured rock aquifer in Eastern Botswana: challenges in Africa hydrology and water resources, in: *Proceeding of the Harare Symposium IAHS Publ.*, 1984, p. 144.
- [6] A.N. Ibrahim, Z.Z.T. Harith, M.N.M. Nawawi, Resistivity imaging and borehole investigation of the Banting area aquifer, Selangor, Malaysia, *Environmental Hydrology* 11 (2003) 7.
- [7] M.A. Sacdan, S. Musa, M.H. Zainal Abidin, Geophysical method at research centre of soft soil Malaysia (RECESS), F.Y.P. Thesis, UTHM, 2008.
- [8] M.J. Kaledhonkar, O.P. Sing, S.K. Ambast, N.K. Tyagi, K. C. Tyagi, Artificial groundwater recharge through

- recharge tube wells: a case study, *Agricultural and Groundwater* 84 (2003) 28-32.
- [9] Loganathan, A.N. Kiat, Z.A. Sulaiman, Groundwater resources study of the Sri Gading Area, Johor and Rembau- Tampin area, Negeri Sembilan, Fourth Malaysia Plan Project (1981-1985), Geology Survey Department, Ministry of Primary Industries, 1987.
- [10] D. Daly, The GIS groundwater newsletter, *Geological Survey, Ireland*, 25 (1994).
- [11] M.F. Al Ajlouni, R. Abd. Rahman, A.G. Rafek, M. Mokhtar, N.E. Ahamad Basril, Aquifer storage in UKM Bangi campus as sub Langat river basin, *Water Resources Management, International Journal of Soft Computing Applications* 1 (2007) 55-61.
- [12] J.A. Osunbitan, D.A. Okunade, H.O. Fapohunda, Evaluating the quantity and quality of groundwater for irrigation in the basement complex of Il-Ife, Nigeria, *Environmental Hydrology* 13 (2005) 8.
- [13] H.D. Yeh, S.Y. Yang, H.Y. Peng, Aquifer parameter estimation for a constant-flux test performed in a radial two-zone aquifer, *Adv. Water Resources* 26 (2003) 747-757.
- [14] Maju Teknik Kota, The construction works of tube well in UTHM, Technical Report, 2007.
- [15] S.K. Kamra, Enhancing groundwater recharge in North-West Indo-Gangeric plains, in: *Proceedings of the Groundwater Used in North-West India*, 2004, p. 202.
- [16] Department of Irrigation and Drainage Malaysia, *Urban Stormwater Management Manual for Malaysia*, Perbadanan Nasional Malaysia Press, vol. 4,5,9, Malaysia, 2000.

Removal of Cu^{2+} Ions from Aqueous Solutions by Adsorption on Libyan Soil

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Abstract: Heavy metals are well recognized as potential health hazards as they can neither be degraded nor biologically detoxified. This experimental study aims to investigate the possible use of Libyan local soil, Ashkida soil, mined in the Southern Province of Libya as a low cost adsorbent to remove copper ions from aqueous solutions. In this work, the effects of various parameters such as adsorbent dosage, initial concentration of copper, agitation rate, contact time and solution pH level on the adsorption efficiency are investigated through batch experiments at room temperature. The results indicate that the optimum conditions for copper removal from aqueous solutions are 60 minutes contact time, 10 g/L adsorbent dose and 500 rpm agitation rate at natural pH value. The results are fitted to Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms. A satisfactory agreement between the experimental data and the model-predicted values is expressed by the correlation coefficient, r^2 , and the total mean error, E%. Freundlich model offers the best representation of adsorption process revealing a monolayer adsorption capacity, q_{max} , of 27.03 mg/g. A comparison of kinetic models applied to the adsorption of copper ions on the adsorbent is evaluated by simple first order, pseudo first order and pseudo second order kinetic models. Kinetic parameters, rate constant, equilibrium sorption capacities and related correlation coefficients for each kinetic model are determined revealing that the pseudo second order kinetic model is in a better correlation with the experimental data in comparison with the other isotherms.

Key words: Copper, adsorption, Libyan soil, isotherms, kinetics.

1. Introduction

Copper is an important toxic material, as it does not undergo biodegradation. It is introduced into natural waters by a variety of industrial wastewaters including those discharged from textile, leather tanning, electroplating, and metal finishing industries. It is accumulation in human body at high levels can cause serious health problems and it can ultimately become lethal.

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A number of techniques for treating contaminated effluents have been developed over the years. The most important of these techniques include chemical precipitation, filtration, ion exchange, reverse osmosis and membrane systems. However, all these techniques have their inherent advantages and limitations in application. In recent years, adsorption has proven to be an effective method to remove dissolved metal ions from liquid wastes. Removal of heavy metals from industrial wastes using several adsorbents is an increasing interest in the scientific community. However, in order to minimize processing costs, several recent investigations have focused on the use of low cost adsorbents such as dolomite [1], olive stones [2], by-product lignin [3], sugar beet pulp [4], coconut pollens [5], Jordanian pottery [6], limestone [7], natural iron oxide-coated sand [8], olive cake [9], cement kiln

dust [10, 11], clay materials [12-19]. Adsorbents, mainly clay minerals, are readily available and offer cost effective alternatives to conventional treatment of wastewater. Activated carbon is regarded as the most effective heavy metals adsorbent. Due to its high cost, low cost alternative adsorbents have attracted the attention of several investigators. As an abundant and low cost material, a Libyan soil is put to test as an adsorbent of copper.

The objective of this work is to investigate the removal of copper ions from aqueous solutions using Ashkida Soil from Southern Libya. The effects of various parameters affecting adsorption are investigated and data are tested against a number of adsorption isotherms. Kinetic experiments at different copper concentrations at different temperatures are also performed. The activation energy involved in the adsorption process is determined from the best kinetic model constants.

2. Materials and Methods

2.1 Adsorbent (Ashkida Soil)

Ashkida soil is brown in color and obtained from Ashkida region which is located in Wadi Alshati in southwest Libya approximately at 27°33'16"N and

Table 1 Results of the chemical composition of Ashkida soil*.

Compound	Wt%	Std. Err.
Fe ₂ O ₃	68.69	0.23
SiO ₂	8.56	0.14
Al ₂ O ₃	6.79	0.13
CaO	5.97	0.12
P ₂ O ₅	2.27	0.07
SO ₃	0.901	0.045
MgO	0.481	0.024
MnO	0.34	0.017
TiO ₂	0.305	0.015
Na ₂ O	0.177	0.011
K ₂ O	0.151	0.008
SrO	0.109	0.005
V ₂ O ₅	0.0915	0.0046
LOI	5	--

* Average values of four different samples.

14°26'40"E. The adsorption process is performed using soil samples of particle sizes ≤ 300 μm. The composition of the Ashkida soil used in this investigation is measured by X-ray fluorescence (Table 1).

2.2 Chemicals and Metal Concentrations Analysis

A 10,000 mg/L standard stock solution is prepared by dissolving the required amount of Cu(NO₃)₂ into 1 L of deionized water. A flame atomic absorption spectrometer (Varian SpectrAA-50) is used to determine the concentrations of Cu(II) in the solutions using air/acetylene flame at an analytical wavelength of 249.2 nm. The analysis of each sample is automatically carried out in triplicate and the mean is computed.

2.3 Optimum Conditions

The optimum time is obtained by adding 0.5 g of adsorbent to 100 mL of aqueous solution with 500 ppm of Cu(II) in 250 mL plastic bottles and shaken for 0 min, 5 min, 10 min, 30 min, 1 hr, 2 hr, 3 hr, 6 hr and 24 hr at room temperature using an agitation speed of 200 rpm. All samples are filtered by glass wool, and the filtrate is collected to determine the Cu(II) concentration.

Adsorption experiments are conducted under a constant initial Cu(II) concentration of 500 mg/L. The solution pH is varied within 2-11 levels by adding of 0.1 N hydrochloric acid or 0.1 N sodium hydroxide solution. The duration of adsorption is 1 hr and the agitation rate is kept constant at 200 rpm. The pH measurements are achieved by pH meter (Model: HI 8417, HANNA Instrument). In order to assess the effect of agitation on metal removal efficiency, experiments are conducted under various agitation rates, 0, 50, 100, 200, 500, 1000, 1500 and 2000 rpm, at 25 °C, for 1 hr using an adsorption dose of 0.5 g/100 mL, an initial Cu(II) concentration of 500 mg/L and solution pH=7.

The adsorbent doses effect on removal of Cu(II) ions is investigated under constant conditions (25 °C, 1 h equilibrium time, 200 rpm agitation rate, pH 7 and initial concentration 500 mg/L) with adsorbent doses of

0.1, 0.3, 0.5, 0.8, 1.0, 1.5 and 2 g for 100 mL aqueous solutions.

2.4 Adsorption Isotherms

A comparison of the adsorption models Freundlich, Langmuir, Temkin and Dubinin-Radushkevich to find the most representative one is based on the batch adsorption results. The batch adsorption experiments are carried out by using 0.5 g doses of adsorbent added to 100 mL of Cu(II) solutions in 250 mL plastic bottles. Aqueous solutions are prepared such that their initial concentrations are within 50-1000 mg/L of Cu(II), agitated at 200 rpm, 25 °C and pH 7 for an optimum time duration of 1 hr.

2.5 Adsorption Kinetics

In order to examine the controlling mechanism of adsorption process such as mass transfer and the chemical reaction, the experimental data are assessed by simple first order, pseudo first order and pseudo second order kinetic models.

2.6 Statistical Analysis

The data are analyzed with a parametric two-way analysis of variance (*ANOVA*) to test the significant differences between treatments ($p = 0.05$). The goodness of fit between the experimental data and predicted values is expressed by the correlation coefficient r^2 (values close or equal 1). Just because r^2 is close to 1, this does not mean that the fit is necessarily good [20]. Therefore, the conformity between the experimental data and the model predicted values is expressed by the total mean error (E%), Eq. (1) [21, 22].

$$E\% = \frac{\sum_{i=1}^n |q_{e(Eper.)} - q_{e(Calc.)}|}{\sum_{i=1}^n q_{e(Eper.)}} \quad (1)$$

3. Results and Discussion

3.1 Optimum Conditions

The adsorption process is relatively fast, whereas the percentage of Cu(II) removal reaches equilibrium in 60 min of contact time. The Cu(II) removal efficiency at 60 min is 79.2%. It is evident that there is no benefit further agitation beyond 60 min (statistically no significant difference between data from 1 to 24 hr). Therefore, an equilibrium time of 60 min can be regarded as an optimum contact time. Reaching equilibrium in a short time duration is an indication that the adsorption sites are well exposed, and bonding of the Cu(II) ions to active sites occurs preferably on the solid surface, with no significant ion diffusion towards the inside of the particle [2, 4].

The removal percentage increases as the pH level increases. The sorption of Cu(II) ions is primarily affected by the surface charge on the adsorbents, which in turn is influenced by the pH of the solution. The low metal adsorption at low pH can be explained by the competitive sorption between proton and Cu(II) ions. As the solution pH increases, the number of negatively charged sites increases, which result in further sorption of Cu(II) ions. The change in H⁺ and OH⁻ ions in the solution cause the surface functional groups on adsorbent minerals to protonate or deprotonate by adsorption of H⁺ or OH⁻ ions. Above the pH value of 6.0, metal ions can be precipitated with OH⁻ ions, and precipitation plays an important role in controlling Cu(II) concentrations.

The increased amount of soil, up to 1.0 g, increases the percentage removal of copper. This is an expected result as the amount of adsorbent increases, the number of adsorbent particles surrounded by metal ions increases; therefore, these particles can accommodate more ions onto their surfaces [23]. Despite the significant removal percentage of Cu(II) as the adsorbent doses increased from 1.0 to 2.0 g, statistical analysis shows that there are no significant differences between 1.0 and 1.5 g and between 1.5 and 2.0 g of adsorbent dose. Therefore a 1 gram dose of adsorbent can be regarded as an efficient amount to perform the investigation.

The removal of copper ions increases as the agitation rate increases from 50 to 500 rpm. Increasing agitation rate decreases the boundary layer resistance to mass transfer surrounding particles. A statistical test shows that there is a significant difference between the percentage of heavy metals removal as agitation rate from 50 to 500 rpm and no significant difference between the percentages of Cu(II) removal from as agitation rate is increased from 500 to 1500 rpm. Therefore, the optimum agitation rate corresponds to the highest of 83.49% is 500 rpm.

3.2 Equilibrium Studies

Three isotherms, Freundlich, Langmuir and Temkin show that adsorption of copper rises sharply at the initial stage for two C_e values (Fig. 1) an indication of presence of plenty radial sites. It can be observed that adsorption corresponding to equilibrium concentrations above 20 mg/L is reduced dramatically due to lesser available active site at the end of the adsorption process. However, Dubinin-Radushkevich is excluded as it does not fit with the experimental data.

3.2.1 Langmuir Isotherm

Langmuir isotherm has found successfully application in many real sorption processes and is expressed as:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (2)$$

Where, q_e (mg/g) and C_e (mg/L) are the amount of adsorbed Cu(II) per unit weight of adsorbent and unadsorbed Cu(II) concentration in solution at equilibrium, respectively.

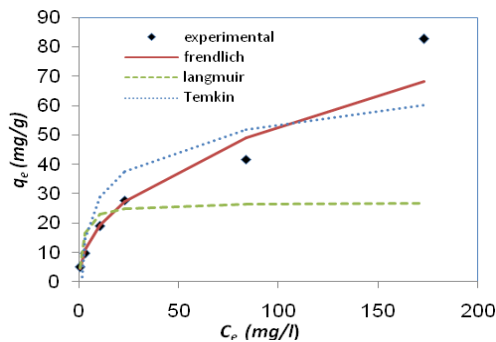


Fig. 1 Equilibrium isotherms of copper on Ashkida soil.

The constant K_L is the Langmuir equilibrium constant and the K_L/a_L gives the theoretical monolayer solution capacity, q_{max} . Therefore, a plot of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercepts $1/K_L$. The values of the Langmuir constants a_L , K_L and q_{max} with the correlation coefficient are listed in Table 2 and the Langmuir isotherm is plotted in Fig. 1 together with the experimental data points. The mean total error (E%) between this model with the experimental data is 3.86%. We note that the monolayer saturation capacity (q_{max}) is 27.03 mg/g. The total mean error is higher than Freundlich isotherm value.

3.2.2 Freundlich Isotherm

The Freundlich isotherm equation is given as:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where, K_F is Freundlich constant and n is Freundlich exponent. K_F and n can be determined from the linear plot of $\log q_e$ versus $\log C_e$. The values of the Freundlich constant together with the correlation coefficient are presented in Table 2 and the theoretical Freundlich equation is shown in Fig. 1. The mean total error, E%, of 0.6% is much lower than those corresponding to the other two models. It is evident from Fig. 1 that Freundlich equation represents the best fit of the experimental data.

3.2.3 Temkin Isotherm

The linear form of Temkin isotherm is represented by Eq. (4):

$$q_e = \frac{RT}{b} \ln(A) + \frac{RT}{b} \ln(C_e) \quad (4)$$

A plot of q_e versus $\ln C_e$ enables one to determine the Temkin constants A and B (Table 2) and the corresponding theoretical plot of this isotherm is shown in Fig. 1. The correlation coefficient is also listed in Table 2. The mean total error, E%, of 14.32% associated with this model is higher than the Langmuir's and Freundlich's.

3.2.4 Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich equation has the following form:

$$q_e = q_m e^{-\beta \varepsilon^2} \quad (5)$$

Where, q_m is the Dubinin-Radushkevich monolayer capacity (mg/g), β a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = \frac{RT}{M} \ln \left(1 + \frac{I}{C_e} \right) \quad (6)$$

Where, R is the gas constant (8.314 J/mol·K), T is the absolute temperature and M is the molecular weight of the adsorbed.

The constants, q_m and β obtained for Dubinin-Radushkevich isotherm model are tabulated in Table 2. The correlation coefficient of 0.531 indicates that the Dubinin-Radushkevich isotherm model is inappropriate for the equilibrium experimental data as the maximum adsorption capacity, q_m , is unrealistic.

3.3 Kinetic Studies

In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the adsorption rate. A number of models such as homogeneous surface diffusion and heterogeneous diffusion models have been extensively applied in batch experiments to describe the transport of adsorbate inside the adsorbent particles [24-26]. The conformity between experimental data and the model predicted values is expressed by the correlation coefficient, r^2 . A relatively higher r^2 value implies that the tested model describes the kinetics of Cu(II) adsorption better.

Table 2 Langmuir, Freundlich, Temkin and Dubinin-Radushkevich constants.

Isotherm	Constants values			
Langmuir	K_L (L/g)	q_{max} (mg/g)	r^2	E%
	0.536	27.03	0.890	3.86
Freundlich	K_F	n	r^2	E%
	6.67	2.217	0.982	0.6
Temkin	B	A (L/g)	r^2	E%
	1.25	221.8	0.756	14.32
Dubinin-Radushkevich	q_m (mg/g)	β (mg ² /J ²)	r^2	q_m (mg/g)
	2×10^9	7×10^8	0.531	2×10^9

3.3.1 Simple First Order Model

The sorption kinetics may be described by a simple first order equation [27, 28]. The change in bulk concentration of the system can be described using the following linear form:

$$\log C_t = \frac{k_1}{2.303} t + \log C_o \quad (7)$$

Where, C_t and C_o are the concentration of Cu(II) at time $t=t$ and $t=0$ in mg/L respectively, and k_1 is the first order rate constant, (1/min.).

The experimental results show that $\log C_t$ versus t (Fig. 2) for different initial concentrations of Cu(II) deviates considerably from the theoretical data. A comparison of the results and the correlation coefficient is shown in Table 3, which indicate the failure in expressing this adsorption process by the simple first order kinetics. It is proposed that simple kinetic models such as first order rate equation are not applicable to the adsorption system with solid surfaces, which are rarely homogeneous like Ashkida soil, as the effect of transport phenomena and chemical reactions are often experimentally inseparable [27, 29].

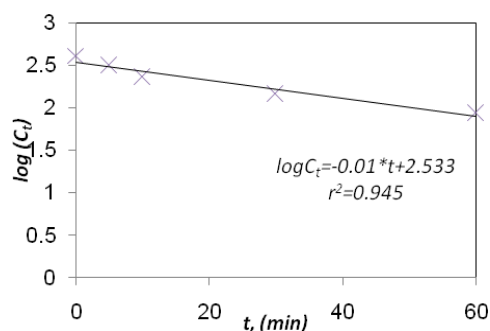


Fig. 2 A simple first order adsorption kinetics of Cu(II) on Ashkida soil.

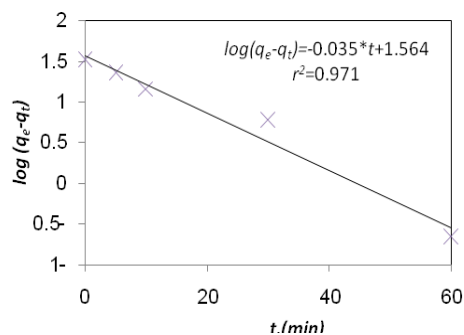
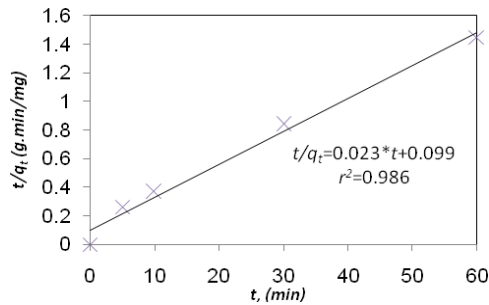


Fig. 3 A pseudo first-order adsorption kinetics of Cu(II) on Ashkida soil.

Table 3 Comparison of the simple first order, pseudo first and second order adsorption and calculated experimental q_e values.

$q_{e \text{ exp.}}(\text{mg/g})$	Simple 1st order		Pseudo 1st order			Pseudo 2nd order		
	$k_1(1/\text{min})$	r^2	$k_1(1/\text{min})$	$q_{\text{ecal}}(\text{mg/g})$	r^2	$k_2(\text{g/mg}\cdot\text{min})$	$q_{e \text{ cal.}}(\text{mg/g})$	r^2
41.61	0.02303	0.945	12.406	36.64	0.971	0.0053	43.48	0.986

**Fig. 4** The pseudo second-order adsorption kinetics of Cu(II) on Ashkida soil.

3.3.2 Pseudo First-Order Model

The sorption kinetics may also be described by a pseudo first order equation [25, 27, 30]. Integration of the linear form of the differential equation and using the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ is yields:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

Where q_e and q_t are amounts of adsorbed copper in (mg/g) at equilibrium and at a time t , respectively, and k_1 is the equilibrium rate constant of pseudo first-order adsorption (1/min).

Fig. 3 shows a plot of the linear form of pseudo first-order model at all concentrations studied. The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t are used to determine the pseudo first-order constant k_1 and equilibrium adsorption density q_e . The experimental data show a considerable deviation from the theoretical data. A comparison of the results and the correlation coefficients in Table 3 reveal that the correlation coefficients for the pseudo first order kinetic model obtained at all the solution concentrations are relatively low. And the theoretical q_e values calculated by the pseudo first-order kinetic model offer no reasonable values. This suggests that this adsorption system is not a pseudo first-order reaction.

3.3.3 Pseudo Second-Order Model

The adsorption kinetics may also be described by a pseudo second-order equation [25, 30-32]. Applying the boundary conditions to the linear form of the integrated differential equation the model becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

Where, k_2 is the equilibrium rate constant of pseudo second-order adsorption (g/mg·min). The slopes and intercepts of plots t/q_t versus t (Fig. 4) are used to calculate the pseudo second-order rate constants k_2 and q_e shows a good agreement between the experimental data and the pseudo second-order kinetic model for different initial Cu(II) concentrations. The computed results obtained from the pseudo second-order kinetic model are provided in Table 3. The correlation coefficient for pseudo second-order kinetic model is 0.986 and the calculated q_e value agrees very well with the experimental data.

4. Conclusions

This study successfully concludes that Cu(II) can be adsorbed from aqueous solutions in significant amounts by Ashkida soil. In batch adsorption studies, removal of the metal ions increases with the increase in contact time, amount of Ashkida soil and pH level. The optimum conditions for Cu(II) removal are 60 minutes contact time, and a pH level equal 7 at 25 °C. The increase in initial metal ion concentration increased the amount of metal uptake per unit weight of the soil (mg/g). The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Freundlich isotherm provides the best correlation and the lowest total error for sorption of copper onto Ashkida soil. The adsorption capacity of copper is 27.03 mg/g.

The pseudo second-order kinetic model tends to agree

very well with the dynamical behavior for the adsorption onto Ashkida soil for different initial concentrations over the whole range studied. The rate constant increases linearly with an increase in temperature, an indication of endothermic processes are involved.

References

- [1] G.M. Walker, G. Connor, S.J. Allen, Copper (II) removal onto dolomitic sorbents, *Chem. Eng. Res. and Design* 82 (2004) 961-966.
- [2] G. Blazquez., F. Hernainz, M. Calero, L.F. Ruiz-Nunez, Removal of cadmium ions with olive stones: the effect of some parameters, *Process Biochem.* 8 (2005) 2649-2654.
- [3] D. Mohan, S. Chander, Removal and recovery of metal ions from acid mine drainage using lignite a low cost sorbent, *J. Hazard. Mater.* 3 (2006) 1545-1553.
- [4] E. Pehlivan, S. Cetin, B.H. Yanık, Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash, *Journal of Hazardous Materials B135* (2006) 193-199.
- [5] G.O. Agiri, O. Akaranta, I.O. Ajay, Studies on dyed coconut (*Cocos nucifera*) pollens for removal of Cu(II) and Zn(II) from aqueous solution, *African Journal of Biotechnology* 7 (2007) 929-932.
- [6] O. Khazali, R. Abu-El-Halawa, K. Al-Souod, Removal of copper(II) from aqueous solution by Jordanian pottery materials, *Journal of Hazardous Materials B139* (2007) 67-71.
- [7] H.A. Aziz, M.N. Adlan, K.S. Ariffin, Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: post treatment by high quality limestone, *Bioresour. Technol.* 6 (2008) 1578-1583.
- [8] N. Boujelben, J. Bouzid, Z. Elouear, Adsorption of nickel and copper onto natural iron oxide coated sand from aqueous solutions: Study in single and binary systems, *Journal of Hazardous Materials* 163 (2009) 376-382.
- [9] A.Y. Okasha, H.G. Ibrahim, M.M. Aboabboud, A.N. Awad, Removal of copper from aqueous solutions by adsorption technique onto low cost material, in: the 3rd National Conference on Basic Sciences, 25-27/4/2009, Gharian, Libya.
- [10] H.G. Ibrahim, A. Y. Okasha, A.M. Alsari, M.S. Elatrash, Removal of chromium from tannery wastewater effluents by fixed bed system, in: the 3rd National Conference on Basic Sciences, 25-27/4/2009, Gharian, Libya.
- [11] M.S. Elatrash, A.Y. Okasha, H.G. Ibrahim, Copper removal from aqueous solutions by using portland cement kiln dust, in: The TIES and GRASPA Conference (2009), Bologna, Italy.
- [12] N.W. Harvey, V. Chantawong, Adsorption of heavy metals by ballclay: their competition and selectivity, *Journal of Tokyo University of Information Sciences*, (2001), pp. 78-86.
- [13] M. Fomina, G.M. Gadd, metal sorption by biomass of melanin-producing fungi grown in clay-containing medium, *Journal of Chemical Technology and Biotechnology* 78 (2002) 23-34.
- [14] E. Menntasti, O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, Adsorption of heavy metals on namontmorillonite, effect of pH and organic substances, *Water Research* 37 (2003) 1619-1627.
- [15] T. Nemeth, I. Mohai, M. Toth, Adsorption of copper and zinc ions on various montmorillonites: an XRD study *acta mineralogica-petrographica*, Szeged 46 (2005) 29-36.
- [16] S.M.I. Sajidu, I. Persson, W.R.L. Masamba, E.M.T. Henry, D. Kayambazinthu, Removal of Cd²⁺, Cr³⁺, Cu²⁺, Hg²⁺, Pb²⁺ and Zn²⁺ cations and AsO₄³⁻ anions from aqueous solutions by mixed clay from Tundulu in Malawi and characterization of the clay, *Water SA* 4 (2006) 519-526.
- [17] W. Omar, H. Al-Itawi, Removal of Pb²⁺ ions from aqueous solutions by adsorption on kaolinite clay, *American Journal of Applied Sciences* 7 (2007) 502-507.
- [18] M. Doula, A. Dimirkou, Use of an iron-overexchanged clinoptilolite for the removal of Cu²⁺ ions from heavily contaminated water samples, *Journal of Hazardous Materials* 151 (2008) 738-745.
- [19] S.T. Akar, T. Akar, Z. Kaynak, B. Anilan, A. Cabuk, O. Tabak, T.A. Demir, T. Gedikbey, Removal of copper(II) ions from synthetic solution and real wastewater by the combined action of dried *Trametes versicolor* cells and montmorillonite, *Hydrometallurgy* 97 (2009) 98-104.
- [20] S.C. Chapra, R.P. Canale, *Numerical Methods for Engineers*, 3rd edition, McGraw-Hill Co, Singapore, 1998.
- [21] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes in Pascal: The Art of Scientific Computing*, Cambridge University Press, 1989.
- [22] A. Ayar, S. Gursal, A. Gurten, O. Gezici, On the removal of some phenolic compounds from aqueous solutions by using a sporopollenin-based ligand-exchange fixed bed isotherm analysis, *Desalination* 219 (2008) 160-170.
- [23] R. Gong, Y. Dingc, H. Liua, Q. Chen, Z. Liub, Lead biosorption and desorption by intact and pretreated *Spirulina maxima* biomass, *Chemosphere* 1 (2005) 125-130.
- [24] O.A. Fadali, E.E. Ebrahiem, Y.H. Magdy, A.A.M. Daifullah, M.M. Nassar, Removal of chromium from tannery effluents by adsorption, *J. Environ. Sci. Health, Part A Environ. Sci. Eng.* 9 (2005) 465-472.
- [25] P. Wu, W. Wu, S. Li, N. Xing, N. Zhu, P. Li, L. Wu, C. Yang, Z. Dang, Removal of Cd²⁺ from aqueous solution by adsorption using Fe-montmorillonite, *Journal of Hazardous Materials* 169 (2009) 824-830.
- [26] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.* 32 (1998) 344-349.
- [27] M.A. Hossain, M. Kumita, Y. Michigami, S. Mori, Kinetics of Cr(VI) adsorption on used black tea leaves, *J. Chem. Eng. Japan* 38 (2005) 402-406.
- [28] C.Q. Eligwe, N.B. Okolue, C.O. Nwambu, C.I.A. Nwoko, Adsorption thermodynamics and kinetics of mercury (II), cadmium(II) and lead(II) on lignite, *Chem. Eng. Technol.* 22 (1999) 45-49.
- [29] D.L. Sparks, *Kinetics of Soil Chemical Processes*, 1st edition, Academic Press, New York, USA, 1989, pp. 18-29.
- [30] M. Ozacar, Equilibrium and kinetic modeling of adsorption of phosphorus on calcined alunite, *Adsorption* 9 (2003) 125-132.
- [31] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dyes on cross-linked chitosan beads, *J. Hazard. Mater.* 2 (2002) 233-248.
- [32] Y.S. Ho, G. McKay, Pseudo-second order model for adsorption processes, *Process Biochem.* 34 (1999) 451-465.

Physicochemical Characterization of Surface Water of the Area of Gafsa

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Abstract: Water exploits an essential part in all the durable development, the exploitation of this natural resource, its management and its position, its mineralization, its underground course and the mode of its resurgence. The area of Gafsa is known by its very important hydrous potential which is geographically in the zone of transition between central Tunisia and the Saharan platform, these two great fields are separated by the fault of Gafsa which plays an important part in the structuring of the basins of the area, the hydrous resources of Gafsa make subsoil water the principal source of supply water, in the absence of an important network of surface. The zones of studies present requirements out of water which do not cease growing with the progress of the industrial activities and the concentration of the agricultural activities: The objective of this work is to analyze the water of the various zones of the area of Gafsa and to treat it to make it possible most drinkable. The analyzes like measurement of pH, measurement of electric conductivity and measurement of dry residue were made in the laboratory of the chemical group of Mdhila in Tunisia and in laboratory of Ion exchanger Materials of Vitry in France, the processes of treatment as opposite osmosis are also programmed in this same laboratory. The results are very encouraging to start the study and the design of a station of potabilisation of water in the area of Gafsa.

Key words: Durable development, the area of Gafsa, hydrous potential, to analyze, to treat, dry residue, potabilisation.

1. Introduction

Each year one counts three million case of deaths due to diseases related to the water, of which two million deads is caused by the diarrhea. Contaminated water is the cause for approximately 80% of the diseases in the poor countries. Former work concerning the analyzes of water can be classified in three categories: For waste water one finds the various analyzes which were made on the water effluents produced with the phosphate mines in the power station of Jordan [1, 2], the technique, which was used to analyze the anions (Cl^- , NO_3^- , and SO_4^{2-}) and heavy metals, was the ionic chromatography. One also finds the technique of spectrometry to analyze the isotopes

^1H and ^{18}O in Germanic [3]. For industrial water one finds the various analyzes which were made on water of drainage into Germanic [4, 5], one quotes the atomic emission to measure the concentrations of the Na^+ cations in water of drainage. Other technique such as the atomic absorption is used by apparatus (PERKIN ELMER 5100 Zeeman). This apparatus is equipped with the thermoelectric system of atomization (furnace) improving considerably the limits of detection and allows the proportioning of trace element, it is also reserved for the analysis of the metal elements (Rb, Cd, Cr, Pb, Ni, Co) to the state of traces in various mediums: grounds, manure, plants, water, seamen circles (crustacean), micro-organisms (acarina) [6, 7]. For drinking water, the needs are increasingly important in Tunisia, one finds the project of desalination of sea water with El Bibane [8] since one noted a lack of drinking water in the south-east of Tunisia, water is characterized by a high degree of salinity. It is to be

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also noted that economic development and social in this area induced an increase in the requirements out of water. This situation brought to the construction of the water desalination stations to Gabès, DJerba and Zarzis. The Tunisian experiment as regards desalination, is amply enriched with the start up by the desalination station by Gabès in June 1995 [9]. In order to precisely define the degree of potability of water, international standards were established fixing the limiting contents in particular not to exceed for a certain number of substances harmful and likely to be present in water. The taps waters are in general consumed at the regional level because their transport would increase the cost. There exists ten of such sources in Tunisia, the area of Gafsa, located in the South-west of Tunisia, covers a surface of 8990 km² (5.5% of the surface of the country) and shelters a population of 327,900 inhabitants distributes out of 11 delegations. This area is known as the climate arid and semi-arid, it is cut out in three areas of catchment areas which are: basin of Gafsa Northern, basin of Southern Gafsa and basin Moulares-Redayef, the analysis of spring waters of this area is the subject of our work, for that, 11 samples were taken in various zones of this area.

2. Materials and Methods

With an aim of studying the geochemistry of taps waters of the area of Gafsa, a sampling campaign was made during which 9 samples were taken. These samples were the subject of various analyzes carried out in the research center of the company of phosphates of Gafsa. The analysis of the major elements was made on filtered water with 0.45 µm. It concerns to chlorides, sulfates, alkalinity, the elements alkaline (Na and K) and the elements alkaline-earth (Ca and Mg). The proportioning of the anions as chlorides was made by the method of titration. Titration was carried out by a silver nitrate solution N/10, in the presence of potassium chromate. The method used for the analysis of sulfates is gravimetry. It consists in making precipitate these ions in an acid medium, by barium

chloride (BaCl₂) of known title (10%), in the presence of potassium chromate (K₂Cr₂O₄). Alkalinity was determined by the volumetric method (Rodier, 1978), which is based on the neutralization of a volume of water to analyze by an inorganic acid of known normality, in the presence of an indicator. Proportioning of the cations were made by the method of the atomic absorption spectrometry, the K⁺ and Na⁺ were proportioned by the method of atomic absorption in emission, by using a flame with air/acetylene and the ions Ca²⁺ and Mg²⁺ were proportioned by absorption, these elements are dispersed in an atomic state in the flame with air acetylene. The pH and conductivity were measured using a pH meter and a conductivity meter.

3. Results and Discussion

A drinking water is water which one can drink without health risk. In order to define a drinking water precisely, standards were established which fix in particular the limiting contents not to exceed for a certain number of substances harmful and likely to be present in water. The fact that a water is in conformity with the standards drinkable, this does not mean that it is free from polluting matters, but that their concentration was considered to be sufficiently weak not to endanger the health of the consumer. According to these standards, only the techniques of treatment of water of taps used with the area of Gafsa are: the ventilation which is a simple technique making it possible only to eliminate part of the gases which obstruct the other stages of treatment; it is carried out by gas splashing (standard N₂) or by cascade (falls of water) which supports the passage of gases towards the atmosphere and disinfection by chlorine [10].

The results of measurement of the pH of water of the area of Gafsa (Fig. 1) show that all the samples have a pH located in the interval of the standard of Grenoble (the standard most employed) [11]. The highest value(8.31) characterizes water of Zannouch, located at the basin Gafsa-North, whereas the lowest value (7.4) is measured in water of Moulares, located at the

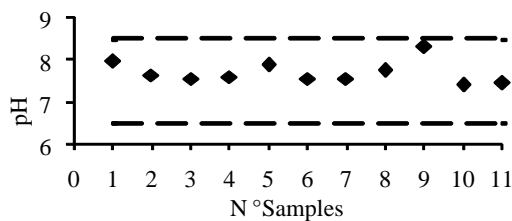


Fig. 1 pH of the water samples.

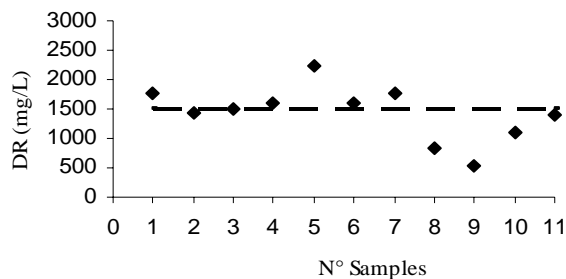


Fig. 2 Dry residue of the water samples.

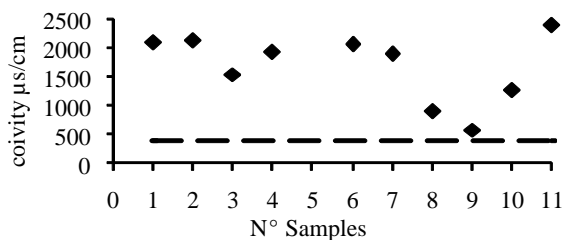


Fig. 3 Conductivity of the water samples.

Moulares-Redayef basin.

We notice starting from Fig. 2 that 6 samples out of 11 have a salinity close to the standard of Grenoble (1,500 mg/L), the low values of salinity (820.65 and 534.23 mg/L) are measured in Zannouch and Sidi Aich, strongest salinity (2,220.89 mg/L and of 1,780.5 mg/L) is recorded in Metlaoui and Redayef (Fig. 2). The low values of salinity observed in the center of the Northern basin of Gafsa are in relation to the food of the tablecloth by the wadis (Wadi Sidi Aich).

The electric conductivity of all the samples (Fig. 3) is higher than the standard of Grenoble (<400 µs/cm), the highest value is 2,810 recorded on the level of Redayef and the low value of conductivity (582 µs/cm) is measured in Zannouch.

3.1 Contents of Major Elements

3.1.1 Contents of Cations

One notices starting from the analyzes of the concentration of the cations of water of the area of

Gafsa that the contents of cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) vary from a sample with another, this is with the variation of the geochemical characteristics of the tablecloths related to these water samples.

Fig. 4 shows that 6 samples out of 11 (Redayef, Elguettar, Zarroug, Mélaoui, Ksar and MDhilla) do not respect the standard of Grenoble (50 mg/L) and the other samples respect this standard. We notice starting from Fig. 5 that the contents of the water samples of the area of Gafsa of Ca^{2+} vary in the following way: the majority of the samples have a content of Ca^{2+} which exceed the standard of Grenoble, 2 samples out of 11 (Sidi Aich and Zannouch) are close to this standard of Grenoble. We can then affirm that hardness is high for almost all the samples. For the sodium content (Fig. 6) we have 2 samples out of 11 (Redayef and Mélaoui) which do not respect the standard of Grenoble because

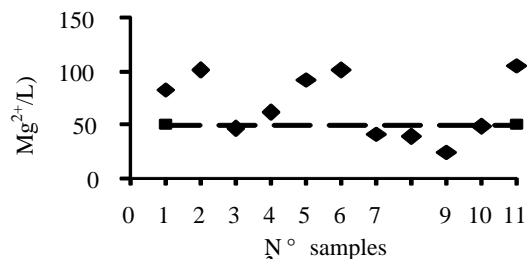


Fig. 4 Representation of Mg^{2+} (mg/L).

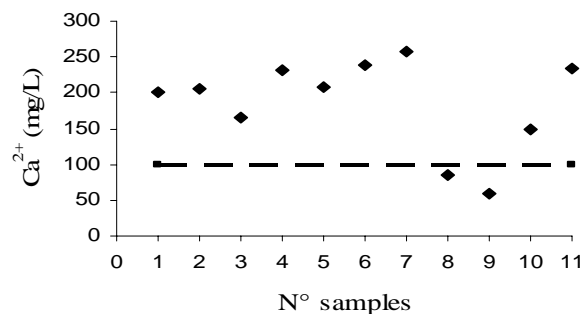


Fig. 5 Representation of the Ca^{2+} (mg/L).

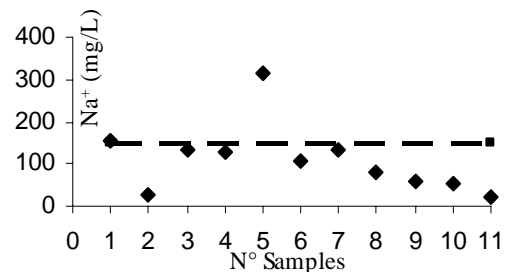


Fig. 6 Representation of the Na^+ (mg/L).

the place of corresponds to field Moulars-Redayef from where hardness is high.

3.1.2 Contents of Anions

Fig. 7 shows that 9 samples out of 11 (Redayef, Elguettar, Ennour city, Zarroug, Metlaoui, Ksar, Douali, Moulares and M'dhilla) do not respect the standard of Grenoble (250 mg/L) and the other samples respect this standard. We notice starting from Fig. 8 that for the water contents of the area of Gafsa Cl one finds 5 samples out of 11 (Redayef, Ennour city, Zarroug, Metlaoui and Douali) do not respect the standard of Grenoble (200 mg/L) and the other samples respect this standard. The results of analysis is concentration of fluorine (Fig. 9) for water of taps of the area of Gafsa which showed that there are 2 types of water: a minority of samples (Zannouch and Sidi Aich) having a lower quantity of fluorine or equalizes with 1.5 mg/L thus respecting the standard of Grenoble, a majority of samples (Redayef, Elguettar, Ennour city, Zarroug, Metlaoui, Ksar, Douali, Moulares and M'dhilla) having a quantity of fluorine higher than 1.5 mg/L not respecting thus the standard of Grenoble. For the content of element NO_3^- it appears in the form of trace in all the water samples of taps of the area of Gafsa. By comparing the results of the analyzes of water of the area of Gafsa with the standards of pure water potabilities of Grenoble, one notices that there is water not showing the good physical and chemical characteristics and do not conform to the standards intended for human consumption, for these reasons, it is necessary to treat them before their use by the population.

3.2 Origin of Mineralization of Water

The relations between total mineralization and the contents of the major elements of water of taps of the area of Gafsa show good positive correlations with calcium, sodium, sulfates and the chlorides (Figs. 10-14). This confirms that the salinity of water of the studied area is controlled mainly by the concentrations of these elements and especially the sulfates (sulfates

being dominant anions).

3.3 Nature of Waters

The coefficient resulting from the chart Fig. 15 is ($R^2=0.488$) what shows a positive correlation indicating that these two elements come from the dissociation of anhydride.

The chart of the concentrations of Na^+ according to that of Cl^- shows a good correlation ($R^2=0.99$) what

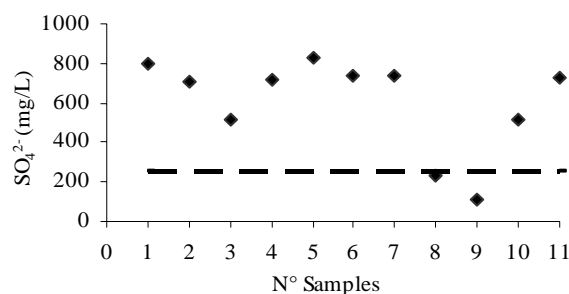


Fig. 7 Representation of SO_4^{2-} (mg/L).

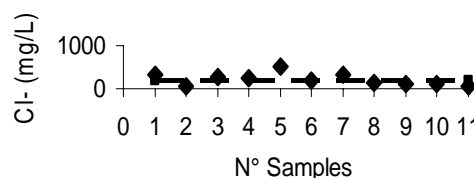


Fig. 8 Representation of Cl^- (mg/L).

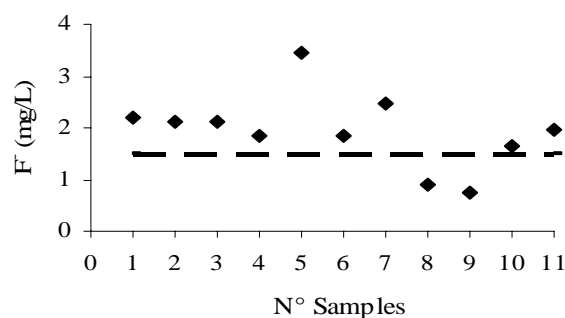


Fig. 9 Representation of F^- (mg/L).

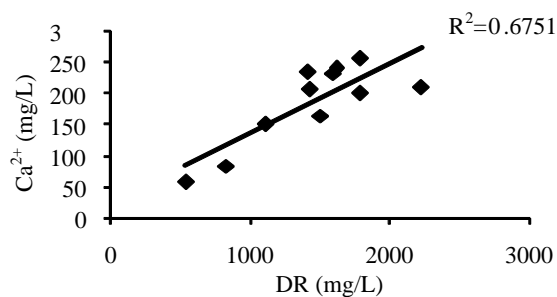
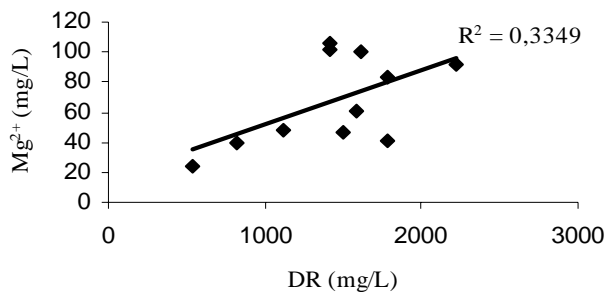
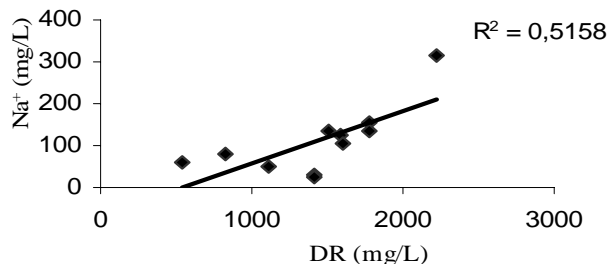
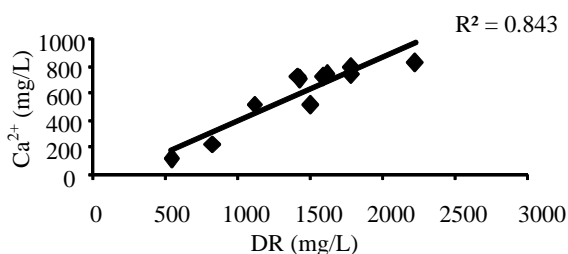
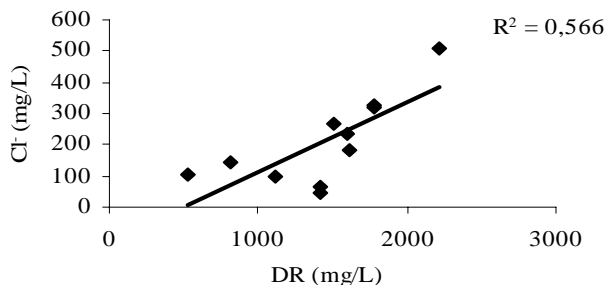
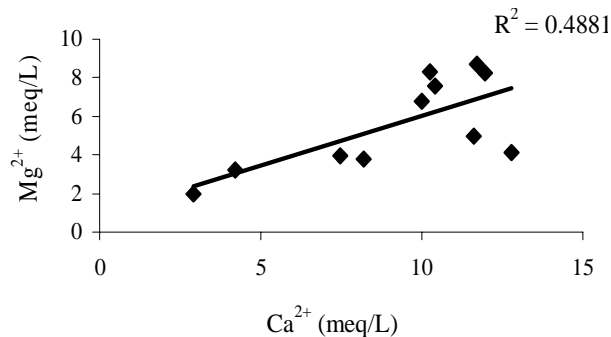
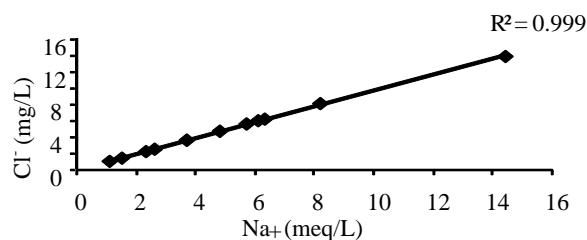
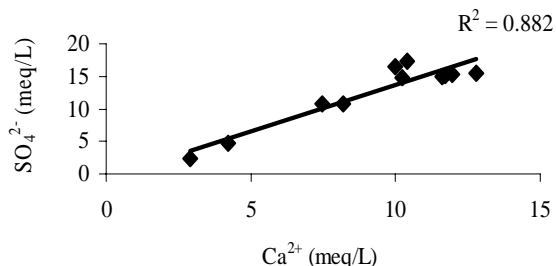


Fig. 10 Evolution of Ca^{2+} .

Fig. 11 Evolution of Mg^{2+} .Fig. 12 Evolution of Na^+ .Fig. 13 Evolution of SO_4^{2-} .Fig. 14 Evolution of Cl^- .Fig. 15 Ratio of Ca^{2+}/Mg^{2+} .Fig. 16 Ratio of Na^+/Cl^- .Fig. 17 Ratio of Ca^{2+}/SO_4^{2-} .

indicates that these two elements have the same origin which is the dissolution of Halite $NaCl$ (Fig. 16). The coefficient resulting from the chart Fig. 17 is ($R^2=0,88$) what shows a good positive correlation indicating that these two elements come from the dissociation of the gypsum ($CaSO_4$).

The results of the geochemical analyzes of water of the area of Gafsa according to the diagram of piper make it possible to determine their chemical facies where the sulfates and calcium dominate. This is explained by the influence of the interactions water-rock, these rocks are of sablo-argillaceous nature with gypseous interactions and by the infiltration of rainwater after deterioration of the gypsum and limestone. Thus starting from diagram of Piper, one can quote the following chemical facies: water chlorinated and sulfato-calcic taken on the level of the samples of Redayef, Ennour city, Zarroug, Metlaoui, Ksar, Moulares and water chlorinated and Sulfato-magnesian taken on the level of the samples of Douali, Sidi Aich and Zannouch.

The representation of the chemical composition of water of the area of Gafsa in the diagram of Scholler Berkloff makes it possible to distinguish several families from water which is characterized by facies where the sulfates dominate: water sodi-magnésio-

chloruro-sulphated taken on the level of the samples of Redayef and Metlaoui and water calci-magnésio-chloruro-sulphated taken on the level of the samples of Elguettar, Ennour city, Zarroug, Ksar, Douali, Sidi Aich, Moularés and M'dhilla. Since the various chemical facies derive from/to each other, one can then determine the way followed by the solutions during the process of concentration or dilution. Thanks to the description of the composition of water, two types of water are distinguished easily: sulfato-magnesian Sulfato-calciquee water and water whose element more dominating is the sulfate which is due to the dissolution of the gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and contained in the Plio-Quaternary formation of this zone.

4. Conclusion

This study enables us to analyze water of taps of the area of Gafsa. We are mainly interested in the analysis of the major elements of the taken samples, by comparing the results of these analyzes with the standard of Grenoble one noticed that there is water not showing good physical and chemical characteristics especially those of Metlaoui, Redayef and Douali. The study of the relationship between the major elements and salinity shows that the latter is controlled mainly by the concentrations of these elements especially by sulfates. The exploitation of the diagrams of Scholler Berkloff and Piper made it possible to know the various families of studied spring waters. This work can also be regarded as a first big step of a procedure of

water treatment of the area of Gafsa so that the population concerned extracts the maximum of profit.

References

- [1] J. Anwar, Mine Water and the Environment Springer-verlag, Evaluation of the Effluent Water Quality Produced at Phosphate Mines in Central Jordan, Water and the Environnement Study Center, Al-Karak-Jordan, 2004, pp.133-137.
- [2] O. Rimawi, Springer science+Business Media B.V., Reuse of Mining Wastewater in Agricultural Activities in Jordan, 2009, pp.695-703.
- [3] R. Sadaq, P. Pufahl, Oxygen and carbon isotopes in the Jordanian phosphorites and associated fossils, Abster, 7th jord Geol conf, 2001, pp. 81.
- [4] K. Weise, Forster, Ecological Biotechnologie Leningrad: Khimiya, 1990.
- [5] V. Goncharuk, Nanofiltration in pre-treatment of drainage waters of the dumps for solid domestic wastes, Journal of Water Chemistry ant Technology, 29 (2007) 102-109.
- [6] M. Britskec, Atomic-Absorption Spectroscopie Analysis, Moscow, Khimiya, 1982.
- [7] M. Lur'e, Analitical Chemistry of Watewa-ters, Moscow: Khimiya 1984.
- [8] A. Ounalli, Elsevier Desalination 137, Project of desalination of sea water in El Bibane, Arrange national renewable energy (ANER) Tunisie, 2000, pp. 293-296.
- [9] K. Fathi, C. Habib, ELSEVIER DESALINATION 136, Performances station of desalination of Gabes ($22,500\text{m}^3/\text{j}$) after five years of Sonede operation, Division Production South East Gabes Tunisia, 2000, pp. 263-272.
- [10] Service of study of the SONEDE, Statistical Report, appendix, 2008.
- [11] Decree (of the 12/20/2001) Standard of Grenoble, available online at: <http://grenoble.eau.pure.free.fr/analyses.htm>.

Impact of Urban Water Pricing on Future Water Demand: A 'Socioeconomic' Study in Greece

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Abstract: The main aim of this study is to assess various aspects of the current water policy, investigate the perspectives of water saving, evaluate water price elasticity and explore new approaches toward sustainable water management in the water sector, through a questionnaire survey that has been performed in the city of Volos, Greece, concerning the residential sector. The appropriate design of water management measures presupposes the investigation of the influence of some selected variables to consumers' behavior. The price of water, the size of the dwelling, the indoor and outdoor uses, the educational level, the income of consumers as well as rainfall and temperature levels are examined, the residential water demand curve is estimated and projections of future water demand under different pricing policies are performed.

Key words: Demand management, price elasticity, public awareness, residential water use, integrated water policy, water conservation.

1. Introduction

Data concerning water use traditionally presents three columns of water use: withdrawals in the domestic, agriculture and industrial sector respectively [1-3]. Although agriculture (and specifically irrigation) appears to be the most consumptive sector in most countries, residential water consumption is usually the most important use in an urban context and its management results in the most controversial decision from a socioeconomic point of view [4].

The study and evaluation of suitable social interventions as well as the application of financial tools and measures which could contribute significantly to saving water, which are nowadays the top choices of a sustainable water policy, lie within this framework [5, 6].

Nowadays, water utilities face the challenge of developing new water policies by adopting advanced technologies for demand management through a series of incentives, reuse of treated wastewater, installation of water saving and conservation equipments, consumer's awareness and education, while having at the same time to introduce changes in pricing procedures and full cost recovery, that includes environmental costs and induces conservation in order to comply with the principles of the Water Framework Directive.

Water use can be expressed as a mathematical function of one or more independent variables and its mathematical form as well as the selection of the independent variables depends not only on the type and aggregation of water demand, but also on the data availability. It is evident that the definition of the above differs significantly among both water sectors (agricultural, residential, industrial, commercial, etc.) and geographical regions.

There are many applications and statistical models to

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be found in the international bibliography, according to the availability and the type of data, which evaluate the water demand curve in the residential sector and define the factors that affect water demand as well as the way they affect each other. A variety of methods and econometric models depending upon the nature and availability of data in order to estimate water demand [7-9] have been performed in many studies.

The potential explanatory variables that have been used in studies of residential water demand mostly refer to water price, population, income, housing, weather, family composition and other, which are represented by various and different expressions.

Among the above variables, water price and its specification in water demand models is an econometric issue of great importance. Howe and Linaweaver [10] set the stage for a discussion on the relevance of average and marginal prices for the demand model specification by arguing that consumers react to marginal rather than average prices. Many recent studies include either the average price [8, 11], the marginal price [7, 12], or both [13-16] started using the so-called 'perceived price', which is usually a combination of marginal and average prices. Perceived prices have subsequently been used in other studies as well [17]. Other water demand studies include a difference variable in addition to the marginal price [18].

In the framework of demand management, it is vital to analyze and to understand the characteristics of water demand. How demand is formulated, which factors determine it, how demand responds to changes in income and relative prices and eventually how future demand will be shaped [4, 19]. Thus, the analysis of demand is an essential component in designing effective water demand management [20].

2. The Methodological Approach

The impact of urban water pricing on future water demand could be accessed through the following three-step methodological approach.

In the first step, collection of data both from various

authorities, public organisations, water utilities and target population is performed.

Data concerns socioeconomic profile of the target region, climatic information and water related data (water consumption levels, water pricing structure).

Some of the above are selected and checked concerning their aptness to water demand. A basic and simple equation of some observations (y), which depend on a set of variables (x), is found in Hsiao [21] and follows the form:

$$y_{it} = a + \sum_{k=1}^K \beta_k x_{kit} + v_i + u_{it}$$

$$i = 1, 2, \dots, N$$

$$t = 1, 2, \dots, T \quad (1)$$

Where,

- Y: the dependent variable in observation i at time t ;
- X_{kit} : the vector of specific selected variables;
- α, β_k : coefficients to be estimated;
- v_i : the unexpected regime of the dependent variable;
- u_{it} : the error term.

According to the type of data collected in the previous step, the appropriate expression of the above form is decided and the suitable econometric model is used in order to estimate water price elasticity.

A log transformation of Eq. (1) is used, all the explanatory variables are replaced and fixed effects model provides the value of water price elasticity.

In the last step of the proposed approach, future water demand projections are performed through prediction models.

The system "IWR-MAIN Water Demand Analysis Suite", which is a tool for the prediction of future water demand and the Build Forecasting Model is used in this analysis and the residential water consumption Q for month m and for the year of prediction y is evoked by the following equation:

$$Q_y = Nq^* \left(\frac{X_{i,y}}{X_{i,b}} \right)^{\beta_i} d_m \quad (2)$$

Where,

N : the number of water measurement devices;

q^* : the specific consumption per capita per day in the base year;

d_m : the number of days in each month;

$X_{i,y}$: the value of variable i in the year of prediction y ;

$X_{i,b}$: the value of variable i in the base year b ;

β_i : the elasticity of variable I .

The entire methodology described above could be presented in the Fig. 1.

3. Results and Discussion

3.1 The Study Area and the Questionnaire Survey

The survey is performed in the wider region of the city of Volos, which belongs to the River Basin District of Thessaly - RBD (Fig. 2).

Water for domestic uses is the second dominant of water uses in Greece and accounted for almost 12%. Regarding water demand per residential water use, RBD of Thessaly owes the third rank (69.0 hm³), following the RBD of Attica (420.0 hm³) and Central Macedonian (99.8 hm³), where the two metropolitan areas of Greece, Athens and Thessaloniki respectively exist [22]. The Municipal Water Utility of the city of Volos, which is responsible for the municipalities of Volos, Nea Ionia and Esonia, supplies the urban complex of Volos (120,000 residents) with an estimated average water consumption of about 350 liters per counter per day.

In the city of Volos-Greece the number of water counters has increased from 28,569 in 1979 to 71,133 in 2005, while the annual water production has increased 2.60 times for the same time period.

The broader study area has been divided into four main sectors, according to the segregation of the Municipal Water Utility of the city of Volos. Sectors 1, 2 and 3 cover the municipality of Volos, whereas sector 4 the municipalities of Nea Ionia and Esonia. Demographic data is retrieved from the National Statistical Service and the percentage of each sector's participation in the sample is calculated, aiming at an uniform geographical distribution. Field questionnaire survey through face-to-face interviews is performed and probability sampling is used for the selection of the respondents.

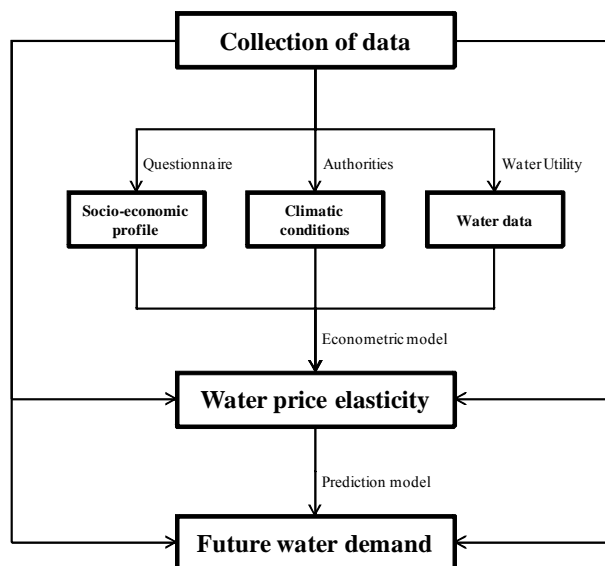


Fig. 1 Methodological approach.

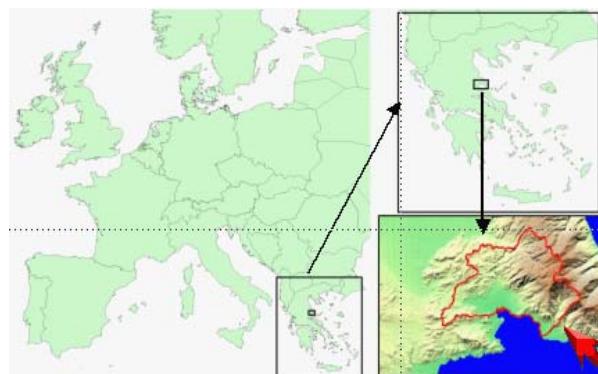


Fig. 2 The study area.

One hundred twelve questionnaires are collected and after being examined thoroughly for shortages and possibility of bias.

The questionnaire used in the interview consists of three parts, which are presented in Table 1. The first part defines the social identity of the sample through the investigation of its social characteristics and its financial situation (sex, age, education, income, etc.). The second part includes several questions regarding water consumption and uses in the urban area of Volos (outdoor water use, leakages, use of water conserving devices). In this part of the questionnaire, the consumer assesses and hierarchically defines weights to potential factors that form water consumption patterns and contribute to water conservation. In the last part, consumers' willingness to pay is examined, as well as

Table 1 Sample questionnaire.

Outline of the questionnaire	
A. General characteristics of consumers	
1.	Name/Address/Phone number/Water counter number
2.	Type of dwelling/ Floor/Respondent's sex/Respondent's age/ Respondent's educational level/Ownership of the dwelling/ Members of the family/Years of residence in the dwelling/ Square meters of dwelling/Number of rooms
3.	Family income/Percentage of family income for water bill
B. Water use and consumption	
1.	Number of bathrooms/Number of taps/Number of washing machines (clothes and dishes)
2.	Outdoor uses
3.	Use of water conservation devices
4.	Control of leakages/Frequency
5.	Evaluation of variables affecting water demand (family members, size of dwelling, floor, outdoor uses, income, educational level, water price, temperature, rainfall)
6.	Evaluation of variables affecting water conservation (water pricing policy, use of water conservation devices, construction of dual water supply network, control of leakages, public awareness and education)
C. Consumers' attitude	
1.	Would you be willing to participate in a water conservation programme?
2.	Would you be willing to be informed about water conservation programmes?
3.	Would you be willing to pay an extra amount annually in order to contribute to the amelioration of water services? If yes, how much?

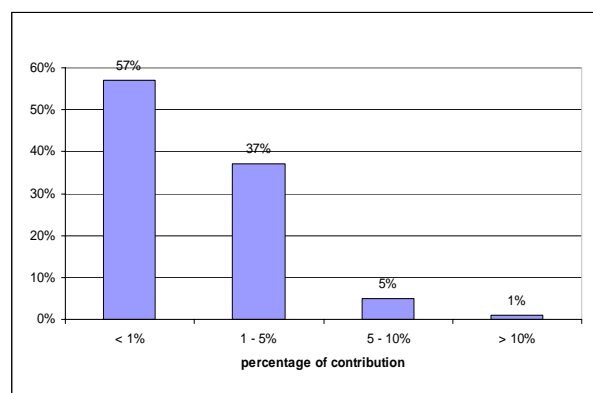
their attitude towards conservation programs.

3.1.1 Water Pricing Policy and Willingness to Pay

Tariff structures in Greece, typically include an increasing block rate system (progressive volumetric rate for different consumer categories), in addition to a fixed monthly standing charge that depends on the diameter of the pipe connecting the consumer to the network. The water bill also includes sewerage cost

expressed as a standard percentage of the water consumption cost. A respective increasing block rate system, which sets the price of the initial blocks of water at a low rate and gradually increases the rate according to increased rates of consumption, has prevailed in the city of Volos, Greece after 1985. From 1985 to 1991 the residential customers were being charged based on a three-block rate structure, whereas from 1991 to 1997 according to a four-block pricing scheme. Since then, five water brackets have prevailed combined with a fixed service charge of 15 m³/trimester. Table 2 shows the price for each block for the residential sector from 1997 (base year of the implementation of five brackets water charging system) until 2005 as well as increases occurred the next eight years in relation to the base year.

Despite the vast increase of the water price, especially for high consumers, 57% declare that the contribution of water bill to their family income is less than 1% (Fig. 3).

**Fig. 3** Contribution of water bill to total family expenses.**Table 2** Water prices and percentage increases in water rate structure in the city of Volos.

m ³ per months	1997 (base year)	1998	1999	2000	2001	2002	2003	2004	2005
	€/m ³	€/m ³ %	€/m ³ %	€/m ³ %	€/m ³ %	€/m ³ %	€/m ³ %	€/m ³ %	€/m ³ %
0-15	0.32	0.34 6.25	0.35 9.38	0.36 12.50	0.36 12.50	0.37 15.63	0.38 18.75	0.39 21.88	0.40 25.00
16-38	0.38	0.40 5.26	0.42 10.53	0.43 13.16	0.44 15.79	0.45 18.42	0.46 21.05	0.48 26.32	0.50 31.58
39-60	0.50	0.53 6.00	0.54 8.00	0.56 12.00	0.57 14.00	0.59 18.00	0.61 22.00	0.64 28.00	0.67 34.00
61-80	0.50	0.53 6.00	0.54 8.00	0.56 12.00	0.59 18.00	0.62 24.00	0.65 30.00	0.69 38.00	0.73 46.00
>81	0.56	0.59 5.36	0.61 8.93	0.63 12.50	0.68 21.43	0.73 30.36	0.79 41.07	0.86 53.57	0.93 66.07

Although, water charges slightly involve in residential expenses, 49% of the respondents are reluctant to pay extra for service improvements, indicating the lack of water and environmental consciousness and the low reliability of the utility's infrastructure and services (Fig. 4). Even those who are willing to pay for the amelioration of water services (42%) would accept only an amount of up to 30 € annually, whereas only very few would consent to a higher amount (from 45 € till 300 € annually).

3.1.2 Water Saving Devices

Water saving devices can be installed in kitchens, in bathrooms, on toilets, on washing machines, and on flash tanks. Results of adopting such measures showed a total reduction in water consumption of about 20 percent [23]. Although only 5% has already installed, numerous of those who don't use water conserving devices would be interested in being informed as well as in participating in water conservation programs. Thus, with suitable planning and application of cultural and technical methods, it is possible to optimize consumption in the near future.

3.1.3 Dual Water Supply Network

Residential water consumption is divided into indoor and outdoor water use. Indoor uses include toilets, showers/bath, washing clothes, cooking/cleaning and dishwashing. Outdoor uses consist of irrigation, gardening, swimming pools, and car washing [5].

While indoor use depends mainly on the residents' habits, outdoor use depends on the size of the area as

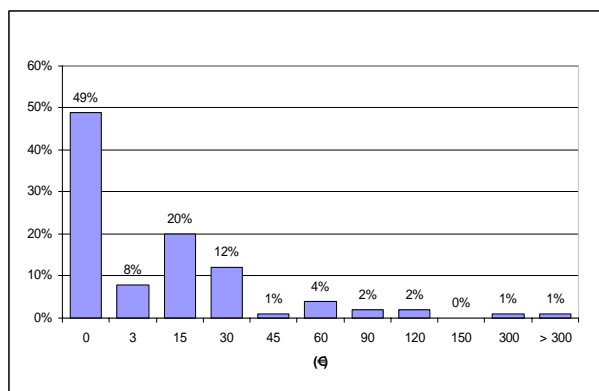


Fig. 4 Consumers' willingness to pay.

well as on the weather conditions in the area under study. In the case of the urban complex of Volos, the variable of outdoor use concerns mostly the washing of balconies and the watering of plants. It is a very important parameter when studying potential variables affecting water demand, since outdoor use geometrically increases the household's water consumption.

It has been proven in California that the prohibition of certain outdoor uses, such as washing of sidewalks and outdoor areas can lead to a 29% decrease in consumption [24]. As water consumed for outdoor uses doesn't have to meet high quality standards and as almost 3/4 of the sample consumers spends a considerable bulk of water in this use, the construction of a dual water supply network could be an effective solution in water conservation.

3.1.4 Public Participation in Water Conservation Programs

The water supply authorities ought to work out campaigns, in order to help consumers understand the need and the importance of water demand management and activate them towards a demand oriented water use policy.

The domestic consumers' willingness to be informed on programs and water conservation services is at a very high level in the city of Volos. The overwhelming majority of consumers (90%) wish to be informed by the Municipal Water Utility of the city of Volos on the water supply problems of the city as well as on water related issues. The most preferable way of information includes a special edition (flyer) dispatched together with the water bill. In addition, local media (radio, TV, newspapers) are considered an effective mean.

Before applying any water conservation program, one should check the possibility of failing to decrease the water demand. It is therefore of great importance that 87% of the sample would be willing to take part in water conservation programs. There have been water conservation programs, where water saving devices were handed out to the consumers, and the consumers

had to install them by themselves, which turned out to be inefficient, since the consumers never installed these devices [25]. The public's contribution as well as the general environmental education of consumers is considered of great importance for the successful implementation of demand management programs. Consumers are more willing to participate in certain actions and programs, when they understand the benefits and the advantages of such actions.

3.1.5 Leakages' Control

61% of the sample admits that they check for network leakages. This means that a significant part of the consumers deals with possible network damages and the consequent water leakages. The leakage control entails double benefit, since on the one hand water is being conserved and on the other hand the financial interests of the Water Utility are secured since there is no water loss which can't be charged.

The majority of those controlling water leakages (27%) checks for damages once per year, whereas another 15% checks once per month and 13% checks once every two months (Fig. 5).

3.2 Elasticity of Demand for Residential Water Use

Time series data of water consumption levels, including three-month period records from 1997-2005 (36 time series observation in total), are retrieved by the Municipal Water Utility of the city of Volos and used in the analysis.

According to consumers' water records, the average consumption is 38.2 m³ per 3 months.

Price structure and changes in pricing policy are also collected by the Municipal Water Utility of the city of Volos. Price is inserted in the model as the difference between marginal price and the difference variable and are adjusted by the consumer price index (CPI).

Monthly climatic data (temperature in mm and precipitation in °C) are collected from the records of the meteorological station of the city of Volos. The peak values of rainfall and temperature are noticed at the third and fourth trimester of 2001, while the lowest

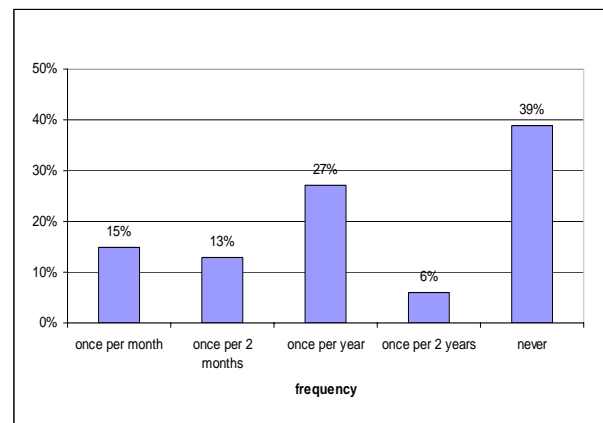


Fig. 5 Frequency of water leakages' control.

values are presented at the third of 2004 and first of 2003 respectively.

The size of the house in square meters is stated in the model as a continuous variable and dummy variables for outdoor uses, educational and income level are also used as independent variables.

In order to derive direct price elasticity estimates of demand for water, a log transformation of Eq. (1) is used and solved with the statistical package STATA (fixed – effects model), water demand evaluation at the mean of the explanatory variables evokes as follows:

$$\ln(C) = -3.632(\ln P)^2 - 0.953(\ln P) + 3.288 \quad (3)$$

The own price elasticity is negative and less than unity in absolute value, so the water demand in the city of Volos is relatively inelastic and water consumption changes less than proportionately with price. A 10% increase in price can lead to a water consumption reduction of 9.53%. This high value means that the current water policy can act as an incentive to water conservation. The model's coefficient for temperature (T) is 0.02, meaning positive in sign and statistically significant (P -value<0.05). It has the expected sign since a 10% increase in temperature leads to a small increase of only 0.2% in water consumption. However, the coefficient of precipitation (R) is 0.19 and is estimated with the opposite sign than expected.

3.3 Future Estimation of Residential Water Demand

In order to predict residential water demand, the variables described above are also used. Variables'

coefficients are estimated using the fixed-effects model. The base year used is 2005 and projections of water consumption levels are made from 2005 to 2017 under different scenarios of water pricing policies.

For the residential sector of the city of Volos, eight potential different pricing scenarios are implemented (Table 3). In the first Scenario, the price of water remains stable from 2005 to 2017. Scenario 2 supposes that there is an increase in water price so that the real price of water will remain stable and equal to the real price of water in 2005 (do nothing scenario). Scenarios 3, 4 and 5 assume a 5%, 10% and 15% increase of the real price of water every four years respectively. In

scenarios 6, 7 and 8 the price of water remains the same from year 2005 to 2009 and the next four years it increases by 5%, 10% and 15% respectively.

In Fig. 6 the estimated consumptions are presented.

In the first two scenarios there isn't actually any increase in the real price of water and consequently there is an increase in water consumption. It is evident that in the first scenario, water consumption levels rise and this could be explained by the fact that under this scenario although the water pricing scheme remains stable, there is a decrease in the real price of water throughout years, as the price is divided by the consumer price index which every year steps up. This

Table 3 Fluctuations of prices under different pricing policies.

Scenario 1					Scenario 5				
m ³ /month	2005 (€/m ³)	2009 (€/m ³)	2013 (€/m ³)	2017 (€/m ³)	m ³ / month	2005 (€/m ³)	2009 (€/m ³)	2013 (€/m ³)	2017 (€/m ³)
0-15	0.400	0.400	0.400	0.400	0-15	0.400	0.518	0.670	0.867
16-38	0.500	0.500	0.500	0.500	16-38	0.500	0.647	0.838	1.084
39-60	0.670	0.670	0.670	0.670	39-60	0.670	0.867	1.122	1.452
61-80	0.730	0.730	0.730	0.730	61-80	0.730	0.945	1.222	1.582
>81	0.930	0.930	0.930	0.930	>81	0.930	1.203	1.557	2.015
Scenario 2					Scenario 6				
m ³ /month	2005 (€/m ³)	2009 (€/m ³)	2013 (€/m ³)	2017 (€/m ³)	m ³ / month	2005 (€/m ³)	2009 (€/m ³)	2013 (€/m ³)	2017 (€/m ³)
0-15	0.400	0.450	0.506	0.570	0-15	0.400	0.450	0.532	0.629
16-38	0.500	0.563	0.633	0.713	16-38	0.500	0.563	0.665	0.786
39-60	0.670	0.754	0.848	0.955	39-60	0.670	0.754	0.891	1.053
61-80	0.730	0.822	0.924	1.040	61-80	0.730	0.822	0.971	1.148
>81	0.930	1.047	1.178	1.325	>81	0.930	1.047	1.237	1.462
Scenario 3					Scenario 7				
m ³ /month	2005 (€/m ³)	2009 (€/m ³)	2013 (€/m ³)	2017 (€/m ³)	m ³ / month	2005 (€/m ³)	2009 (€/m ³)	2013 (€/m ³)	2017 (€/m ³)
0-15	0.400	0.473	0.559	0.660	0-15	0.400	0.450	0.557	0.690
16-38	0.500	0.591	0.698	0.825	16-38	0.500	0.563	0.697	0.863
39-60	0.670	0.792	0.936	1.106	39-60	0.670	0.754	0.934	1.156
61-80	0.730	0.863	1.020	1.205	61-80	0.730	0.822	1.017	1.259
>81	0.930	1.099	1.299	1.535	>81	0.930	1.047	1.296	1.604
Scenario 4					Scenario 8				
m ³ /month	2005 (€/m ³)	2009 (€/m ³)	2013 (€/m ³)	2017 (€/m ³)	m ³ / month	2005 (€/m ³)	2009 (€/m ³)	2013 (€/m ³)	2017 (€/m ³)
0-15	0.400	0.495	0.613	0.759	0-15	0.400	0.450	0.583	0.754
16-38	0.500	0.619	0.766	0.949	16-38	0.500	0.563	0.728	0.943
39-60	0.670	0.829	1.027	1.271	39-60	0.670	0.754	0.976	1.263
61-80	0.730	0.904	1.119	1.385	61-80	0.730	0.822	1.063	1.376
>81	0.930	1.151	1.425	1.765	>81	0.930	1.047	1.354	1.753

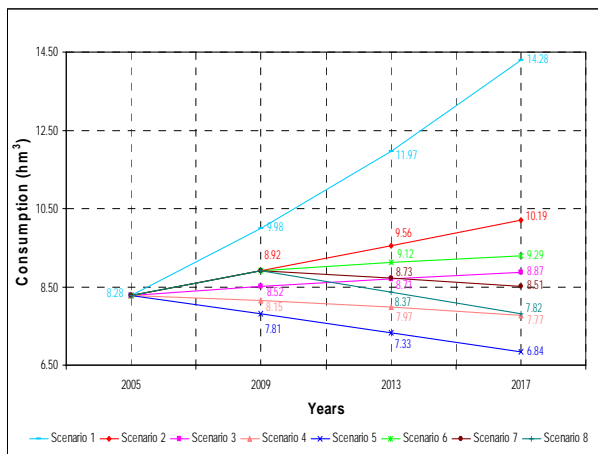


Fig. 6 Fluctuations in future water consumption levels.

is an extreme concept for the stabilization of water prices but provides an explicit view of water demand evolution, in case no water demand management policy takes place in the future.

It should also be noted that the highest increase in water consumption both for 2009-2013 (6.2%) and 2013-2017 (6.6%) is presented under scenarios 5 and 8.

4. Conclusions and Suggestions

In this study, factors affecting the demand for urban domestic water consumption within the city of Volos, Greece are investigated. The value of elasticity with respect to marginal and difference price is estimated to be -0.95, meaning that price elasticity is inelastic (decrease by less than one percent for every one percent increase in price), an observation that has also been verified in many researches so long.

While the price elasticity of demand has turned to be inelastic, consumers respond to price changes, as a high decrease in future consumption levels will occur, if a pricing scenario with a 15% increase in the price of water is implemented.

Further decrease in water consumption levels could be achieved through improvements in the presentation of water price and consumption information on water bills, as it will increase customers' price responsiveness.

Public awareness campaigns are necessary and should be launched in cooperation with stakeholders in

order to inform the users about the importance of water resources. They will aim to inform the public about the role of Water Utility in water resources management, develop an understanding of the significance of water saving, familiarize consumers with and facilitate the use of water saving techniques and increase the awareness of environmental issues related to water utilization.

Consumers' willingness to participate in educational as well as in conservation programmes will strengthen the effectiveness of such measures.

All efforts and interventions in policy formulation and water resources planning should be performed in accordance with public participation.

The results of this study could be safely extrapolated and used by policy makers and water planners in other areas where the socio-economic profile, the climatic conditions and the cultural habits are similar to those of the study area.

References

- [1] P.H. Gleick, *Water in Crisis: a Guide to the World's Fresh Water Resources*, Oxford University Press, Oxford, UK, 1993.
- [2] I.A. Shiklomanov, Appraisal and assessment of world water resources, *Water International* 1 (2000) 11-32.
- [3] FAO, *AQUASTAT 2003*, Food and Agriculture Organization of the United Nations, Rome, Italy, available on line at: <ftp://ftp.fao.org/agl/aglw/aquastat/aquastat2003.xls>.
- [4] F. Arbues, M.A. Garcia-Valinas, R. Martinez-Espineira, Estimation of residential water demand: a state-of-the-art review, *Journal of Socio-Economics* 32 (2003) 81-102.
- [5] D.D. Baumann, J.J. Boland, W.M. Hanemann, *Urban Water Demand Management and Planning*, McGraw Hill Press, United States of America, 1997.
- [6] H. Wang, S. Lall, Valuing water for Chinese industries: a marginal productivity assessment, *Sinosphere* 3 (1999) 27-50.
- [7] L.E. Danielson, An analysis of residential demand for water using micro time-series data, *Water Resources Research* 4 (1979) 763-767.
- [8] R.B. Billings, D.E. Agthe, Price elasticities for water: a case of increasing block rates, *Land Economics* 1 (1980) 73-84.
- [9] J.A. Weber, Forecasting demand and measuring elasticity, *Journal of American Water and Wastewater Association* 5

- (1989) 57-65.
- [10] C.W. Howe, F.P. Linaweaver, The impact of price on residential water demand and its relation to system design and price structure, *Water Resources Research* 1 (1967) 13-32.
- [11] T.F. Hogarty, R.J. Mackay, The impact of large temporary rate changes on residential water use, *Water Resources Research* 6 (1975) 791-794.
- [12] R.A. Lyman, Peak and off-peak residential water demand, *Water Resources Research* 9 (1992) 2159-2167.
- [13] J.J. Opaluch, Urban residential demand for water in the United States: further discussion, *Land Economics* 2 (1982) 225-227.
- [14] J.J. Opaluch, A test of consumer demand response to water prices: reply, *Land Economics* 4 (1984) 417-421.
- [15] R.C. Martin, R.P. Wilder, Residential demand for water and the pricing of municipal water services, *Public Finance Quarterly* 1 (1992) 93-102.
- [16] J.S. Shin, Perception of price when information is costly: evidence from residential electricity demand, *Review of Economics and Statistics* 67 (1998) 591-598.
- [17] M.L. Nieswiadomy, Estimating urban residential water demand: effects of price structure, conservation, and education, *Water Resources Research* 3 (1992) 609-615.
- [18] M.L. Nieswiadomy, D.J. Molina, Comparing residential water demand estimates under decreasing and increasing block rates using household data, *Land Economics* 3 (1989) 280-289.
- [19] R. Griffin, R. Sickles, Demand specification for municipal water management: evaluation of the stone-gearry form, *Land Economics* 3 (2001) 399-422.
- [20] K. Bithas, C. Stoforos, Estimating urban residential water demand determinants and forecasting water demand for Athens metropolitan area, 2000-2010, *South-Eastern Europe Journal of Economics* 1 (2006) 47-59.
- [21] C. Hsiao, *Analysis of Panel Data*, Cambridge University Press, New York, 1986.
- [22] S. Tasoglou, S. Dimitropoulou, Use of Freshwater Resources (GR-EEA CSI 018), National Centre for Environment and Sustainable Development, 2010, available on line at: <http://www.ekpaa.greekregistry.eu>.
- [23] G.N. Bidhendi, T. Nasrabadi, H.R. Vaghefi, H. Hoveidi, H.R. Jafari, Role of water-saving devices in reducing urban water consumption in the Mega-City of Tehran, case study: a residential complex, *Journal of Environmental Health* 8 (2008) 44-47.
- [24] M.A. Renwick, R.D. Green, Do residential demand side management policies measure up? An analysis of eight California water agencies, *Journal of Environmental Economics and Management* 40 (2000) 37-55.
- [25] H.E. Campbell, R.M. Larson, R.M. Johnson, M.J. Waits, Grant Research Performed for the Arizona Department of Water Resources. Some Best Bets in Residential Water Conservation: Results of a Multivariate Regression Analysis, City of Phoenix (1990-1996), 1999, available on line at: <http://www.asu.edu/copp/morrison/bestbets.pdf>.

Treatment of O-nitro-phenol Wastewater with Magnetization-Enhanced Oxidation by NaClO Solution

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Abstract: O-nitro-phenol wastewater which contains refractory organic matters can not be degraded by conventional biological methods. In this work, o-nitro-phenol wastewater was effectively treated using magnetization-enhanced oxidation by NaClO solutions. The pollutant concentrations in wastewater were 250 mg/L o-nitro-phenol, 2,000 mg/L COD_{Cr} and 150 times color. The experimental results show that, using the method in this work, 94.4% o-nitro-phenol, 94.2% COD_{Cr} and 100% color can be removed at pH 6, 200 mg charcoal, 8 mL oxidizer, 5 min reaction time in 1000 mL wastewater. The treatment can be enhanced under magnetic field. COD_{Cr} and o-nitro-phenol removal can keep unchanged while the reaction time can be reduced to 3 min when the intensity of magnetic field was 60 mT.

Key words: Magnetization oxidation, O-nitro-phenol, NaClO.

1. Introduction

O-nitro-phenol is poisonous wastewater. When its concentration is high (such as its mass concentration is more than 1,000 mg/L), the treatment method can use resin to absorption [1], but when its mass concentration isn't high enough (such as the mass concentration is 250 mg/L), the resin-absorption method isn't economical. The biochemical process and the effect usually isn't ideal because of the high toxicity and high mineral salt contents. So searching a technical-economical method to treat with this kind of wastewater is more and more animate. Now there are more and more reports about wastewater treatment directly or indirectly using magnetic field. The research contents come down to mechanism of degradation, analysis of physics, degradation kinetic, analysis of all kinds of factors which affect the process of magnetic-degradation and application on engineering [2, 3]. But the combination of magnet and chemical oxidation method treating organic wastewater isn't

reported. This paper is about experimental studies using magnetization-enhanced oxidation by NaClO solution to treat the o-nitro-phenol wastewater, and the effect is perfect. Its merits are high effect and easy operation.

2. Experimental Part

2.1 Appliance and Reactant

Magnetic stirring apparatus, adjustable electromagnet, NaClO, catalytic agent (granular active carbon).

2.2 Experimental Steps

Put the beakers with 100 mL wastewater on the magnetic stirring apparatus, and regulate the pH of solution, then add some NaClO and catalytic agent. After some reaction, then filtrate the water sample, take the filter liquor to determinate its COD_{Cr} and chromaticity, at last, count their removal rate (The GB is used to determinate COD_{Cr}, the multiple dilution method is used to determinate the chromaticity). When the magnetization-enhanced experiment is done, putting the beakers in the magnetic field, then the

P. Zhang (1985-), female, post graduate student, dedicating in studying the potion using to deal with wastewater.

experiment is operated on the same conditions as before.

3. Results and Discussion

3.1 The Targets of Wastewater

The level of o-nitro-phenolis AR. The concentration of o-nitro-phenolis is 250 mg/L, COD_{Cr} is 2 000 mg/L, chromaticity is 150 times, pH 6.0.

3.2 Discussion on Reaction Mechanism

Granular active carbon has mighty adsorption effect. The pollutant adsorpted on the surface is high concentration, and easily oxidated by NaClO. The surface of granular active carbon offers many active centers, the oxidation reaction and the reduction are easily going in these active centers. After the magnetic treatment, the removal rate of COD_{Cr} and chromaticity have some elevation. The reason is that if the reaction system situated in the magnetic field, the rank of element is more regular and more easily absorbed in the center of granular active carbon. Then the rate of reaction is enhanced, and the removal rate of pollutant is enhanced.

3.3 The Selection of the Quantity of Oxidant

100 mL water sample, the quantity of granular active carbon is 200 mg, pH 6.0, reaction time is 30 min. The quantity of oxidant is tested (concentration of NaClO is 2.5%), the results is as Table 1.

Table 1 showed that when the oxidant doesn't add into the reaction system, the o-nitro-phenol, COD_{Cr} and chromaticity has some removal rate. This is because that the absorption of the granular active carbon. As soon as adding the oxidation, these removal rate will have marked election. And the more the quantity of oxidant, the more the removal rate it is. When the quantity of oxidant is 12 mL, the removal rate of o-nitro-phenol will enhance slowly (there are a little intermediate product which is hardly oxidated), but the removal rate of COD_{Cr} has a little decline. The

reason is that there are much Cl⁻ in the solution, when the concentration of Cl⁻ is high, it will react with K₂Cr₂O₇ and generate Cr³⁺. Then the [(NH₄)₂Fe(SO₄)₂ · 6H₂O] using in the titration process will enhance and then COD_{Cr} will be higher than true value. Although the HgSO₄ can be used to bury the disturbance of Cl⁻, it is useful to little Cl⁻. Concluding it, the best quantity of oxidant is 8.0 mL/100 mL water sample.

3.4 The Selection of Reaction Time

100 mL water sample, the quantity of granular active carbon is 200 mg, pH 6.0, the quantity of oxidant is 8.0 mL. The reaction time is tested, the results are as Table 2.

As the increase of reaction time, these removal rate will enhance gradually. But when the reaction time is more than 5 min, the removal rate of chromaticity will reach 100%, and the removal rate of o-nitro-phenol and COD_{Cr} won't increase. This is because that when the organics are oxidated, there are some intermediate product and some of them are hard to be oxidated on the condition of this experiment. Although the reaction time is enhanced, these intermediate product can't be oxidated. So 5 min reaction time is OK in this experiment.

Table 1 Selection of oxidant.

Quantity of oxidant (mL)	Removal rate of o-nitro-phenol (%)	The removal rate of COD _{Cr} (%)	The removal rate of chromaticity (%)
0	46.5	45.6	4
4.0	88.9	89.7	97
8.0	94.4	94.2	100
12.0	94.7	92.5	100
16.0	95.0	89.6	100

Table 2 Selection of reaction time.

Reaction time (min)	The removal rate of o-nitro-phenol (%)	The removal rate of COD _{Cr} (%)	The removal rate of chromaticity (%)
3.0	93.5	93.2	98
5.0	94.5	94.2	100

10.0	94.0	93.8	100
20.0	94.2	93.2	100
30.0	94.5	94.2	100

3.5 The Selection of the Solution' pH

100 mL water sample, the quantity of granular active carbon is 200 mg, the quantity of oxidant is 8.0 mL, the reaction time is 5 min, pH is changed, the results are as Table 3.

The higher the acidity of the solution, the better the removal rate of COD_{Cr} and chromaticity is. When the pH ≥ 7.0, the effect is bad. This is because that when the pH ≥ 7.0, the main style of NaClO is ClO⁻, and the oxidizing ability of ClO⁻ is worse, and the organization of o-nitro-phenol has changed, which isn't good to oxidate. But when the pH is less than 7.0, the main style is HClO, the difference of the standard electrode potentials between HClO and ClO⁻ is 1.209.6 V, so the oxidizing ability of HClO is high, and the organization of o-nitro-phenol in the wastewater doesn't change, it is easy to oxidate. Based on a comprehensive analysis of it, the pH 6.0 is the ideal value.

3.6 The Quantity of Granular Active Carbon

100 mL water sample, pH=6.0, the quantity of oxidant is 8.0 mL, reaction time is 5 min, the quantity of granular active carbon is tested. The results are as Table 4.

Table 4 shows that when the granular active carbon isn't added into the system, some removal rate of them is existent, this is caused by the oxidation. But as soon as the granular active carbon is added into the system, the removal rate of COD_{Cr} and chromaticity will be enhanced significantly. This shows that the effect of the granular active carbon is significant. So the quantity of the granular active carbon is 200 mg/100mL water sample.

3.7 The Influence of the Magnetic Field

100 mL water sample, pH=6, the quantity of the catalytic agent is 0.2 g, the oxidant is 8 mL. Under the

influence of the 60 mT magnetic field, the change of the removal rate of COD_{Cr} is as Table 5.

When there is magnetic field, the removal rate of COD_{Cr} will reach 94.2% after 2 min. It saves 3 min.

Table 3 Selection of pH of solution.

pH of solution	The removal rate of o-nitro-phenol (%)	The removal rate of COD _{Cr} (%)	The removal rate of chromaticity (%)
2.0	95.0	95.1	100
4.0	94.7	94.8	100
6.0	94.4	94.2	100
7.0	92.1	91.1	96
8.0	87.6	86.3	82

Table 4 Selection of granular active carbon' quantity.

The quantity of catalytic agent (mg)	The removal rate of o-nitro-phenol (%)	The removal rate of COD _{Cr} (%)	The removal rate of chromaticity (%)
0	85.2	85.5	92
100	89.9	90.1	95
200	94.4	94.2	100
400	95.3	95.2	100
500	95.5	95.4	100
800	95.6	95.8	100

Table 5 The influence of applied magnetic field.

Reaction time (min)	The removal rate of o-nitro-phenol (%)	The removal rate of COD _{Cr} (%)	The removal rate of chromaticity (%)
1	92.3	92.5	95
2	94.4	94.2	100
3	94.7	94.6	100
4	94.9	94.8	100
5	96.0	95.8	100

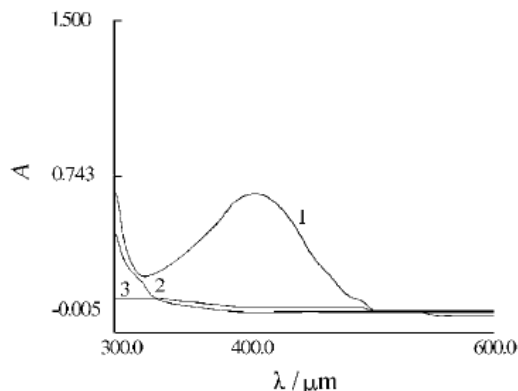


Fig. 1 UV spectrogram of the pre-treating and post-treating wastewater.

1. pre-treatment, UV spectrogram of wastewater; 2. un-magnetize, UV spectrogram of wastewater after oxidation treatment; 3. post-magnetize, UV spectrogram of wastewater after oxidation treatment.

Therefore, the more the reaction time, the higher the removal rate of COD_{Cr} it is.

Table 6 The targets of pre-treatment and post-treatment.

Target	o-nitro-phenol	COD _{Cr}	Chromaticity (%)	pH
Pre-treatment	250.0mg/L	2000 mg/L	400	6
Un-magnetize		112		
Un-oxidation (5min)	13.2 mg/L	mg/L	0	6
Post-magnetize post-oxidation (5min)	94.7 mg/L	94.6 mg/L	100	6

4. Conclusions

(1) The UV spectrogram of the pre-treating and post-treating wastewater is shows as Fig. 1. When the wastewater isn't treated, there is a significant absorption peak in the UV area. When it is oxidated, the peak in 400 nm will disappear, the line in 300 nm is also lower. This shows that oxidating treatment has

some effect on the removal of pollutant in the wastewater. After the treatment of magnetic field, the absorption peak is barely disappeared, which shows that the effect of magnetic field is significant.

(2) The results is as Table 6. It shows that, the effect of experiment is significant, the method of this experiment can be used in the treatment of o-nitro-phenol wastewater.

Acknowledgments

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References

- [1] H. Jiang, Q.X. Zhang, J.L. Chen, Study on the treatment of o-nitrophenol wastewater with polymeric adsorbent, ion exchange and adsorption 6 2000 540-556.
- [2] M. Luo, Z. Lu, Effects of magnetic field on CaCO₃ crystallization, Journal of East China Univ. of Sci. and Technol. 2 (2000) 177.
- [3] W.G. Dong, Z.X. Yang, G.Y. Yue, Certain physisal and chemistrical characters of magnetic water, Journal of Taishan Medical College 3 (1992) 234.

Simulation of Water Quality of Neijiang River Based on RMA4 Model

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Abstract: Using the RMA4 water quality model to simulate the water quality of Neijiang river in Zhenjiang, the result showed that: in the dry season the ranges of the concentration of various pollutants simulation of Neijiang were BOD₅ 3.2-5.2 mg/L, COD_{Mn} 4.7-6.8 mg/L, NH₃-N 0.46-1.8 mg/L, TP 0.23-0.48 mg/L, and in the rainy period, the ranges of the concentration of various pollutants simulation of Neijiang were BOD₅ 0.69-0.73 mg/L, COD_{Mn} 1.9-2.3 mg/L, NH₃-N 0.25-0.38 mg/L, TP 0.14-0.17 mg/L. These simulated values were closed to the monitoring values of pollution concentrations of Neijiang, which indicated that RMA4 was certain practical in the river water quality simulation, and simulation results have a certain degree of reliability, and it provides a scientific planning and management method for the river pollution control.

Key words: RMA4, Neijiang river, water quality simulation, environment planning.

1. Introduction

Zhenjiang Neijiang is a 8.8 km² water region between the Zhenjiang City and the outside Yangtze River divided by the Zhengrunzhou. The rivers connected with the Neijiang are Yunliang River, the ancient canal, Hongqiao Port, attempt running diversion canal and approach channel. Fig. 1 shows the whole map of Neijiang water system.

Neijiang is a part of the tidal flow regime of the Lower Yangtze area, and in the whole year it mainly charged by the rain-flood run-off and at the same time affected by ocean tides, so the diffusion, migration and transformation processes of pollutants in Neijiang are more complicated. The aim of establishment of Neijiang water quality model is to try to determine the quantitative relationship of these mutual restricted factors, and in other words, the water quality model is a mathematical method to describe the physics, chemistry, biology, ecology and many other aspects of

variation and interaction occurred between the various water quality components participate in the water cycle. It can be used to water quality simulation and water quality evaluation, forecasting, early warning and predicting of water quality, and to develop pollutant discharge standards and water quality planning, so it's an important tool for water pollution prevention and control.

2. RMA4 Water Quality Model

2.1 RMA4 Basic Equation

Water quality model (RMA4) is designed to simulate the depth average convection-diffusion processes

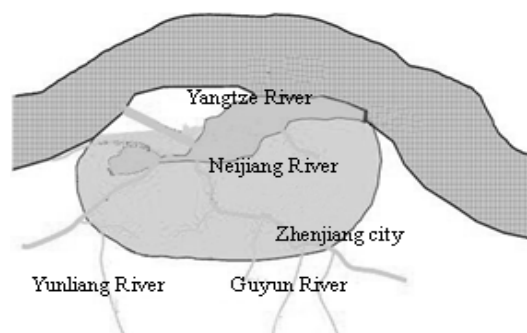


Fig. 1 The whole map of Neijiang water system.

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Table 1 The concentration of boundary contaminations (units: mg/L).

Water quality factors	BOD ₅		COD _{Mn}		NH ₃ -N		TP	
	High water season	Low water season	High water season	Low water season	High water season	Low water season	High water season	Low water season
Yinhang channel	0.7	3.2	2	4.8	0.26	0.45	0.14	0.26
Yunliang River	1.1	11.1	5	23.9	0.91	4.66	0.32	1.87
Guyun River	0.9	6.5	3.9	10.6	0.99	2.69	0.34	1.18
Hongqiao port	1.6	12.9	7.7	16.8	4.1	14.44	0.84	1.39

of the water environment [1, 2]. It can be used to study the pollutants transport and diffusion numerical simulation of reservoirs, rivers, bays, estuaries and coastal areas, and the optimization of the sewage outfall, the oil spill evaluation, the aquatic habitat management. Basic equation is as follows [2]:

$$h \left(\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} - \frac{\partial}{\partial x} D_x \frac{\partial c}{\partial x} - \frac{\partial}{\partial y} D_y \frac{\partial c}{\partial y} - \sigma + kc + \frac{R(c)}{h} \right) = 0 \quad (1)$$

Where, h - water depth; c - concentration of a given components of pollutants; t -time; u , v -the velocity of x and y direction; D_x , D_y -turbulent mixing (diffusion) coefficients; k -the first attenuation of contaminants; σ -the source/sink of elements; $R(c)$ -the rate of rainfall/evaporation.

2.2 Basic Parameters

(1) The diffusion coefficient

The equation includes two directions of diffusion coefficients of D_x and D_y . They are artificial physical assumptions, and valuate through the observation data. To the problems of the water environment, diffusion is often a very important media transfer process. Therefore, choosing an objective, rational analysis of the diffusion coefficient of water quality is very important.

(2) Physical decay

Considered the material attenuation according to the first order reaction kinetics. For conservative substances, attenuation coefficient is 0; for non-conservative substances, attenuation coefficient is greater than 0. The smaller the attenuation coefficient is, the slower the material decays; the greater the attenuation coefficient is, the faster the material decays.

3. Neijiang Water Quality Model Based on RMA4

3.1 Set the Initial Conditions

According to the characteristics of the Neijiang River, set Yinhang Channel, Yunliang River, Guyun River and Hongqiao port for the open boundary conditions. Referring to the monitoring data from the environmental monitoring stations, the pollution concentration of the boundary pollutants is shown in Table 1. The concentration of pollutants within the river area monitored at the same time is shown in Fig. 2, and this is the basis to test whether the water quality model is right and wrong.

3.2 Determination of Water Quality Parameters

Collection a large number of references domestic and abroad referring to river pollutants attenuation coefficient, as well as laboratory measurements to determine that in RMA4 the attenuation coefficients of the BOD₅, COD_{Mn}, NH₃-N and TP were 0.05 d⁻¹, 0.05 d⁻¹, 0.15 d⁻¹ and 0.15 d⁻¹. According to Dickie Hudson formula which is solving the diffusion coefficient and the experimental monitoring data to determine the diffusion coefficient of BOD₅, COD_{Mn}, NH₃-N and TP in RMA4 is 1.0 sec/m².

3.3 Operation of the Model

Enter the initial conditions and operating parameters then obtained the RMA4 model simulation results. Figs. 3 and 4 are separately given for the pollutant concentration curve of each river represent spots V13-V19 during the low water season and high water season.

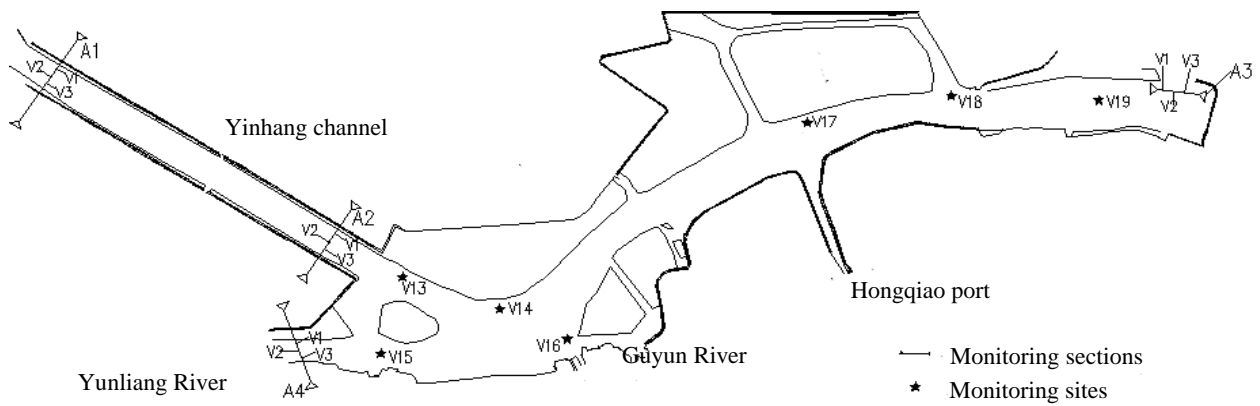
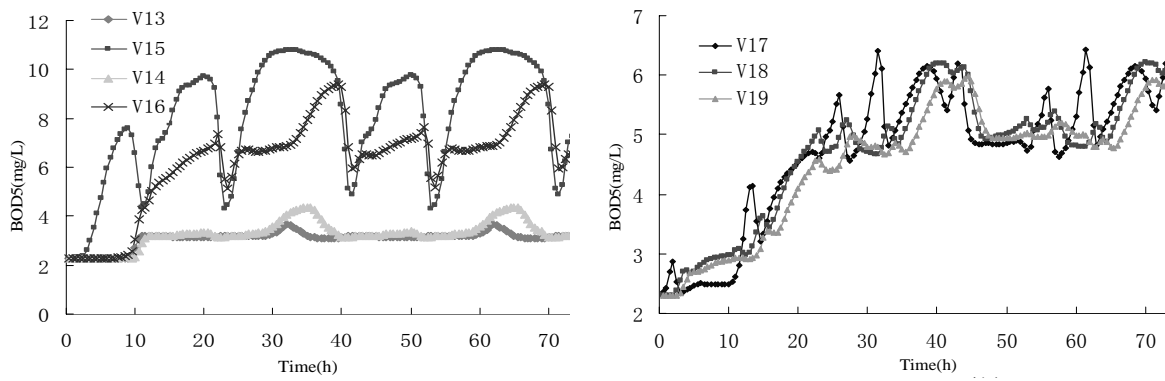
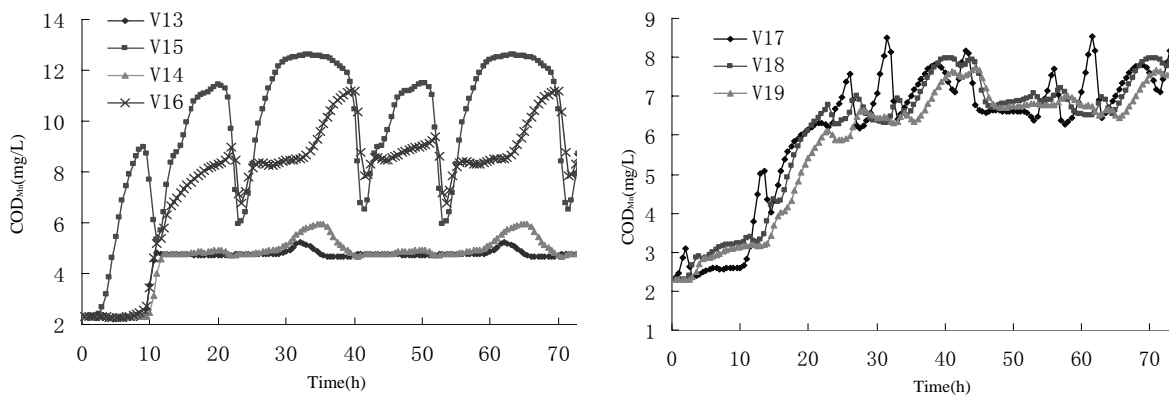


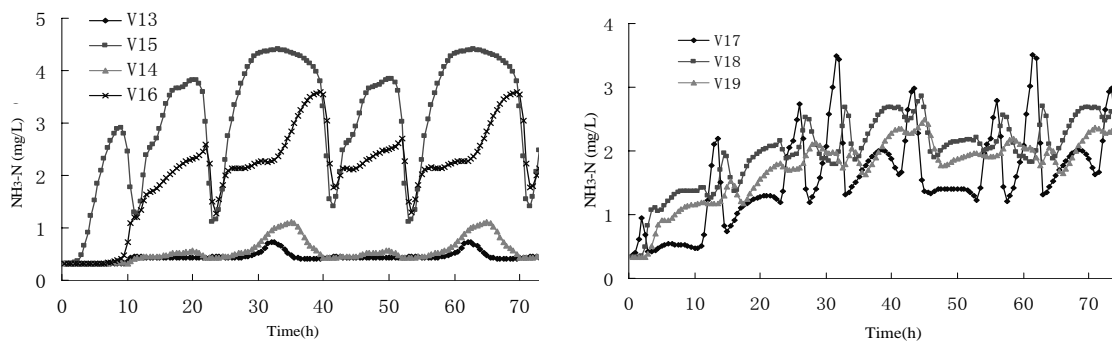
Fig. 2 The layout diagram of hydrology and water quality observed profile in Neijiang.



(1) concentration curve of BOD₅



(2) concentration curve of COD_{Mn}



(to be continued)

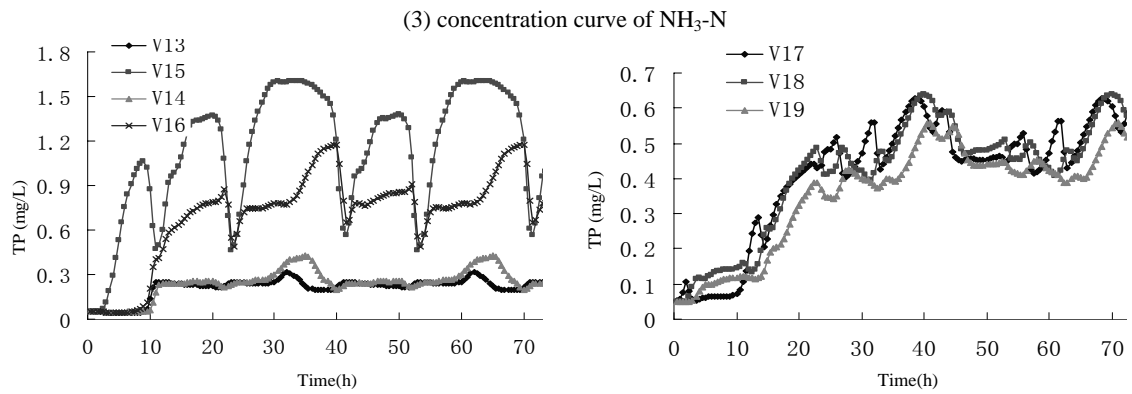
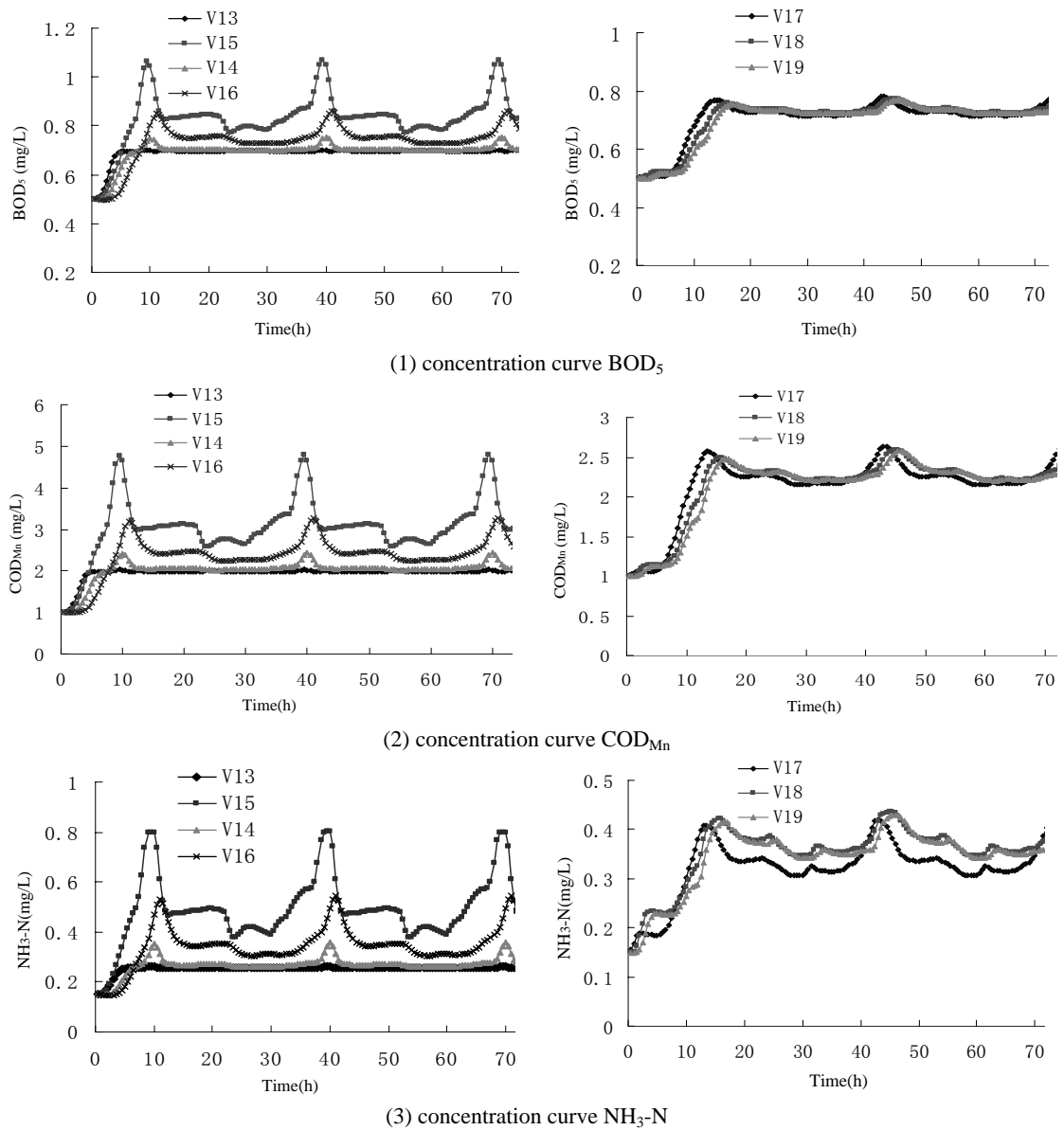
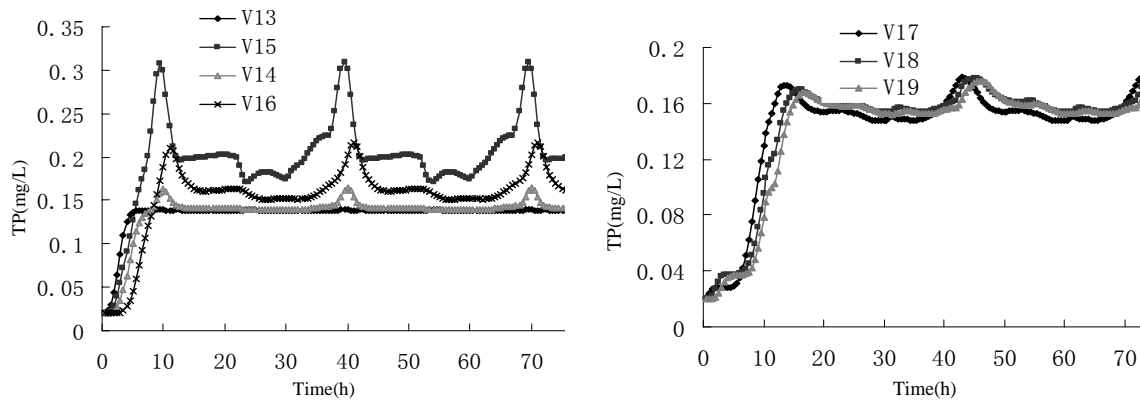


Fig. 3 The concentration curve of pollutant in Neijiang during low water season.



(to be continued)



(4) concentration curve TP

Fig. 4 The concentration curve of pollutant in Neijiang during the high water season.**Table 2** The water quality monitoring results of Neijiang (units: mg/L).

Monitoring point	Wharf No.3		Downstream of Hongqiao port		Jiaonan dam	
	Low water season	High water season	Low water season	High water season	Low water season	High water season
Water quality factors						
COD _{Mn}	5.2	2.2	8.2	2.3	5	2.1
BOD ₅	2.7	0.8	5.85	0.9	3.8	0.7
NH ₃ -N	0.66	0.23	0.59	0.22	1.28	0.22
TP	0.31	0.173	0.29	0.165	0.24	0.12

In the low water season the concentration range each pollutant simulation in Neijiang are: BOD₅ 3.2-5.2 mg/L, COD_{Mn} 4.7-6.8 mg/L, NH₃-N 0.46-1.8 mg/L, TP 0.23-0.48 mg/L; in the high water season the concentration range of of each pollutant simulation in Neijiang are: BOD₅ 0.69-0.73 mg/L, COD_{Mn} 1.9-2.3 mg/L, NH₃-N 0.25-0.38 mg/L, TP 0.14~0.17 mg/L. The simulation values are coincided with the pollutant concentrations of Neijiang water listed in Table 2.

4. Conclusions

In this paper, we used the the RMA4 water quality model to simulate the migration and transformation process of the pollutants in Neijiang, and the simulated values and monitoring values were comparative fit

within a certain range, indicating that RMA4 is certain practicality in river water quality simulation, and the simulation results have a certain reliability, too. Using the model to simulate the dynamic process and water quality conditions of river water could refer the references for management to regional environmental planning.

References

- [1] SMS Tutorials Vresion 8.1, Brigham Young University-Environmental Modeling Research Laboratory, 2004.
- [2] Users Guide to RMA4 WES Version 4.5, US Army, Engineer Research and Development Center Waterways Experiment Station Coastal and Hydraulics Laboratory, 2003.

Elemental Analysis of Air Suspended Particles in Rasht City Using Instrumental Neutron Activation Analysis

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Abstract: Instrumental neutron activation analysis (INAA) has turned out to be particularly useful in the analysis of suspended particles. This work describes the INAA characterization of air particulate matter collected in Rasht city, Iran. The particulate matter was collected in two sampling sites for elemental analysis in the period of winter-summer 2009. Samples have been transferred to the environmental laboratory of radiation applications research school. Neutron exposures were performed in Tehran Research Reactor, and measurements were carried out using HPGe detectors coupled to gamma ray spectrometer. In these filter samples, the elements, Al, As, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, Hg, K, La, Mg, Mn, Na, Sb, Sc, Ti, V and Zn were determined using different irradiation and counting protocols. Results show that mean concentration of most air-pollutants in Rasht are lower than those measured in other cities in Iran (Tehran, Shiraz, Isfahan). Collected data were also compared with reported results for other cities in the world.

Key words: Instrumental neutron activation analysis, air pollutants, particulate matter, Rasht city, toxic elements.

1. Introduction

Air supplies us with oxygen which is essential for our bodies to live. Air is 99.9% nitrogen, oxygen, water vapor and inert gases. An air pollutant is known as substances in the air that can cause harm to human and environment [1]. There are several main types of pollution and well-known effect of pollution which are commonly discussed. One type of air pollution is the particulate matter (PM) in the air. Particulate matter or fine particles are tiny particles of solid or liquid suspended in gas. Sources of particulate matter can be man-made or natural. Natural particulate originate mainly from volcanoes, dust storm, forest and grassland fires, living vegetation and sea spray. Human activities such as the burning of fossil fuels in vehicles, power plants and various industrials processes also generate significant amount of aerosols [2]. A large

number of studies have been carried out on the elemental compositions of particulate and association between human exposure to this type of pollution and occurrence of sever health injuries. Arsenic is a human carcinogen [3], cadmium may give rise to various renal alterations, manganese is characterized by various psychiatric, movement disorders [4] and chromium compounds are toxic and carcinogenic. Bronchial tree is the major target organ for the carcinogenic effect of chromium compounds. Mercury can effect on the kidney and chronic exposure to vanadium compounds revealed a continuum in the respiratory effects, ranging from slight changes in the upper respiratory tract like coughing to more serious effects such as chronic bronchitis and pneumonitis [5]. Another type of pollution is the release of noxious gases, such as sulfur dioxide, carbon monoxide, nitrogen oxides and chemical vapors.

According to WHO (World Health Organization) assessment of the burden of disease due to air pollution, more than 2 million premature death each year can be

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attributed to the effect of urban outdoor air pollution and indoor air pollution (caused by the burning of solid fuels).

More than half of this disease burden is borne by the population of developing countries [6]. Recognizing the need of human for clean air, WHO Air quality guidelines have been published since 1987. The guidelines are intended to provide background information and guidance to (inter) national and local authorities in order to make risk assessment and risk management decisions [7]. They also provide a basis for setting standards or limit value for air pollutants. Depending on specific groups at risk should be protected and degree of risk considered, national standards may differ from country to country and may be above or below the respective WHO guideline values. As a part of development of air quality monitoring programs, the main aim of this research was to determine concentration of elements in the air of Rasht city, the capital of Iranian Northern Province of Guilan, and to compare obtained results with those measured in other cities and WHO air quality guidelines.

2. Experimental Methods

Particulate matter was collected at two sampling sites A and B all located in Rasht city, Iran. Samples were collected on whatman 41 filter using air sampler operating at $6 \text{ m}^3 \cdot \text{h}^{-1}$ for 12 h. The collection was carried out during winter-summer 2009 and 100 samples were collected in that period.

Instrumental neutron activation analysis was employed to determine the composition of the elements in material collected on the air filter. For elemental analysis, the filters were cut into four parts. Using pneumatic sample transfer system, one quarter of the filter was irradiated along with standard of elements SN-D-1/2 supplied from IAEA (International Atomic Energy Organization) for 2 minutes at the Tehran research reactor. The thermal neutron flux utilized was about $3 \times 10^{13} \text{ n cm}^{-2} \cdot \text{s}^{-1}$. Samples and standard were

measured immediately after irradiation to determine V, Al, Ca, Mg, Ti and Cu. After one hour decay time (for decay of short half life radionuclides) the same sample and standard were measured again to determine K, Ba, Cl, Mn and Na.

For determination of Zn, Sc, Sb, As, Br, Cr, Fe, Hg, La and Co second quarter of the same filter and standards were irradiated for 2 h and were measured after one and two weeks decay times.

Measurements were carried out using HPGe detector with 10 percent relative efficiency coupled to gamma ray spectrometer. The quantities of the elements in each sample were calculated through comparative method, the radioisotopes used in these determinations are listed in Table 1 [8].

The blank of the filter was also analyzed and considered in these calculations, with the quantity of each element in the filter and having the volume of air suctioned, the concentration of elements in the air was

Table 1 Radionuclides, their main photopeak energy and half life.

Element	Radionuclide	Energy (keV)	Half life
Al	^{28}Al	1779	2.24 m
As	^{76}As	559	26.30 h
Ba	^{139}Ba	166	83.30 m
Br	^{82}Br	554	35.40 h
Ca	^{49}Ca	3084	8.27 m
Cl	^{38}Cl	2168	37.20 m
Co	^{60}Co	1173	5.27 y
Cr	^{51}Cr	320	27.70 d
Cu	^{66}Cu	1039	5.10 m
Fe	^{59}Fe	1099	44.50 d
Hg	^{203}Hg	279	46.60 d
K	^{42}K	1525	12.40 h
La	^{140}La	1596	1.68 d
Mg	^{27}Mg	1014	9.45 m
Mn	^{56}Mn	847	2.58 h
Na	^{24}Na	1368	15.00 h
Sb	^{122}Sb	564	2.72 d
Sc	^{46}Sc	889	83.80 d
Ti	^{51}Ti	320	5.76 m
V	^{52}V	1434	3.75 m
Zn	^{63}Zn	1115	243.00 d

Table 2 Comparison of average concentration of the measured air-pollutants ($\mu\text{g}\cdot\text{m}^{-3}$) in Rasht with those measured in other cities.

Element	Rasht Min-Max mean \pm SD 2009	Esfahan mean 2008	Tehran mean 2001 [9]	Shiraz mean 2000 [10]	Beijing mean 2008 [11]	Pavia mean 1999 [12]	Milan mean 1998 [13]
Al	1.60E-01 – 6.51E+00 1.71E+00 \pm 1.24E+00	4.48E+00	2.86E+00	2.56E+00	4.69E+00	-	-
As	9.32E-05 – 5.50E-02 3.52E-03 \pm 7.20E-03	3.39E-02	2.92E-02	-	5.82E-02	3.00E-03	4.60E-03
Ba	1.03E-02 – 1.05E-01 3.69E-02 \pm 2.70E-02	1.20E-01	-	-	-	5.70E-02	1.12E-01
Br	9.52E-03 – 3.78E-01 3.82E-02 \pm 5.70E-02	3.21E-02	2.21E-01	4.13E-01	-	4.15E-02	3.42E-01
Ca	1.15E+00 – 1.11E+01 3.53E+00 \pm 1.84E+00	2.02E+01	5.34E+00	1.33+01	1.20E+01	-	-
Cl	1.24E+00 – 6.17E+00 2.66E+00 \pm 9.90E-01	6.02E+00	1.42E+00	-	-	-	-
Co	7.67E-04 – 9.31E-03 3.35E-03 \pm 2.00E-03	6.37E-03	3.81E-03	-	4.23E-03	1.70E-03	4.30E-03
Cr	5.68E-04 – 9.98E-02 1.94 E-02 \pm 2.00E-02	3.25E-02	1.07E-02	1.50E-02	2.32E-02	2.50E-02	6.50E-02
Cu	2.32E-02 – 1.93E-01 1.13E-01 \pm 4.00E-02	1.56E-01	8.05E-02	1.22E-01	1.57E-01	4.65E-02	6.50E-02
Fe	7.90E-01 – 5.66E+00 2.19E+00 \pm 1.28E+00	8.31E+00	2.27E+00	2.62E+00	5.87E+00	2.60E+00	2.70E+00
Hg	1.07E-04 – 1.65E-03 5.58E-04 \pm 4.40E-04	2.08E-03	5.29E-04	-	-	8.00E-04	1.70E-03
K	1.00E-01 – 3.60E+00 7.32E-01 \pm 6.50E-01	3.68E+00	1.09E+00	-	-	1.05E+00	9.34E-01
La	9.91E-05 – 9.65E-03 1.79E-03 \pm 2.00E-03	6.20E-03	2.13E-03	-	-	1.00E-03	1.50E-03
Mg	2.10E-01 – 3.50E+00 7.04E-01 \pm 4.80E-01	2.34 E+00	8.60 E-01	-	-	2.96E+00	3.10E+00
Mn	1.04E-02 – 9.76E-02 3.69E-02 \pm 2.00E-02	1.43E-01	5.57E-02	5.30E-02	2.96E-01	5.25E+00	7.80E-02
Na	4.80E-01 – 3.70E+00 1.23E+00 \pm 6.20E-01	3.22 E+00	1.13 E+00	-	-	-	-
Sb	8.91E-04 – 9.97E-03 2.47E-03 \pm 1.70E-03	3.90E-03	1.38E-02	-	4.37E-02	1.20E-02	5.70E-02
Sc	1.01E-04 – 1.97E-03 5.71E-04 \pm 4.60E-04	1.84E-03	5.07E-04	8.00E-04	-	5.50E-04	1.00E-03
Ti	2.33E-02 – 4.80E-01 1.44E-01 \pm 9.30E-02	7.11E-01	2.23E-01	-	3.37E-01	1.09E-01	7.60E-02
V	1.01E-03 – 1.26E-02 4.01E-03 \pm 2.50E-03	2.27E-02	2.43E-02	9.00E-03	1.35E-02	1.68E-02	3.40E-02
Zn	2.04E-02 – 1.80E+00 1.69E-01 \pm 2.50E-01	2.14E-01	5.07E-01	8.50E-02	1.09 E+00	2.16E-01	2.39E-01

calculated. For verification and evaluation of analytical method, two IAEA's standard reference materials (SL-1 and SD-N-1/2) were chosen and the accuracy and precision of the analytical procedure were estimated by comparison to the certified values. Uncertainty components associated with analytical techniques (including counting statistics, reported standard mass and sampling) were determined and total uncertainty of the measurements were estimated to be within 10-30% in 95% confidence level.

3. Results and Discussion

Table 2 shows the mean concentration of elements in TSP samples collected in Rasht, Esfahan, Tehran, Shiraz, Milan, Pavia and PM₁₀ samples collected in Beijing.

Results show that the levels of most air pollutants in Rasht are lower than those measured in other cities in Iran by the same technique. Compared to other cities in the world except for few elements, mean concentration

Table 3 WHO air quality guidelines for inorganic pollutants.

Element	Guideline ($\mu\text{g}\cdot\text{m}^{-3}$)	Accessed life-time risk level
Arsenic	66.0E-03	1:10000
	6.6E-03	1:100000
	5.0E-03	1:1000000
Cadmium (VI)	5.0E-03	-
	2.5E-03	1:10000
Chromium	2.5E-04	1:100000
	2.5E-05	1:1000000
	1.0	
Mercury *	1.0	
Vanadium **	1.0	
Manganese	1.5E-01	

* For inorganic Mercury as an annual average.

** For an average time of 24 hours.

of elements in air of Rasht are lower than those reported for Milan and Pavia. Besides, these concentrations are lower than concentrations obtained from measurements of PM_{10} samples collected in Beijing.

Table 3 contains WHO guidelines for concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) of As, Cd, Cr, Mn, Hg and V in ambient air [7].

Considering protection of the public and ecosystems from the adverse effect of air pollution, mean concentrations of the measured pollutants in Rasht may be used along with WHO air quality guidelines for risk assessment of the exposed population. Results from this comparison show that mean concentrations of the measured inorganic pollutants in Rasht are in agreement with WHO air quality guidelines for inorganic pollutants. Due to considerable differences in element concentrations, depending on the day of sample collection, more detailed studies are needed to control the emission of pollutants in this region.

4. Conclusions

As a part of development of air quality monitoring programs in order to determine and control the emission of pollutants in different cities in Iran, concentration of elements in the air of Rasht city, the capital of Iranian Northern Province of Guilan, were determined and were compared with those measured in other cities. Although obtained results show that the levels of measured air-pollutants in Rasht are lower than those measured in other cities in Iran by the same

technique but due to great variability among concentrations depending on the day of sample collection denoted by the standard deviation of the mean concentrations, more detailed studies are needed to control the emission of pollutants in this region.

References

- [1] EPA: Air Pollutants, available online at: http://www.epa.gov/ebtpages/air_pollutants.html.
- [2] P. Brimblecombe, Air Composition & Chemistry (2nd ed.), Cambridge University Press, 1996.
- [3] E.A. Woolson, Man's perturbation of the arsenic cycle, in: W.H. Lederer, R.J. Fensterheim (Eds.), Arsenic: Industrial, Biomedical and Environmental Perspectives, Proceedings of the Arsenic Symposium, Gaithersburg, MD. Van Nostrand Reinhold, New York, 1983.
- [4] H.A. Roels et al., Assessment of the permissible exposure level to manganese in workers exposed to manganese dioxide dust, British Journal of Industrial Medicine 49 (1992) 25-34.
- [5] C.E. Lewis, The biological action of vanadium: the signs and symptoms of occupational vanadium exposure, AMA Arch Ind Health 19 (1959) 497-503.
- [6] World Health Organization, Reducing risks, promoting healthy life, World Health Report, Geneva, 2002.
- [7] Air Quality Guidelines for Europe (2nd ed.), WHO Regional Publication, European Series, No.91, 2000.
- [8] M. Sohrabpour, H. Mirzaee, S. Rostami, M. Athari, Elemental concentration of the suspended particulate matter in the air of Tehran, Environment International 25 (1991) 75-81.
- [9] M. Athari, M. Sohrabpour, S. Rostami, Elemental characterization of TSP and two size fractions of airborne particulate matter from Tehran by INAA and AAS, Journal of Radioanalytical and Nuclear Chemistry 260 (2004) 351-356.
- [10] K. Hadad, S. Mehdizadeh, M. Sohrabpour, Impact of different pollutant sources on Shiraz air pollution using SPM elemental analysis, Environment International 29 (2003) 29-43.
- [11] T. Okada, M. Katsuno, D. Naoi, S. Nakao, S. Tanaka, Trends in hazardous trace metal concentrations in aerosols collected in Beijing, China from 2001 to 2006, Chemosphere 72 (2008) 917-924.
- [12] E. Rizzio, G. Bergamaschi, A. Profumo, M. Gallorini, The use of neutron activation analysis for particle size fractional and chemical characterization of trace elements in urban air particulate matter, Journal of Radioanalytical and Nuclear Chemistry 248 (2001) 21-28.
- [13] H. Bem, M. Gallovinci, E. Rizzio, M. Krzemiska, Comparative studies on the concentrations of some elements in the urban air particulate matter in Lodz city of Poland and Milan, Italy, Environment International 29 (2003) 423-428.

Investigate the Parameters Effect on Thermogravimetry Analysis (TGA) Performance for SO_x Additive in FCC Units

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Abstract: Although the FCC process has been used for more than half a century, new and important developments continue to be made in several areas. Some of these new developments are a direct response to environmental regulation. Sulfur oxides (SO_x ⇌ SO₂+SO₃) emitted from fluid catalytic cracking units (FCCU) are one of the most hazardous atmospheric pollutants, which may cause serious environmental problems such as the formation of acid rain and the destruction of the ozone layer. Thus, great attention has been focused on the SO_x removal from FCC in last few years. The present papers will focus on the spinel material studies include three samples they were prepared by acidic method, solid solution MgAl₂O₄, solid solution with cerium 10%Ce/MgAl₂O₄, iron mixed spinel with cerium 10%Ce/MgAl_{2-x}FeO₄.MgO and two samples solid solution with cerium introduce by vanadium as second co-catalyst prepared by basic method, 1% V/10%Ce/MgAl₂O₄.MgO were tested in TGA for oxidation half cycle to study some parameters effect on performance of SO_x additives in TGA under condition similar to those of FCC units. Thermogravimetry analysis experiments have been used to demonstrate the pick-up and release of sulfur oxides in the development of additives for SO_x control in the FCCU.

Key words: FCCU, SO_x, TGA, spinel.

1. Introduction

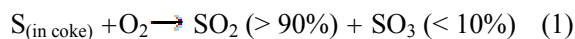
Fluid catalytic cracking (FCC) is a central technology in modern refining [1]. The FCC unit is used to upgrade heavy oils and residue fuels to gasoline, diesel fuel, and light gases. Sulfur oxides, SO_x ⇌ (SO₂ + SO₃) emission from a FCC regenerator are the result of the some aromatic sulfur in feed condensing with the coke on the catalyst. The most of sulfur in coke on the spent catalyst can vary depending upon feed type, process condition and catalyst properties.

The most promising technology at this time is a situ control of the SO_x using catalyst technology. This approach to reducing SO_x was outlined in the 1970's and numerous early formulations were tried [2]. It is very important to design high effective SO_x reducing materials for this purpose. SO_x transfer additive must [3]:

(1) Be able to oxidize SO₂ to SO₃ under the FCC regenerator conditions, Eqs. (1) and (2).

(2) Be able to chemisorb the SO₃ in the form of stable metal sulfates in the FCC regenerator, Eq. (3).

(3) Be able to reduce sulfates to release sulfur as H₂S in the FCC reactor, Eq. (4).



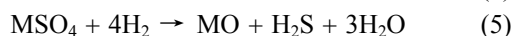
Formation metal sulfate:



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Reaction of metal sulfate:



Over the past several years, cerium oxide CeO_2 has come under intense scrutiny as catalyst and as structure and electronic promoters of heterogeneous catalytic reaction. Undoubtedly, the utilization of CeO_2 is as the key component for the treatment of exhaust gas from automobiles [4, 5], other catalytic applications such as the use of CeO_2 in removal of Sox from fluid catalytic cracking (FCC) flue gases [6-8]. Ceria reducibility enhances the oxidation of SO_2 to SO_3 under FCC regeneration condition by reacting with SO_2 to give substoichiometric cerium oxide, which is then reoxidized by oxygen. According to its basic sites allow the adsorption of SO_2/SO_3 with formation of sulfates. In addition, it helps the desorption of sulfates as hydrogen sulfide under reductive conditions.

So, the spinel MgAl_2O_4 , magnesium-rich spinel $\text{MgAl}_2\text{O}_4 \cdot y\text{MgO}$ was impregnated with cerium oxide that meet all the criteria to be interest for this reaction [7-18].

Vanadium pentoxide [17] is an excellent oxidation-catalyst and is especially useful for oxidation of SO_2 to SO_3 . However, V_2O_5 cannot use in a FCC unit because it reacts with zeolites present in a FCC catalyst [9]. A lower amount (< 3%) of vanadium may be used in combination with cerium (5-10%) to catalyze the oxidation as well as the reduction [17-29].

Moreover, the fraction (replacement of aluminum in the MgAl_2O_4 spinels with iron) can improve the regenerability of $\text{MgAl}_{2-x}\text{Fe}_x\text{O}_4$ spinels, but the higher content of iron in $\text{MgAl}_{2-x}\text{Fe}_x\text{O}_4$ spinels can promote coke formation. So the control of the appropriate iron content important [12, 17, 20].

In present work, spinel MgAl_2O_4 , magnesium-rich spinel $\text{MgAl}_2\text{O}_4 \cdot y\text{MgO}$ impregnated with cerium oxide prepared according to acidic and basic methods. Addition iron and vanadium as promoter to solid solution spinel $\text{MgAl}_2\text{O}_4 \cdot \text{MgO}$ also were prepared, characterized by TGA technique and XRD. It is evaluated as potential SOx transfer catalyst under conditions similar

of those of a typical FCCU.

2. Experimental Works

TGA experiments have been used to demonstrate the pick-up and release of sulfur oxides in the development of additives for SOx control in the FCCU.

The additive picks-up SOx as SO_3 in the regenerator and subsequently reduces and release sulfur as H_2S on the reactor side of the FCCU. This sequence of events forms the technical basis for the operation of the SOx removal additive. The TGA follows the pick-up of SO_3 as weight gain. As hydrogen is added to the catalyst containing the bond sulfate, the sulfate is reduced to sulfide and is release as H_2S . The reduction and release is observed as weight loss. This experiment was divided into four zones:

Zone A: Under N_2 , the sample was heated to 700 °C, at rate of temperature 20 °C/min. This takes about 35 min.

Zone B: Nitrogen was replaced by a gas containing 1.4% vol. SO_2 , 6.5% O_2 , and balance N_2 . The flow was 200 mL/min. The temperature was kept constant at 700 °C. This condition was maintained for 30 min.

Zone C: Passage of SO_2 -containing gas was cut-off and replaced by nitrogen. The temperature was brought to desired temperature. This is a 15 min. time zone.

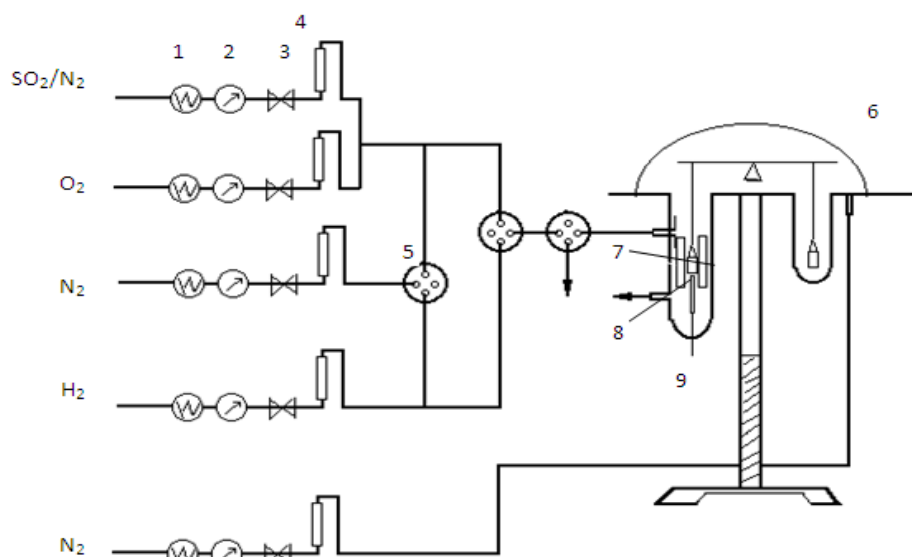
Zone D: Nitrogen was replaced by hydrogen. This condition was maintained for 20 min.

In our work was used a WRT-2 thermogravimetric analyzer illustrate in Fig. 1. Typically a 10-15 mgs. particle size 60-80 mesh No. sample was placed on a quartz sample pan. TG scale 2×100 mg, DTG scale 0.2 mg/min. The standard experimental condition of TGA are summarized in Table 1.

3. Results and Discussion

3.1 Effect of Oxidation Temperature

The spinel materials studies include three samples, they were prepared by acidic method [21], solid solution MgAl_2O_4 , solid solution with cerium 10% $\text{Ce}/\text{MgAl}_2\text{O}_4 \cdot \text{MgO}$, iron mixed spinel with cerium 10%



1- adjustment valve, 2- pressure valve, 3- stop valve, 4- flow meter, 5- way valve, 6- microbalance system, 7- sample pan, 8- heater, 9- platinum thermocouple.

Fig. 1 Schematic diagram of thermogravimetry (TGA).

Table 1 Standard experimental condition for SO₂ adsorption and sulfates reduction.

Conditions	Oxidation/Adsorption	Reduction/Desorption
Temperature (°C)	700	500-700
SO ₂ (% by vol.)	1.4	--
H ₂ (% by vol.)	--	30 or 100
O ₂ (% by vol.)	6.5	--
N ₂ (% by vol.)	Balance	Balance
Time (minutes)	30	20

CeMgAl_{2-x}FeO₄·MgO and two samples solid solution with cerium introduced by vanadium as a second co-catalyst prepared by basic method [22], 1%V/10% Ce/MgAl₂O₄·MgO were tested in TGA for oxidation half cycle at different oxidation temperature under the following condition in TGA.

A 10-15 mgs of virgin sample placing on a quartz pan and introduce nitrogen. The sample was slowly 20°C/min heated to desired temperature (500, 600 and 700 °C). Nitrogen was replaced by a gas containing 1.42 vol.% SO₂, 6.44 vol.% O₂, 92.14 vol.% N₂, the flow rate was 200 mL/min. The temperature was kept constant at a desired value. The condition was maintained for 30 min, then flashing by nitrogen.

Fig. 2 shows the oxidation step performance for acidic preparation samples. From this figure we can

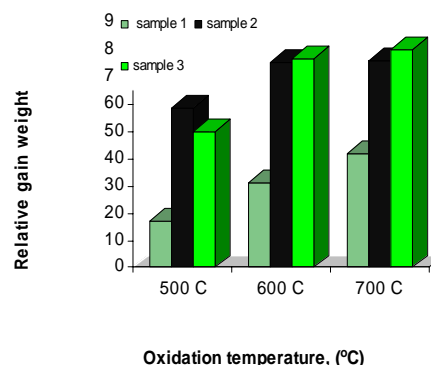


Fig. 2 Relative gain weight vs. oxidation temperature of acidic samples.

observe the gain weight of the sample solid solution sample 1 MgAl₂O₄·MgO which is tested at different temperatures (500, 600, and 700 °C), 17%, 31%, and 42% respectively. The sulfur in the coke mainly oxidized to SO₂ (Eq. (1)), sulfur dioxide should be further oxidized to SO₃ (Eq. (2)). As operational temperature of the regenerator is increased, the formation of SO₃ is less favored. Gibbs free energy change of reaction (2) is -9.5 kJ/mol at 675 °C and -4.4 kJ/mol at 730 °C [7]. The spinel solid solution with cerium sample 2, 10%Ce/MgAl₂O₄·MgO and iron mixed spinel with cerium (sample 3), 10% Ce/MgAl_{2-x}Fe_xO₄·MgO, these two additives were revealed high adsorption SO₂ more than the additive

MgAl₂O₄·MgO. At 500 °C the gain weight was (50-60%), while at 600 °C the gain weight was (75-77%), and at 700 °C slightly more than at 600 °C.

In Fig. 2, sample 2 showed the role of cerium in solid solution spinel, which enhanced the ability of the gas oxygen adsorption on the surface of the catalyst. Hence, cerium oxide modifies the surface property of the catalyst, which resulted the De-SOx activity was improved [23].

At 600 °C and 700 °C the adsorption SOx is similar, because at temperature range between 600-700 °C the cerium was increased the oxidation adsorption of SOx and catalytic performance. We can deduce the oxidation adsorption SOx capacity is depended on the number of active site in the surface of catalyst, which is not related with reaction temperature.

Fig. 3 shows the role of vanadium in solid solution with cerium prepared by basic method. The two samples were subjected to desired oxidation temperature (500 and 700 °C). The sample 28 1% V/10%Ce/MgAl₂O₄·MgO was introduced with vanadium by impregnation procedure reveals high relative gain about 87% more than the sample 30 that is also introduce with vanadium. The both samples at 500 °C oxidation temperature are similar in gain weight about 55-58%.

The solid solution with cerium impregnated with vanadium as a second co-catalyst which was prepared by basic method reveals high relative gain more than the solid solution prepared by acidic method which is introduced with cerium only or both cerium and iron as shown in Fig. 2 samples 2 and 3 respectively. Vanadium pentoxide is excellent oxidation catalyst and especially useful for the oxidation of SO₂ to SO₃ [17-29]. The detail results are summarized in the Table 2. The table shows the relative gain weight for samples prepared by acidic and basic methods at different time (5, 20, and 30 min) within the oxidation half cycle.

The samples are subjected to different oxidation temperature for 30 min. When the passage of the SO₂-containing gas was stopped and replaced by nitrogen,

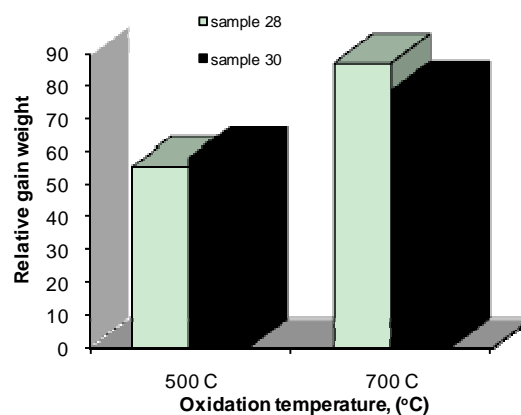


Fig. 3 Relative gain weight vs. oxidation temperature of basic samples.

no weight loss was observed. This indicates that only MgSO₄ is formed which have high stability under FCC condition. The additive MgAl₂O₄·MgO, when promoted by cerium or iron, was found to be most effective De-SOx catalyst.

The temperature was reduced to 450 °C, the nitrogen was replaced by 30% H₂, or H₂/N₂ mixed gas. The temperature was increased gradually until the weight loss. Table 3 shows the reduction temperature for above mentioned samples prepared by acidic and basic methods at different oxidation temperature.

Table 3 shows the oxidation temperature increases reduction temperature is slightly except the MgAl₂O₄·MgO. For the samples which were prepared by basic method impregnated with vanadium exhibit were lower reduction temperature more than the samples solid solution with or without cerium MgAl₂O₄·MgO and 10%CeMgAl₂O₄·MgO respectively. The solid solution with cerium impregnated with vanadium in basic method appeared more sufficiency than the solid solution with cerium prepared by acidic method.

The results confirm that impregnation of vanadium on the single solid solution with cerium spinel was lowered the reduction temperature from 633 °C to 593 °C. This observation is consistent with literature of basic method [24]. If the adsorption temperature increases, the weak adsorbed sulfur species will desorb from the surface of the catalyst, hence, the total amount of the

Table 2 Results of relative gain weight of acidic and basic samples at different oxidation temperature.

Sample No.	Acidic method									Basic method						
	1			2			3			28			30			
	5	20	30	5	20	30	5	20	30	5	20	30	5	20	30	
Gain (Wt.)																
Oxid. Temp.(°C)																
500	4	14	17	11.8	52.5	59	11.8	40	50	10.9	41.7	55.6	13	47.4	58.5	
600	6	24.5	31	21.5	71.8	75.5	19.8	72	77.1	-	-	-	-	-	-	
700	8	32	42	21.8	71.8	76.4	20.2	75	80	24.6	74.8	7.4	13	55.2	78.9	

Table 3 The sulfate reduction temperature of spinel at different oxidation temperature.

Sample	Oxid. Temp. (°C)		
	500	600	700
MgAl ₂ O ₄ ·MgO	613	635	635
10%CeMgAl ₂ O ₄ ·MgO	618	629	633
10%CeMgAl _{2-x} Fe _x O ₄ ·MgO	537	541	569
1%V/10%CeMgAl ₂ O ₄ ·MgO sample 28	574	--	593
1%V/10%CeMgAl ₂ O ₄ ·MgO sample 30	583	--	614

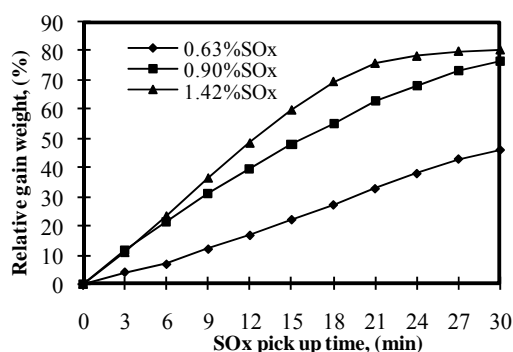
adsorbed SO₂ increases [25], but the reduction is more difficult.

We can observe when incorporating and cerium in the spinel structure, that both cerium and iron function on an oxidant for the oxidation of SO₂ to SO₃ pick-up half cycle. The iron again functions as a promoter for the sulfate reduction.

3.2 Effect of SO₂ Concentration

The solid solution MgAl₂O₄·MgO, solid solution with cerium, 10%Ce/MgAl₂O₄·MgO, iron mixed spinel with cerium 10%Ce/MgAl_{1.8}Fe_{0.2}O₄·MgO that were prepared by acidic method and solid solution with cerium impregnated with 1% by weight vanadium 1% V/10%Ce/MgAl₂O₄·MgO prepared by basic method were studied at low and high concentration (full sulfate) SO₂. The SO_x pick-up half cycle was run in a usual manner with the sample in a flow of a gas mixture containing 0.63 vol.% or 1.42 vol.% SO₂ and 6.44% O₂ in nitrogen at 700 °C for 30 min.

It is shown in Fig. 4 the sample 10%Ce/MgAl_{1.8}Fe_{0.2}O₄·MgO prepared by acidic method was subjected to different concentration from SO₂ (0.63, 0.90, and 1.42 vol.%) respectively with oxygen 6.44

**Fig. 4** Oxidation at different concentrations SO_x of 10%Ce/MgAl_{1.8}Fe_{0.2}O₄·MgO prepared by acidic method.

vol.% in nitrogen at 700 °C for 30 min, SO_x pick-up half cycle. It is very distinctly that the high relative gain at the concentration of SO₂ was increased.

Fig. 5 shows performance of sample, 1%V/10%Ce/MgAl₂O₄·MgO prepared by basic method was subjected to same condition for the acidic sample. It is obviously shown high relative gain weight at a concentration of SO₂ was increased, slightly more than in the acidic sample. The vanadium plays important role when it is introduced to the solid solution with cerium 10%Ce/MgAl₂O₄·MgO to improve oxidation of SO₂ to SO₃.

The spinel materials studied include solid solution with cerium 10%Ce/MgAl₂O₄·MgO and iron solid solution cerium 10%Ce/MgAl_{1.8}Fe_{0.2}O₄·MgO prepared by acidic method were exposure to SO₂ at low and high concentration 0.63, 1.42 vol.% respectively. Solid solution MgAl₂O₄·MgO was exposure only to high concentration SO₂ 1.42 vol.% these reveals in Fig. 6.

The samples as shown in Fig. 6 iron mixed spinel with with cerium 10%Ce/MgAl_{1.8}Fe_{0.2}O₄·MgO and solid solution with cerium 10%Ce / MgAl₂O₄·MgO reveals

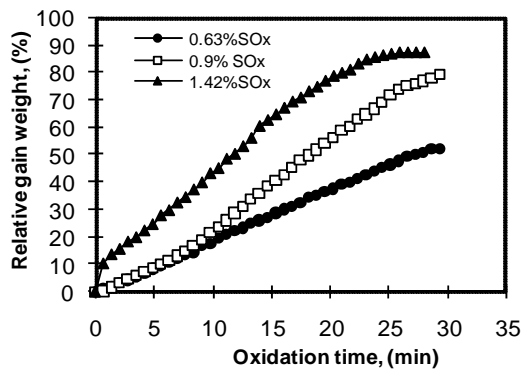


Fig. 5 Oxidation at different concentrations SOx of 1%V/10%Ce/MgAl₂O₄·MgO prepared by basic method.

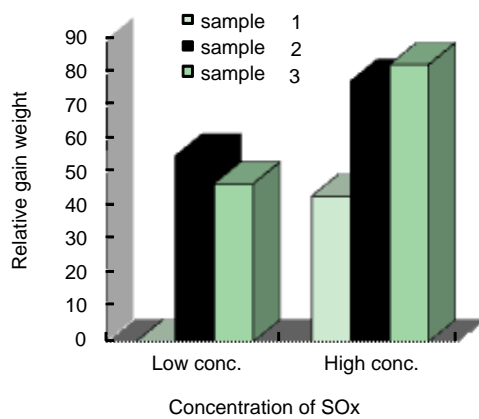


Fig. 6 Oxidation step at different concentration of SOx for acidic samples.

higher relative gain about 77-82% at high concentration SO₂ 1.42 vol.% in comparison with solid solution MgAl₂O₄·MgO low relative gain weight about 43%. At low concentration 0.63 vol.% SO₂, solid solution with cerium 10%Ce/MgAl₂O₄·MgO appear higher relative gain weight than iron mixed spinel with cerium 10% Ce/MgAl_{1.8}Fe_{0.2}O₄·MgO.

In Fig. 7 the solid solution with cerium was impregnated with vanadium as a second co-catalyst prepared by basic method for both samples 28 and 30.

At high concentration of SO₂ 1.42 vol.% is revealed high relative gain for both samples about 87% and 79% vol. respectively. At low SO₂ concentration 0.63% vol. the increasing in relative gain is similar. The solid solution with cerium impregnated with 1% vanadium prepared by basic method reveals high relative gain weight more than iron mixed solid solution with cerium 10%Ce/MgAl_{1.8}Fe_{0.2}O₄·MgO and solid solution with cerium 10%Ce/MgAl₂O₄·MgO they were prepared by acidic method as shown in Fig. 6. The detail results are summarized in Table 4. In this table it shows the relative gain weight for the samples prepared by acidic and basic method at different time (5, 20, and 30 min) within the oxidation half cycle.

When cerium oxide is supported on the surface a strong interaction occurs between the CeO₂ and the support, which results in more oxygen vacancies being created, more adsorbed oxygen ions will be beneficial to the formation of sulfate. Consequently, the De-SOx activity is improved [12].

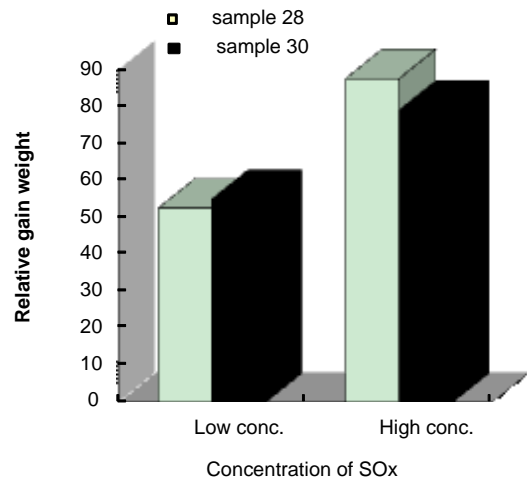


Fig. 7 Oxidation step at different concentration of SOx for basic samples.

Table 4 Results of relative gain weight of acidic and basic samples at different concentrations of SOx.

Sample No.	Acidic method									Basic method					
	1			2			3			28			30		
Gain (wt.)	5	20	30	5	20	30	5	20	30	5	20	30	5	20	30
SOx concn.															
0.63 vol.%	-	-	-	8.3	39.9	55	5.9	31.4	46.8	8.4	37.4	52.5	8.5	32.6	54.9
1.42 Vol.%	8.3	31.4	43.1	20	71.5	77.2	20	74.2	82.1	24.6	77.9	87.4	13.2	58.2	78.9

4. Conclusions

As the adsorption temperature of SO₂ increases, adsorption of SO₂ increases also, therefore the capability of oxidation SO₂ in spinel improved, but reduction is more difficult.

Introduction the vanadium as a second co-catalyst in solid solution with cerium prepared by basic method was enhanced the oxidation of SO₂ to SO₃. This sample has high relative gain weight more than the spinel prepared by acidic method either with iron and cerium or with cerium only. It is distinctly that the high relative gain at the concentration of SO₂ was increased.

References

- [1] J.W. Wilson, Fluid Catalytic Cracking Technology and Operation, Penwell Publishing, Oklahoma, 1977.
- [2] A.I. Vasalos, E.R. Strong, C.K. Hsieh, C.J. D'sauza, Amoco's new ultract process for SO_x control, in: API 42nd Midyear Meeting, May10, 1977, pp. 20-77.
- [3] J.S. Yoo, A.A. Bhattacharyya, C.A. Radlowski, De-SO_x catalyst: the role of iron in iron mixed solid solution spinels, MgO·MgAl_{2-x}Fe_xO₄, Ind. Eng. Chem. Res. 31 (5) (1992) 1552.
- [4] J.S. Summers, S.A. Aunes, Interaction of cerium oxide with noble metal, J. Catalyst 58 (1979) 131.
- [5] G. Kim, Ceria-promoted three-way catalysts for auto exhaust emission control, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 267.
- [6] J.S. Yoo, J.A. Jeacker, Catalyst and process for conversion of hydrocarbons, U.S. Patent, 4 469 589 (1984).
- [7] A.A. Bhattacharyya, G.M. Woltermann, J.S. Yoo, J.A. Karch, W.E. Cormier, Catalytic SO_x abatement: the role of magnesium aluminate spinel in the removal of SO_x from fluid FCC flue gas, Ind. Eng. Chem. Res. 8 (1988) 1356.
- [8] R.J. Bertolacini, E.H. Hirschberg, F.S. Modica, Composition for removing sulfur oxides from a gas, U.S. Patent, 4 497 902 (1975).
- [9] A. Corma, A.E. Palomares, F. Rey, Optimization of SO_x additives of FCC catalysts based on MgO-Al₂O₃ mixed oxides produced from hydrotalcites, Appl. Catalysis B: Environmental 1 (1994) 29.
- [10] A. Trovarell, C. Leitenburg, M. Borao, G. Dolcetti, The utilization of ceria in industrial Catalyst, Catalyst Today 50 (1999) 353.
- [11] A. Wang, L.F. Chen, L.C. Lie, Monolayer dispersion capacity of CeO₂ on the surface of the CeO₂/MgAl₂O₄ catalyst and its effect on the De-SO₂ activity, J. Mater. Sci. Lett. 7 (1998) 533.
- [12] J.S. Yoo, A.A. Bhattacharyya, C.A. Radlowski, Advanced De-SO_x Catalyst: mixed solid solution spinel with cerium oxide, Appl. Catalyst B1 (1992) 169.
- [13] J.A. Wang, Z.L. Zhu, L.C. Lie, Pathway of the cycle between the oxidative adsorption of SO₂ and the reductive decomposition of sulfate on the MgAl_{2-x}Fe_xO₄ catalyst, J. Molecular Catalysis A: Chemical 1 (1999) 31.
- [14] A.A. Chin, I.D. Johnson, C.T. Kersge, M.S. Sarli, Additive for vanadium capture in catalytic cracking, U.S. Patent, 4 889 615 (1989).
- [15] G. Kim, SO_x control compositions, U.S. Patent, 5 288 675 (1994).
- [16] S.P. Carla Maria, A.H. Cristiane, A.N. Arnaldo, L.F.M. Jose, Synthesis characterization evaluation of CeO₂/Mg, Al-Mixed oxide as catalyst for SO_x removal, J. of Molecular Catalysis A: Chemical 24 (2005) 184.
- [17] A.N. Awad, L.C. Lie, M.M. Aboabboud, H.G. Ibrahim, Studies the role of transition metals in spinels materials to improve the activity of SO_x additive, in: the 1st International Petroleum Environmental Conference and Exhibition (IPEC-2008), Tripoli/Libya 12-14, May, 2008.
- [18] P. Mars, J.G.H. Masessen, The mechanism and the kinetics of sulfur oxide oxidation on catalyst containing vanadium and alkali oxides, J. Catalyst 10 (1968) 1.
- [19] J.S. Magee, M.M. Mitchell Jr., Fluid Catalytic Cracking Science and Technology, Vol. 76, Elsevier Science Publishers B.V., 1993, p. 531.
- [20] M. Cantú, E. López-Salinas, J.S. Valente, R. Montiel, SO_x removal by calcined MgAlFe hydrotalcite-like materials: effect of the chemical composition and the cerium incorporation method, Environ. Sci. Technol. 24 (2005) 9715.
- [21] L.M. Maganbosco, E.J. Demmel, Synthetic spinels and processes for making them, U.S. Patent, 5 108 979 (1992).
- [22] A.A. Bhattacharyya, W. Cormier Jr., G.M. Woltermann, Alkaline earth metal spinels and processes for making, U.S. Patent, 4 728 635 (1988).
- [23] W.P. Cheng, X.Y. Yu, W.J. Wang, L. Liu, J.G. Yang, M.Y. He, Synthesis, characterization and evaluation of Cu/MgAlFe as novel transfer catalyst for SO_x removal, Catalysis Communications 8 (2008) 1505.
- [24] J.S. Yoo, A.A. Bhattacharyya, C.A. Radlowski, J.A. Karach, New Frontiers in Catalysis, in: Guzcil et al. (Eds.), Elsevier Science Publishers B.V., 1993.
- [25] S.W. Nam, G.R. Gavalas, Adsorption and oxidative adsorption of sulfur dioxide on γ-Alumina, Applied Catalysis 1 (1989) 193.

Identification of the Electricity-Producing Bacteria in Wastewater for Microbial Fuel Cells (MFCs)

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Abstract: A microbial fuel cell (MFC) is a device that converts chemical energy to electrical energy during substrate oxidation by microorganisms. The characterization and identification of these microbial communities will allow better control of this electricity generation with simultaneous removal of carbon and nitrogen. This study aims to investigate the role of natural bacteria in electricity generation by studying three different sources of wastewater: the raw wastewater (RW), wastewater from an aeration tank (AEW) and returned activated sludge (RAS) from an activated sludge treatment plant. The result showed that after the MFC treatment, the number of bacterial strains was reduced from twenty strains to eight strains. Microscopic observation further showed that fifteen isolate before the treatment were gram-positive, and five were gram-negative whereas all isolates after the treatment were gram-positive rods or cocci. The four strains isolated from the RAS inoculums, *β-Comamonas sp.*, *γ-Enterobacter sp.*, *Bacillus cereus sp.* and *Clostridium sp.* produced the highest power density of 67.57 mW/m² which made them potential candidates for electrochemically active bacteria in MFCs. However, the level of chemical oxygen demand (COD) removal was 20% and the total kjeldahl nitrogen (TKN) removal was 66.7%.

Key words: Electricity-producing bacteria, microbial fuel cell (MFC), wastewater, polymerase chain reaction (PCR).

1. Introduction

Microbial communities play an integral and unique role in wastewater treatment especially in biological treatment that removes carbon and nitrogen. Many researchers have attempted to harness the potential of microorganisms in research field such as wastewater treatment and the generation of alternative energy sources including hydrogen, bioethanol, and biofuels. The microorganisms present in microbial fuel cell (MFC) are responsible for carbon and nitrogen removal as well as the simultaneous generation of electricity.

Their structures and functions have been investigated for decades. However, only very limited information was obtained with classical methods that lacked sufficient information on rarely isolated bacteria. As a result, the bacteria often remained unidentified or misidentified [1].

One approach to solve this problem is to use molecular techniques to study the species composition of the microbial communities in the presence of various substrates. Recent developments of techniques such as PCR, denaturant gradient gel electrophoresis (DGGE) and fluorescence in situ hybridization (FISH) have enabled scientists to overcome the limitations of conventional culture-based identification techniques [2]. These new techniques rely on the analysis of the small subunit of the ribosomal RNA (16S rRNA for

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prokaryote) or its corresponding gene, which is universally and abundantly expressed in all living beings [3].

In this paper, a bacterial 16S rDNA library-based method was applied to analyze naturally existed bacterial communities in wastewater for electricity generation. By comparing the gene sequence of the tested samples with the known sequence in GenBank, the dominant bacterial species and the constituent frequencies were revealed. The application of MFC could be an attractive alternative to reduce the cost of wastewater treatment and to generate electricity. MFC is a device that converts chemical energy to electrical energy during substrate oxidation by microorganisms [4, 5]. Electricity can be generated from either pure cultures or mixed cultures, and mixed cultures are more suitable for complex fuels such as wastewater. Mixed-culture MFCs tend to produce more power than pure culture [6]. The reason for this phenomenon remains unknown and needs further investigation.

The role of bacteria for electricity generation has been addressed by Rabaey & Verstraete in 2005 [7], who used bacteria as electron acceptors (anodes). Their different metabolic pathways were used to determine the selection and performance of specific organisms. Bullen et al. in 2006 [8] extensively reviewed biofuel cells and their development. They also highlighted the application of biofuel cells in sewage treatment process. It was noted that sewage digesting bacteria are capable of generating electricity, and the biological oxygen demand of the fuel itself could serve to maintain the system in an anaerobic state. However, the power levels of a practical system have not yet been demonstrated. The advantages of using mixed culture in MFCs include no sterilization requirements and possibility of using continuous processes.

The MFC consists of three basic components: an anode chamber, a cathode chamber and a proton exchange membrane (PEM) that separates the two chambers. The anode chamber provides sufficient medium for the growth of microorganisms. Organic

matter can be oxidized during the metabolic process, generating electrons and protons that are released to the anode and the cathode, respectively. Dissolved oxygen is provided at the cathode chamber to react with the electrons and protons and finally produces electricity once a complete electric circuit is provided.

2. Materials and Methods

The proposed study takes three steps to identify the electricity-producing bacteria communities in microbial fuel cells:

(1) Cultivation, isolation and characterization of bacteria were before the MFC process. The samples of wastewater were collected from three different locations at an activated sludge treatment plant (raw wastewater, RW; aeration tank, AEW & returned activated sludge, RAS).

(2) Operation of the MFC reactor for 10 days using RW, AEW and RAS samples as substrates.

(3) Collection of the biofilm samples: After the MFC process, biofilm samples were collected from the anode of MFC (RW, AEW & RAS) and were cultivated, isolated, characterized and identified using PCR technique.

2.1 Identification of Bacterial Communities

2.1.1 Cultivation, Isolation and Characterization of Bacteria

A dilution method of the wastewater was used and the sample was cultured on nutrient agar (NA, Oxoid) plates. After incubation at 37 °C for 48 h, the isolated colonies were observed under light microscope [9]. Gram staining was carried out to determine the morphological characteristic of the bacteria.

2.1.2 Molecular Determination

Molecular characterization of the microbial communities was carried out by DNA extraction, amplification of 16S rRNA, purification of PCR products and DNA sequencing.

2.1.2.1 Extraction of Total DNA

The isolates were cultivated in nutrient broth (NB,

Oxoid) at 37 °C for 18 h. DNA was extracted using GF-1 bacterial DNA extraction kit (Vivantis) according to the manufacturer's instructions and was suspended in 30 µL of TE buffer or sterile water. The purified DNA was checked by agarose gel electrophoresis (1.0%, containing ethidium bromide).

2.1.2.2 Polymerase Chain Reaction (PCR)

The primers, previously proposed by Lee et al. in 2002 [10], were specific for the amplification of the spacer region of the 16S rRNA genes. Primer sequences were 5'-AGAGTTTGATCCTGGCTCAG-3' and 5'-GGTTACCTTGTACGACTT-3'. Each 50 µL, PCR reaction mix contained Green Go Taq[®] Master Mix (Promega, Madison, WI, USA), primer, sterile ultrapure water and extracted DNA. For each set of PCRs, a control reaction without the template DNA was included. The master mix was prepared according to the manufacturer's instructions. All PCRs were performed in a Mastercycler (epgradient S, Eppendorf, Version 3.608) and the amplification products were separated by horizontal electrophoresis (1% agarose gels). The gels were stained with ethidium bromide and visualized under UV light. Minor differences in band intensity and weak bands were not considered when defining the sequence of the DNA.

2.1.2.3 Purification of PCR Products

A fragment of approximately 1.5 kbp present in all PCR products were removed from the agarose gels and purified with the Wizard Plus SV Minipreps (Promega Corp., Madison, WI, USA) according to manufacturer's protocol.

2.1.2.4 DNA Sequencing and Analysis

Samples were sent to the First BASE Laboratories Sdn. Bhd. for sequencing. BLAST searches of the nucleotide sequences were conducted at the homepage of the National Center for Biotechnology Information (<http://www.ncbi.nlm.nih.gov/>).

2.2 MFC Systems

The MFC reactor was designed and fabricated from

acrylic material. It consisted of two chambers (1 liter) for anode and cathode compartment, which were separated by a Nafion[™] membrane (D=3.6 cm). To increase the porosity of the membrane [11], the Nafion[™] sheet (Alfa Aesar, USA) was pretreated by boiling sequentially in 30% H₂O₂, deionized water (pH 7.0), 0.5 M H₂SO₄ and again with deionized water for one hour each. The anode and cathode were each a single piece of carbon paper (0.5 mm thickness; Advent Research Material, England) with a surface area of 25.75 cm². Electrodes were soaked in deionized water for a period of 24 hours prior to use. They were placed on the distance of 7 cm and connected with copper wires. The cathode chamber of MFC was filled with phosphate buffer (50 mM, pH 7.5) as a catholyte and continuously aerated to supply oxygen. The anode chamber was filled with the wastewater sample. Voltage and current were measured using a digital multimeter (BK Precision 5491A). Power density, P (W/m²) was calculated by $P = iV/A$, where A is the surface area of the anode electrode (m²), i is the current (A) and V is the voltage (V). COD and TKN were measured before and after the MFC operation according to APHA (1998) [12].

3. Results and Discussion

3.1 Bacterial Isolation and Characterization

Table 1 shows the twenty isolates from three different locations at the activated sludge treatment plant, with eight, four and eight strains for RW, AEW and RAS samples, respectively. Gram staining showed that 15 of the samples were gram positive, and five were gram negative. According to their shapes, they could all be classified as either rods or cocci (Table 1). In contrast, only eight isolates were obtained from MFC biofilms, with four for RAS, two for RW and two for AEW samples (Table 2). All these isolates were gram positive.

3.2 Polymerase Chain Reaction (PCR)

As validated by electrophoresis on 1.0% agarose gel

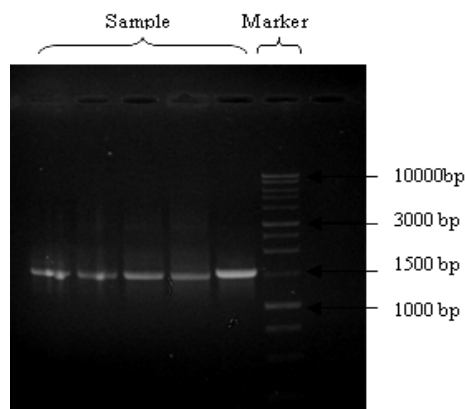
Table 1 Characterization of bacteria isolated from RW, AEW and RAS samples before MFC operation.

Samples	Gram stain	Colonies color	Morphology
RW1	+ve	Yellow	Rod
RW2	-ve	White	Cocci
RW3	-ve	White	Rod
RW4	+ve	White	Rod
RW5	+ve	White	Rod
RW6	-ve	White	Rod
RW7	+ve	White	Rod
RW8	+ve	White	Rod
AEW1	+ve	Yellow	Rod
AEW2	+ve	White (filamentous)	Rod
AEW3	+ve	White	Cocci
AEW4	+ve	White	Rod
RAS1	-ve	White	Rod
RAS2	+ve	Yellow	Cocci
RAS3	+ve	White	Rod
RAS4	+ve	White	Cocci
RAS5	-ve	White	Rod
RAS6	+ve	White	Rod
RAS7	+ve	White	Rod
RAS8	+ve	White	Rod

Table 2 Characterization of bacteria isolated from RW, AEW and RAS samples after MFC operation.

Samples	Gram stain	Colonies color	Morphology
RAS1	+ve	White	Rod
RAS2	+ve	White	Rod
RAS3	+ve	White	Rod
RAS4	+ve	White	Rod
RW1	+ve	White	Cocci
RW2	+ve	White	Cocci
AEW1	+ve	White	Rod
AEW2	+ve	White	Rod

(Fig. 1), the PCR products were around 1500 bps and were generated from the bacterial DNA extracts. PCR is used to amplify a specific DNA sequence. It is extremely efficient and sensitive because it can make millions, or even billions of copies of any specific DNA sequence, even in a complex mixture. PCR was carried out for MFC biofilm samples, and sequencing analyses showed that the isolates could be divided into three different groups: *Proteobacteria*, *Firmicutes* and uncultured bacterium (Table 3). *Proteobacteria* and *Firmicutes* were proved by some researchers to be the major electricity-generating bacteria [13, 14].

**Fig. 1** Agarose gel electrophoresis of PCR products.**Table 3** Results of PCR and sequencing analyses.

Phylogenetic group	Closest relative GenBank database	relative in Max Ident (%)	Sample
<i>Proteobacteria</i>			
β -	- <i>Comamonas sp</i>	98	RAS
δ -	- <i>Aeromonas sp</i>	80	RW
γ -	- <i>Enterobacter sp</i>	95	RAS
<i>Firmicutes</i>			
<i>Bacilli</i>			
	- <i>Bacillus cereus</i>	94	RAS
	- <i>Enterococcus sp</i>	87	AEW, AEW
<i>Clostridia</i>			
<i>Uncultured bacterium</i>			
	- <i>uncultured klebsiella</i>	84	RW

Proteobacteria play an important role in biodegradation, organic removal and floccules formation [15]. *Proteobacteria* and *Firmicutes* contain exoelectrogenic species that can produce power in MFC [16]. The identified *Proteobacteria* were further divided into three sub-groups: β -*Proteobacteria*, δ -*Proteobacteria*, and γ -*Proteobacteria*. The most relative species from GenBank database were identified by NCBI Blast and listed in Table 3. The percentage similarity was calculated and expressed as Max ident. The results indicated that all the max ident were between 80% and 98% which indicated a higher intensity and acceptable. Among the three samples, RAS showed the highest number of communities: four with β -*Comamonas sp*, γ -*Enterobacter sp*, *Bacillus cereus sp* and *Clostridium sp*.

3.3 The Performance of MFC

The MFC was evaluated for 10 days for its voltage

and current production. All operations were done under batch-mode conditions. The average COD concentrations of the samples were 40 mg/L (RW), 515 mg/L (AEW) and 3293 mg/L (RAS). Fig. 2 shows the voltage profile of each sample. We found that the RW and AEW bacterial samples reached their lag phase within two days while for RAS sample the process took longer. It also took longer for the RAS sample to reach its stationary phase as compared to less than six days for the other two samples.

The current profile (Fig. 3) shows that RAS produced higher current than the other samples (in the range of 0.1 mA to 0.6 mA). Although RW was able to reach 0.6 mA, it was unable to maintain this high level: the current dropped within three days and remained at 0.1 mA. This result could be due to the weakness of the protons that were transferred to the cathode chamber. AEW reached 0.5 mA initially but failed to remain at such level for extended period of time. Within two days, it was only able to preserve its current in the range of 0.1 mA to 0.3 mA. RAS managed to rise within one day and reached 0.4mA on the second day, and the current remained between 0.2 mA to 0.6 mA. The pH in the anode chamber of the RAS sample was 6.47-6.90 (Table 4), which might have contributed to its high current profile. Jadhav and Ghangrekar [17] mentioned that a pH of between 6 and 7 would encourage microbial activity and increase the current.

Fig. 4 displays the power density production throughout the operation for all three samples (RW, AEW and RAS). The maximum power densities were 35.96, 50.10 and 67.57 mW/m² for RW, AEW and RAS respectively. RAS with the communities of *β-Comamonas sp*, *γ-Enterobacter sp*, *Bacillus cereus sp* and *Clostridium sp* managed to produce a power density higher than the other samples. The combination of these species may constitute an electrochemically active bacteria community in RAS, which can be further applied in MFC reactors. However, the level of COD removal for RAS was 20% and the TKN removal was 67% (Table 3). Nitrogen removal is not due to

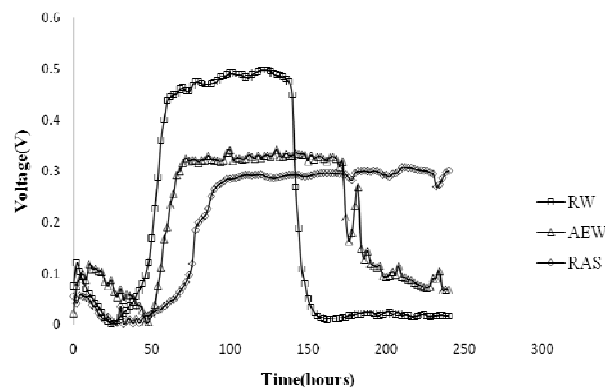


Fig. 2 Voltage profile of each sample over time.

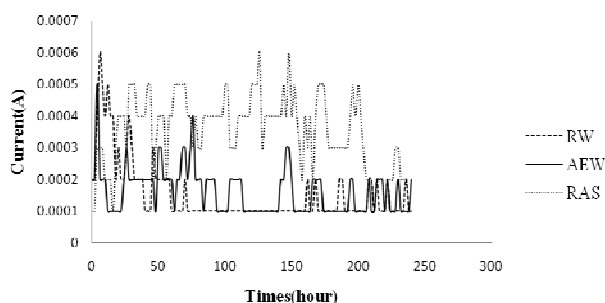


Fig. 3 Current profile over time for each sample.

Table 4 pH, COD and TKN removal performance.

	pH	Average COD removal (%)	Average TKN removal (%)
RW	7.49-7.88	50	67
AEW	6.67-7.02	75	78
RAS	6.47-6.90	20	67

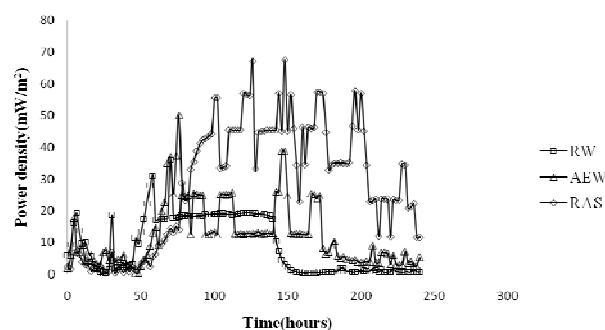


Fig. 4 Power density profile over time.

biological activity but rather through ammonia evaporation at the cathode chamber [16]. During the MFC process, ammonium ion is converted to ammonia and subsequently evaporates into the air. From process biology, we know that nitrogen removal is due to nitrification and denitrification with the existence of oxygen. To get a clearer view of the nitrogen removal

process, further study is needed to determine ammonia-nitrogen, nitrate-nitrogen and nitrite-nitrogen levels.

4. Conclusions

The efficiency and stability of electricity production in MFCs depend on the natural bacterial communities in wastewater. The combination of *β-Comamonas sp.*, *γ-Enterobacter sp.*, *Bacillus cereus sp.* and *Clostridium sp.* in returned activated sludge (RAS) produced the highest power density of 67.57 mW/m². RAS also produced a consistent power density higher than the other samples. However, the COD removal for RAS was only 20% which was significantly lower than that for the other samples. The TKN removal for RAS was 67%.

Acknowledgements

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References

- [1] V. Biovin-Jahns, A. Bianchi, R. Ruimy, J. Garcin, S. Daumas, R. Christen, Comparison of phenotypical and molecular methods for the identification of bacterial strains isolated from a deep subsurface environment, *Applied and Environmental Microbiology* 61 (1995) 3400-3406.
- [2] T. Hoshino, S. Tsuneda, A. Hirata, Y. Inamori, In situ PCR for visualizing distribution of functional gene 'amoA' in a biofilm regardless of activity, *Journal of biotechnology* 105 (2003) 33-40.
- [3] J.L. Sanz, T. Kochling, Molecular biology techniques used in wastewater treatment: an overview, *Process Biochemistry* 42 (2007) 119-133.
- [4] Z. Du, H. Li, T. Gu, A state of the art review in microbial fuel cells: A promising technology for wastewater treatment and bioenergy, *Biotechnology Advances* 25 (2007) 464-482.
- [5] B.H. Kim, I.S. Chang, G.M. Gadd, Challenges in microbial fuel cell development and operation, *Applied Microbial Biotechnology* 76 (2007) 485-494.
- [6] B.E. Logan, S. Cheng, D. Xing, V. Watson, D.F. Call, P.A. Selembro, R. Cusick, G. Rader, Recent advances in the design and operation of microbial fuel and microbial electrolysis cells, in: the 2nd Microbial Fuel Cell Conference, 2009, pp. 23-28.
- [7] K. Rabaey, W. Verstraete, Microbial fuel cells: novel biotechnology for energy generation, *Trends in Biotechnology* 6 (2005) 291-298.
- [8] R.A. Bullen, T.C. Arnot, J.B. Lakeman, F.C. Walsh, Biofuel cells and their development, *Biosensors & Bioelectronics* 21 (2006) 2015-2045.
- [9] A.A. Gorbushina, J. Heyrman, T. Dornieden, M. Gonzalez-Delvalle, W.E. Krumbein, L. Laiz, K. Petersen, C. Saiz-Jimenez, J. Swings, Bacterial and fungal diversity and biodeterioration problems in mural painting environments of St. Martins Church (Greene-Kreienzen, Germany), *International Biodeterioration & Biodegradation* 53 (2003) 13-24.
- [10] Y.K. Lee, H.W. Kim, C.L. Liu, H.K. Lee, A simple method for DNA extraction from marine bacteria that produce extracellular material, *Journal of Microbiological Methods* 52 (2002) 245-250.
- [11] S.V. Mohan, R. Saravanan, S.V. Raghavulu, G. Mohanakrishna, P.N. Sarma, Bioelectricity production from wastewater treatment in dual chambered microbial fuel cell (MFC) using selectively enriched mixed microflora: effect of catholyte, *Bioresource Technology* 99 (2008) 596-603.
- [12] APHA, AWWA, WPCF, Standard methods for examination of water and wastewater, 20th Edition, American Public Health Association, Washington, DC, 1998.
- [13] B.C. Jong, B.H. Kim, I.S. Chang, Enrichment, performance, and microbial diversity of thermophilic mediatorless microbial fuel cell, *Environment Science & Technology* 40 (2006) 6449-6454.
- [14] K. Rabaey, N. Boon, Biofuel cells select for microbial consortia that self-mediated electron transfer, *Applied and Environmental Microbiology* 70 (2004) 5373-5382.
- [15] J. Xin, M. Mingchao, L. Jun, L. Anhuai, Z. Zuoshen, Bacterial diversity of activated sludge in wastewater treatment plant, *Earth Science Frontiers* 15 (2008) 163-168.
- [16] B.E. Logan, *Microbial Fuel Cell*, New Jersey, John Wiley & Son, Inc, 2008.
- [17] G.S. Jadhav, M.M. Ghangrekar, Performance of microbial fuel cell subjected to variation in pH, temperature, external load and substrate concentration, *Bioresource Technology* 100 (2009) 717-723.

Spacial Distribution Characteristics, Activity and Degradation Capability of the Biofilm in Integrated Vertical-flow Constructed Wetland

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Abstract: The spacial distribution characteristics, activity and degradation capability of the biofilm in integrated vertical-flow constructed wetland were investigated. Results showed that the biofilm widely distributed in the substrate of integrated vertical-flow constructed wetland and mainly in the 0-10 cm top layer where the activity of dehydrogenase of the biofilm was also higher than that of other layers. The water quality could also affect the activity of the biofilm, for the TF(1,3,5-Triphenylformazan) amount reduced by the biofilm incubated in water of the higher eutrophication was larger, too. The PCP (pentachlorophenol) removal rate by the substrate with biofilm was 1.5 times that without biofilm. In total, the biofilm of the down-flow chamber appeared larger biomass, higher dehydrogenase activity and stronger degradation capability of organic contamination than that in up-flow chamber and it was the major place for removal of the organic matters in waste water.

Key words: Integrated vertical-flow constructed wetland, biofilm, distribution, activity of dehydrogenase, degradation capacity.

1. Introduction

The wastewater treatment process of the constructed wetland is performed by means of combined physical, biological and chemical functions [1]. During the process of wastewater treatment, it is the special properties, such as large surface area, oxidation and so on [2] that endow the biofilm consisting of various microorganism, some organic and inorganic substance with ability to adsorbing, degrading, converting even utilizing various organic matters effectively [3]. The mechanism of wastewater treatment of the constructed wetland is complicated and there're so much investigations which have been reported on the effect

and the mechanism of its purification to date [4, 5], especially in aspects of the substrate and the microorganism [6, 7], but little about the properties of the biofilm. So the spacial distribution characteristics, dehydrogenase activity and degradation capability of organic contamination were investigated in this study, which could enhance the understanding of the mechanism of purification and the development of the constructed wetland system and provide basis for the construction and management of wetland.

2. Materials and Methods

2.1 Constructing of Integrated Vertical-flow Wetland

Wu [8], with some others, has, for the first time, put forward and designed the process flow of a new kind of sewage disposal system-the integrated vertical-flow

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constructed wetland (IVCW) with the main part composed of two series chambers, the waste water is poured into the up-flow chamber quickly and equably through the water pipes distributed on the surface of it, and then flows down vertically because of the gravity, after that it reaches to the up-flow chamber through the connection layer of the two chambers, then flows up vertically, and finally the treated water is expelled from the system through the collecting pipes distributed on the surface of the up-flow chamber.

2.2 Sampling

According to lattice method, samples were collected by using sampling tubes of 60 cm diameter from each layers divided by 10 cm in the two chambers. And then a mean sample was generated from mixing the samples collected from the same layer.

2.3 Biofilm Cultivation

Slide glasses with dimensions of 76.2 mm×25.4 mm×0.8 mm were immersed in ethyl alcohol and cleaned before being used as carrier for the biofilm to adhere to and then put in the 30 cm depth of the water in experimental area, which was also the IVCW water resource for 10 days and then took the slide glasses to laboratory for experiment.

2.4 Determination of Biomass of the Biofilm

A certain amount of substrates was dried in oven at 105 °C to a constant weight which was the total solids (TS) and then treated at 300 °C for 2 h, 650 °C for 0.5 h to a second constant weight which was the nonvolatile solids. The dry mass of the biofilm accumulated on the slides was assessed by the determination of VSS of the homogenized biofilm, using the equation:

$$VSS=TS-NVSS \quad [9] \quad (1)$$

TS: the total solids weight

NVSS: the nonvolatile solids weight

2.5 Measurement of the Thickness of the Biofilm

The biofilm thickness was measured by using micro-

scopic dividing ruler [10]. The brief experimental procedures are as follows: the diameters of two groups of 50 random sampling substrate particles were measured, one group with biofilm and one group without biofilm. And then two mean values (d_p and d_m) were calculated by using the same equation:

$$d_p = \frac{\sum d^3 i}{\sum d^2 i} \quad (2)$$

Finally the thickness of the biofilm was calculated according the equation:

$$\delta W = (d_p - d_m) / 2 \quad (3)$$

2.6 Determination of Dehydrogenase Activity of the Biofilm

The triphenyl tetrazolium chloride (TTC) colorimetry method [10] was used. The experimental details were that after accurately 2.00 g sampling substrate with biofilm was cultivated at 37 °C for 12 h, coloration activation was then performed and the absorbance value at 485 nm wavelength was measured as a parameter reflecting the dehydrogenase activity.

2.7 Property of Degrading Persistent Organic Matters of the Biofilm

20.00 g neat sand grain sterilized at 170 °C and two 20.00 g substrate sand grain sampled at the top 10 cm of the up-flow chamber and down-flow chamber of the IVCW were separately putted in flasks and then 100 mL 22 mg/L pentachlorophenol solution were added to each samples. After the initial value being measured, the flasks with samples was incubated at 28°C on a rotary shaker operating at 120 rpm. The flask added with 100 mL 22 mg/L pentachlorophenol only was used as control. The concentration of pentachlorophenol was measured using HPLC (Agilent 1100).

3. Results and Discussions

3.1 The Spacial Distribution Characteristics of the Biofilm in IVCW

The VSS (Fig. 1) and the thicknesses (Fig. 2) of the biofilm can be used as a parameter to indicate the quantity and the quality of the organic phase which

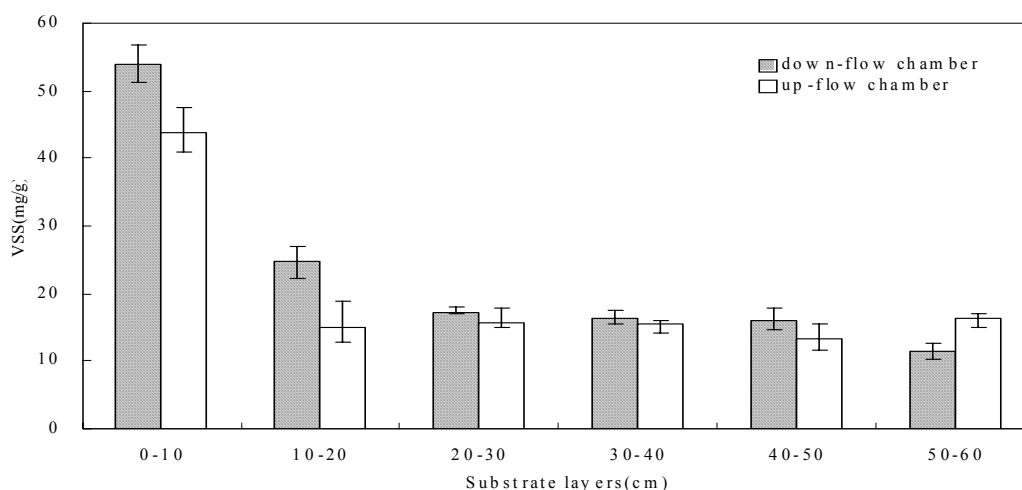


Fig. 1 Solid value of biofilms on the substrate sampled from separate layer in IVCW.

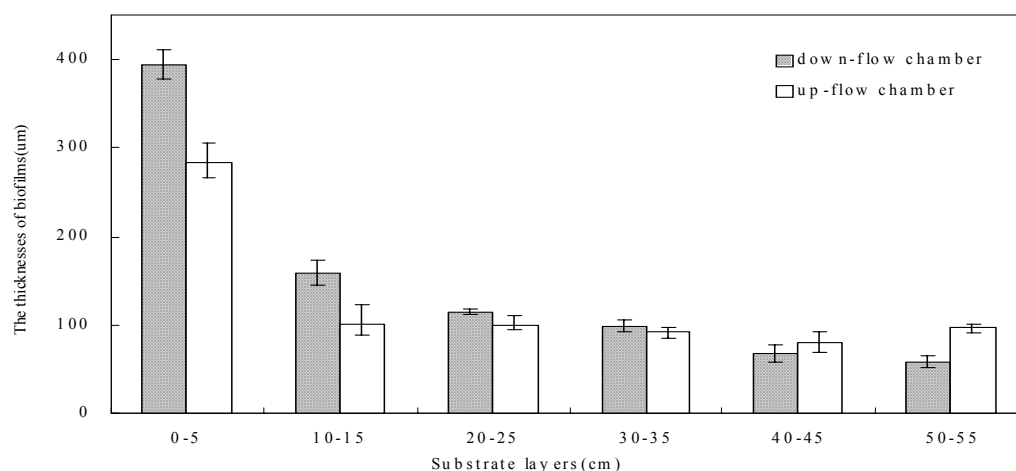


Fig. 2 The thickness of the biofilm on the substrate sampled from separate layer in IVCW.

plays an important role in absorption and degradation of various contaminants and the samples from each layer of the constructed wetland incubated in East Lake were measured.

Fig. 1 and Fig. 2 revealed that the biofilm distributed widely but heterogeneously in IVCW and the biofilm was mostly accumulated in the top 0-10 cm layer and the VSS and the thickness were about 2-3 times that of other layers. In total, both the VSS and the thickness of down-flow chamber were greater than that of the up-flow chamber, meanwhile, the distribution of the biofilm in substrates was consistent with the distribution of microorganisms, especially the aerobic microorganisms [11]. The biomass of the biofilm attached on the substrate of the compound biological

reactor could reach to 65 mg/g [12]. So the development degree of the biofilm was quite high when the mean VSS on the substrate reached to 21.8 mg/g as for the constructed wetland.

The heterogeneity in the down-flow chamber was associated with the water distribution way that the wastewater first flowed through the top layer, so that the organic contamination pellets were intercepted there mostly, and the sufficient oxygen and good development may be the other contributing factors. While the distribution in the up-flow chamber appeared opposite trend, which revealed that the distribution of the biofilm in IVCW was also associated with some other factors such as the root distribution of the plants which mainly distributed at the top layer, the

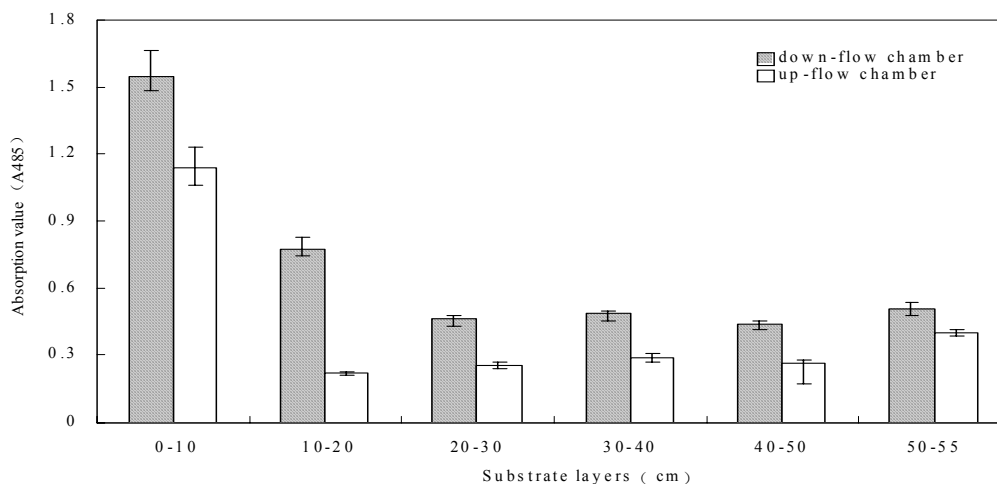


Fig. 3 The dehydrogenase activities of the biofilm of each layer in IVCW.

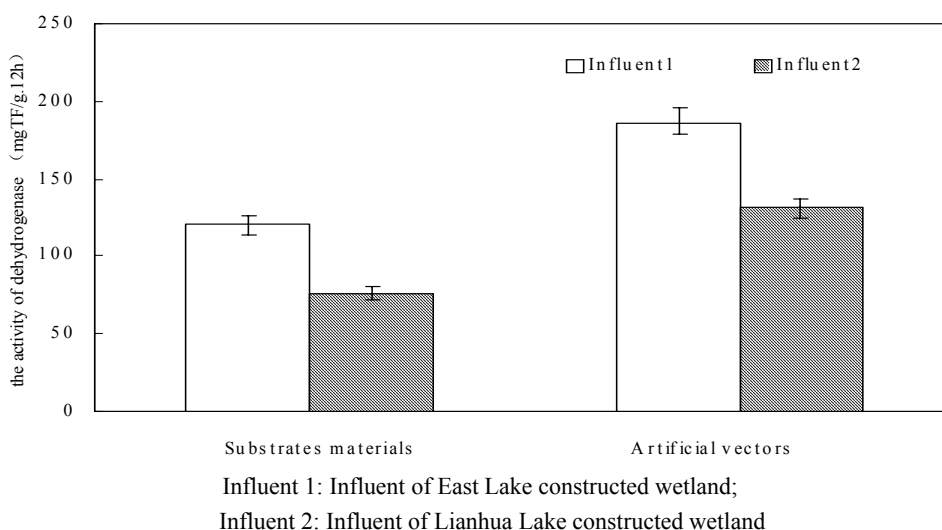


Fig. 4 The activities of the biofilm incubated in different water bodies of different water quality.

accumulation of secretion of the root system of plants and the organism mainly distributed at the top layer, too [11].

3.2 The Dehydrogenase Activities of the Biofilm

3.2.1 The Dehydrogenase Activities of the Biofilm in Different Layers of the IVCW

The removal of the contaminants completed by a series of biological oxidation-reduction catalyzed by various enzymes secreted by the microorganisms in the biofilm, and under the dehydrogenase’s catalyzing the hydrogen of the oxidized organics can be activated and delivered to the acceptor. So the activities of the dehydrogenase (Fig. 3) can indicate the amount of

active organisms and organic degradation efficiency of the biofilm.

As shown in the Fig. 3, the activities of dehydrogenase of the biofilm in different layers appeared significant variation, which was associated with the accumulation state of the biofilm in different layers. The dehydrogenase activity of the biofilm in top 0-10 cm layer, the major space of degradation of the organics in wastewater, was significantly higher than that of the other layers. In total, the activity of the biofilm of down-flow chamber was higher with the mean absorption value at 485 nm wavelength of 0.700 while the up-flow chamber was 0.427.

After operating for one year, the thickness of the

biofilm on the substrates in the surface layer (0-2 cm) was measured and the value reached to 393.48 μm . But the treatment efficiency of the biofilm in the surface layer didn't increase to matching degree with the great accumulation of the biofilm. The result indicated that excessive accumulation of the biofilm could not improve the dehydrogenase activity but result in another possibility of blocking the constructed wetland. After the constructed wetland working for a long time, non-living organisms such as various organic and inorganic particles were in large proportion in the biofilm. As a result, the activity of the biofilm was not equated with the great biomass.

3.2.2 The Activities of the Biofilm in IVCW Incubated in Different Lakes of Different Water Quality

The activities of the biofilm of two wetlands incubated in two lakes (East Lake and Lianhua Lake) of different water quality were determined. Substrates and slide glasses were both put at the water influent as carrier for the biofilm. Sample biofilm for the activity of dehydrogenase determination when their thickness reached to 100 μm (Fig. 4).

Though on different carriers, activities of the biofilm appeared the same trend that the higher level of eutrophication, the stronger activity (The East Lake was more eutrophic) and the average activity incubated in East Lake was 1.5 times that of in Lianhua Lake.

There was distinct difference between the values of dehydrogenase activity of the biofilm obtained from different material carrier, because the factual quantity was different.

In general, in the constructed wetland, environment factors could directly affect the growth rate, biomass, thickness and activity of the biofilm, such as the culture time, the eutrophication state and so on. And in the higher eutrophication water body, it was the more microbes quantity that resulted in the higher attachment frequency, which led to higher growth rate of the biofilm. Differences existed in both thicknesses and activities of the biofilm obtained from substrates cultured in water body of different eutrophication level revealed another fact that both the structure of biofilm and the physiological activities of organisms in the biofilm were different, too.

3.3 The Persistent Pentachlorophenol (PCP) Removal Capacity of the Biofilm

The removal efficiency of the substrate in IVCW (Fig. 5) was good. The average removal rate of the up-flow and down-flow in a week were 71.2% and 83.5% respectively. It was variation of distribution of the biofilm and activity possibly caused by water flow state and the plant species and so on that accounted for the difference in PCP removal rate between the two constructed wetlands. And the average

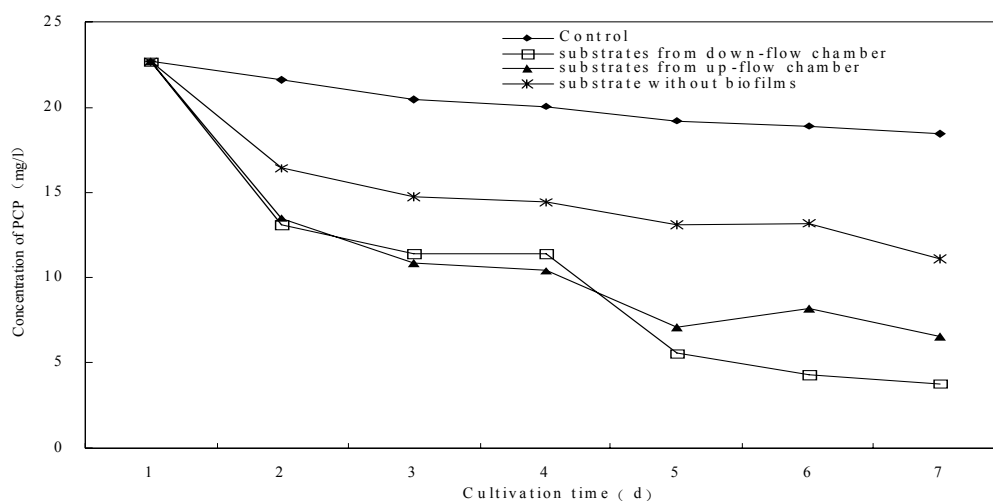


Fig. 5 PCP degradation by the substrate of IVCW.

removal rate of the substrate with biofilm in IVCW was 77.3%, which was 1.52 times that of 51% of the substrate without biofilm, and the contribution rate was 26.3%. Totally, the biofilm prompted the PCP removal capacity of the IVCW.

4. Conclusions

The biofilm distributed widely in the constructed wetland and mainly in the upper layer. Within certain limits, the higher pollution load was beneficial to the formation of the biofilm and improving the treatment efficiency. The removal rate of persistent pentachlorophenol of the constructed wetland increased with the time, which suggested the potential of removing organic contaminants efficiently.

References

- [1] D.A. Hammar, P.F. Breen, S. Perdomo, et al., *Constructed Wetlands for Waste Water Treatment*, Michigan, Lewis Publishers Inc., 1989, pp. 5-20.
- [2] F.A. Comin, Nitrogen removal and cycling in restored wetlands used as filters of nutrients for agricultural runoff, *Water Science Technology* 35 (1997) 255-261.
- [3] T.S. Rao, K.H. Rogers, Biofilm formation in a fresh water environment under photic and aphotic conditions, *Biofouling* 11 (1997) 265-282.
- [4] D. Vrhovesk, K.V. Felde, R.G. Mckinlay et al., Constructed wetland for industrial waste water treatment, *Water Resources* 30 (1996) 2287-2292.
- [5] C.P. Gerbq, M. Green, Optimization of artificial wetland design for removal of indicator microorganisms and pathogenic protozoa, *Water Science Technology* 40 (1999) 363-368.
- [6] A. Drizo, K.R. Reddy, Physico-chemical screening of phosphate removing substrates for use in constructed wetland systems, *Water Resources* 33 (1999) 3595-3602.
- [7] L. Michael, G. Geller, J.R. Gully, et al., Transformations in dissolved organic carbon through constructed wetlands, *Water Resources* 34 (2000) 1897-1911.
- [8] Z.B. Wu, S.P. Cheng, F. He, et al., Design and purification performance of vertical flow constructed wetland, *Chinese Journal of Applied Ecology* 13 (2002) 715-718 (in Chinese).
- [9] Y. Liu, Q.L. Zhao, X.C. Zhen, *Biofilm Technology for Wastewater Treatment*, China Architecture & Building Press, Beijing, 2000 (in Chinese).
- [10] L.X. Yu, G.Q. Wu, X.T. Meng, *Handbook of Microbiological Tests in Environment Engineering*, China Environmental Science Press, Beijing, 1990 (in Chinese).
- [11] S.P. Chen, Y.C. Xia, Artificial wetland with cattail (*Typha angustifolia*), rush (*Juncus efusus*), II : purifying space, *Journal of Lake Sciences* 10 (1998) 62-66.
- [12] Q.L. Zhao, R.C. Huang, Biofilm characteristics in hybrid biological reactor, *Environmental Pollution & Control* 22 (2000) 4-7.

DNA Damage (Comet Assay) as Biomarker of Cd Exposure in Marine Seed Scallops *Mizuhopecten Yessoensis* Age 1 Year

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Abstract: Cadmium-induced DNA degradation in gill cells of the scallop *Mizuhopecten yessoensis* was assessed using the comet assay (single-cell gel electrophoresis). Accumulation of highly toxic cadmium in the gill cells of bivalve is accompanied by the damage of the cell genome revealed as DNA migration in the comet assay. The main mechanisms of Cd effects on the integrity of the DNA structure are discussed.

Key words: Accumulation, cadmium, bivalves, *Mizuhopecten yessoensis*, genotoxicity, comet assay, DNA damage.

1. Introduction

Any organism, irrespective of its position in the evolutionary hierarchy, has key metabolic biochemical systems whose damage can be regarded as a biomarker of inevitable, irreversible destructive processes. Among the major reliable indicators are primarily the alterations (damage) in the structure of DNA, the main carrier of genetic information. Moreover, there are grounds to believe that DNA damage is one of the early stages in a cascading process leading to negative consequences. Understanding of its early mechanisms is particularly important for adequate evaluation of the toxicity of chemicals.

The above said is of primary importance for the study of the toxicity of heavy metals, a large and widespread group of pollutants of the aquatic environment, which are accumulated and long retained by the organisms. Among trace metals found in tissues of various aquatic inhabitants, cadmium occupies a noticeable place: it actively inhibits their vital

processes and, hence, the formation of nutrients. Extensive literature data suggest that bivalve mollusks in particular are able to concentrate this metal [1-3]. It is believed that the ecological danger of cadmium lies in possible distant consequences associated with its accumulation in the organism. Recently increased attention has been given to the study of the ecological and toxicological aspects of the interaction of aquatic organisms with this element, which, due to its physico-chemical properties and biological features, is a potential threat to biological systems.

Biochemical studies have shown that cadmium is a typical polytropic chemical agent, which is able to interact with various macromolecules and structures of the cell and cause a broad spectrum of negative biochemical shifts, from inhibition of individual enzymes and metabolic systems to damage of membrane structures [4-8]. From the ecotoxicological viewpoint, of particular interest is the ability of cadmium to induce oxidative stress [4], which is thought to be a leading pathogenetic mechanism responsible for the disturbance of cell metabolism [9].

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The reasons for the multiple manifestations of cadmium toxicity have not been studied completely, though there is no doubt that such studies are needed because cadmium is present in all components of the ecosystems. Experimental research performed in mammalian and human cells provided evidence for the genotoxicity of cadmium: it exhibits carcinogenic and mutagenic properties and is able to initiate DNA-strand breaks and to cause chromosome aberrations [10, 11]. Extensive studies in this direction have recently been performed using the comet assay, which allows a detection of DNA damage in individual cells with high accuracy [12-16]. However, no due attention has been paid to the interaction of cadmium with the DNA molecule in marine invertebrate cells.

The aim of our study was an experimental investigation of the effect of cadmium accumulation on the extent of DNA damage (assessed by DNA migration in individual cells and the length of the comet tail) in gill cells of the marine seed scallop *M. yessoensis* age 1 year.

2. Materials and Methods

2.1 The Chemicals

Normal melting point (NMP) and low melting point (LMP) agarose was obtained from LKB, Sweden. Ethidium bromide [CAS No. 1239-45-8] was obtained from Sigma. All other chemicals were of analytical grade and millipore water was used as the solvent.

2.2 Sample Collection

For experiments, scallops *Mizuhopecten yessoensis* were collected from a relatively unpolluted site in Severnaya Bay (Peter the Great Bay). To reduce the risk of size/age-related variability, scallops used in the experiments were 1 year old (39±2 mm shell length). Specimens of *M. yessoensis* were acclimated for at least 5 days in a holding tank at 16-18 °C with continuous aeration.

2.3 Exposure Conditions

After adaptation to the laboratory conditions, scallops were divided into two groups and placed for up to 4 days in tanks each containing 40 L of aerated filtered sea water with (experimental tank) or without (control tank) CdCl₂ (0.3 mg·L⁻¹) at 16 °C, at a density of ten molluscs per tank. During this period, the sea water was changed every other day and cadmium dosing was repeated at each water change.

2.4 Isolation of Gill Cells

The procedure for gill cell isolation was generally the same as that described by Wilson et al. (1998) [17]. The adductor muscle was cut with a scalpel to open the scallop. The gills were removed and washed four times in 5 mL of ice-cold calcium-magnesium-free saline (CMFS) consisting of 0.050 M Tris-HCl, pH 7.4, 500 mM NaCl, 12.5 mM KCl, 5 mM EDTA. The gills were then cut into a volume of 2 mL CMFS for 1 min with scissors. The gill cell suspension from each mollusc was transferred to flasks, and 10 mL of CMFS was added. The suspension was shaken gently for 1 h on ice in darkness, and large clusters of gill cells were removed by filtering the suspension through a 40-µm sieve. The isolated gill cells were centrifuged for 5 min at 1500 rpm (250 g), after that the supernatant was removed and cells were resuspended in the remaining CMFS to a concentration of 10⁵ cells/mL. The cells were further prepared according to the comet assay protocol.

2.5 Alkaline Single-Cell Gel Electrophoresis Assay (Comet Assay)

The effect of cadmium on DNA structure was evaluated using single-cell gel electrophoresis (SCGE) [18] known in the literature as the comet assay. This method has received a wide recognition and provides a rapid and sensitive tool for demonstrating DNA damage from chemicals and physical factors in individual cells [12]. Fragments of DNA resulting from DNA strand breaks actively migrate away from the nucleus in the electric field and form a tail, which

resembles a comet. The comet, in essence, represents the cell genome, because under alkaline conditions (at pH greater than 13) the RNA is decomposed and only the DNA-dye complex is fluorescent. In our experiment, the length of migration indicates the presence of cells with single-strand breaks in the DNA molecule.

The alkaline comet assay [18] modified for use with marine organisms [19] was applied to bivalve gill cell suspension to determine the level of DNA strand breakage. To this end, 50 μ L of the cell suspension was added to 100 μ L of 1% low melting point agarose (LKB, Sweden) in 0.04 M phosphate buffer (pH 7.4) at 37 °C, thoroughly mixed, and placed on a glass slide coated with 1% agarose for better adhesion and covered with a cover glass. The sample was placed for 3 min in a fridge for gel to form. The cover glass was carefully removed, each slide was embedded for 1 h in a lysing solution (2.5 M NaCl, 0.1 M EDTA- Na_2 , 1% Triton X-100, 10% DMSO, 0.02 M tris, pH 10) and placed in darkness. After washing with cold distilled water, the slides were transferred to an electrophoresis buffer (300 mM NaOH, 1 mM EDTA- Na_2) and maintained for 40 min. Electrophoresis was carried out at 2 V/cm for 15 min. After neutralization (0.4 M tris-HCl, pH 7.4), the slides were stained with ethidium bromide (2 μ g/mL).

The DNA comets were visualized and registered using a scanning fluorescence microscope (Zeiss, AxioImager A1) equipped with a digital camera AxioCam MRc. Digital images were processed using a CometScore Freeware v.1.5 (http://www.autocomet.com/products_cometscore.php), which allows calculations of the various parameters of comets indicating the level of DNA damage. Three parameters were determined for each comet: (1) the percentage of DNA in the comet tail (%DNA_t); (2) the length of the comet tail (Lt); (3) the tail moment (Mt) calculated by multiplying the tail length (Lt, μ m) by percent of DNA in the tail (%DNA_t).

In control and experimental groups of mollusks, we analyzed 5 slides each containing no less than 50

comets. For each experiment, statistical assessment of results was performed by comparisons of the mean group parameters ($P < 0.05$) of DNA damage in both groups of mollusks using a nonparametric Dunnett's test.

2.6 Data Analysis

Mean and median parameters of comets were compared between treatments by using a one-way ANOVA and Dunnett's test at $p = 0.05$ level. Comparison of the mean of exposed group to the mean of control group was made based on the mean of all cells analysed ($n > 500$) in each group and also on the mean of each individual ($n = 10$) within a group to analyse variability between organism replicates. Also, to compare the variability of %DNA in the comet tail (%DNA_t) and Mt in cells of control and exposed individuals, frequency distributions of the %DNA in the comet tail and Mt of all the cells were analysed. The percentage of DNA in the comet tail, length of the comet tail (Lt) and the tail moment (Mt) of 95% of the control cells were estimated. This number was compared to that found in the exposed cells.

2.7 Analysis of Trace Metals

The trace metal content of the gills of each scallop was analysed individually using atomic absorption spectroscopy with flame atomization and deuterium background correction (Shimadzu AA-6800). Blanks (mixture of nitric and perchloric acids, 3:1, v/v) were processed with the sample at each digestion. Metal concentration was calculated on the basis of the dry mass of tissue, which was dried to constant weight at 85 °C. The experiments were carried out in triplicate. Each mean represents five or seven individual tissue samples \pm standard error. A one-way ANOVA (analysis of variance) was applied to reveal differences between groups, taking a probability limit $P < 0.05$ as significant. Individual samples were compared by Student's *t*-test, using the standard error estimate derived from the corresponding ANOVA.

3. Results and Discussion

Like most bivalve mollusks, *Mizuhopecten yessoensis* exhibits the ability to accumulate cadmium from seawater. During experimental exposure (300 µg Cd/liter, 4 days), the cadmium content in the gills of scallop increased 6.5 to 276.0 µg/g, dry wt., i.e., almost 42 times. A comparative analysis of results obtained and literature data [1-3] suggests that despite the wide variations of absolute values, which are related to specific experimental conditions, *M. yessoensis* can be considered as an effective accumulator of cadmium.

Analysis of the electrophoresis picture of *M. yessoensis* gill cells shows that the DNA molecule in the gill cells of control mollusks (Fig. 1a) forms a symmetrical bright nucleus (a hollow in agarose filled with DNA) and a surrounding “halo” consisting of loops of high-polymer DNA which migrated into agarose. In Cd-exposed experimental mollusks, the DNA molecule in gill cells forms a well-expressed comet. This is evidently due to deep damage of the genome and the migration of low-polymer DNA fragments (Fig. 1b). According to the classification of Collins et al. [20], the comets formed by gill cells of control mollusks can be referred to two classes: C0 and C1. It is sometimes difficult to visually distinguish between the two classes of comets; therefore, they are united into a single group of (C0/C1)-comets characteristic of intact and viable cells [21]. Cadmium-exposed mollusks formed comets that mostly belong to the class C3, suggesting a high level of DNA molecule fragmentation.

We calculated the comet parameters reflecting the extent of DNA damage in gill cells of bivalve (Table 1). Analysis of the data shows that the values of all investigated parameters are significantly higher in the experimental group than in the control. On the other hand, the remarkably high variability of these parameters indicates a heterogeneity of the whole sample of comets. For illustration, experimental data, from which mean values were calculated, were

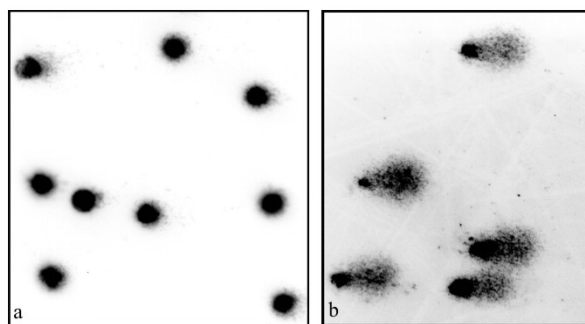


Fig. 1 Microphotographs of the comets formed by the gill cells of *Mizuhopecten yessoensis* under control (a) and experimental (b) conditions.

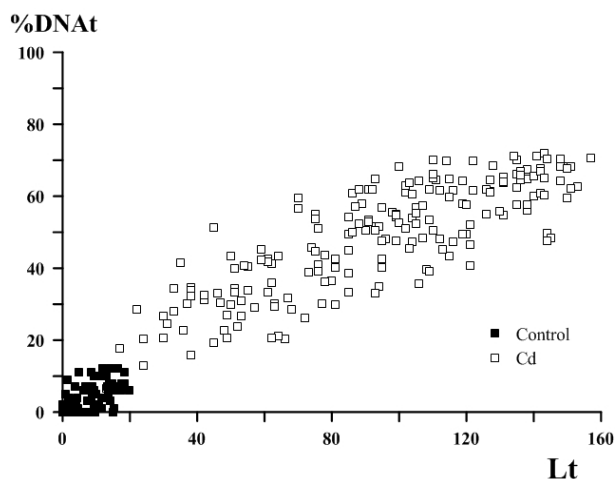


Fig. 2 The correlation between the percent DNA in the comet tail (%DNA_t) and the tail length (Lt) of comets formed by the gill cells of *Mizuhopecten yessoensis* under control and experimental conditions.

Table 1 The main parameters of DNA comets of the gill cells *Mizuhopecten yessoensis* from control and experimental groups.

Group	%DNA _t	Mt	Lt
Control	15.2 ± 2.0	2.3	5.0 ± 3.1
Experimental	32.0 ± 8.5	8.0	90.1 ± 31.5

Note: %DNA_t-the percentage of DNA in the comet tail; Lt-the length of the comet tail; Mt - the tail moment.

represented in the form of the relation between percent DNA and the length of the comet tail (Fig. 2). This kind of bivariate distribution is usually used to characterize populations and demonstrate the extreme values of comet parameters and their relations. Comparison of results (Fig. 2) shows a high heterogeneity of the DNA structure of gill cells in Cd-exposed mollusks. The proportion of DNA migration from the comet nucleus

in intact cells did not exceed 10%-12%, while in cells of experimental mollusks this index was 30%-60% for most comets. Thus, experimental data obtained with the comet assay indicate that the DNA molecule is one of the main targets during cadmium accumulation. Despite the functioning biochemical system of detoxification, cadmium does exhibit genotoxic properties causing a sharp increase in DNA damage.

Analogous experiments have demonstrated the genotoxicity of cadmium causing DNA damage in gill cells of the mussel *Mytilus edulis* (see Ref. [22]) and the crab *Charybdis japonica* (see Ref. [23]), as well as in cells of the marine sponge *Suberites domuncula* (see Ref. [24]) and the diatom *Chaetoceros tenuissimus* (see Ref. [25]). It should be noted that the damaging effect of cadmium manifested itself rapidly and at a relatively low ambient concentration of metal [22, 23].

Unfortunately, research in this area using marine organisms is merely beginning and analysis of the reasons for cadmium genotoxicity is based on few experimental data obtained on mammals. Most investigators believe that DNA damage can be caused by both the direct and indirect effect of metal [10, 11]. The direct mechanisms involve the ability of Cd^{2+} ions to bind with phosphate groups of nucleotides and form rigid complexes with N and O atoms of purines and pyrimidines by means of coordination bonds [26]. It is believed that such interaction of Cd^{2+} can alter the structure and destabilize the double strand of nucleic acids [27]. Moreover, the increased length of DNA migration under cadmium exposure can be a reflection of the increased quantity of single-strand breaks as a consequence of inhibition of biochemical systems of DNA repair [28, 29].

Among the reasons for cadmium genotoxicity, of the greatest interest is Cd-induced increase in the production of reactive oxygen species (ROS) or oxy radicals [30, 31], which trigger the processes of lipid peroxidation [4, 32] and oxidative destruction of DNA [11, 33, 34]. Some investigators believe that highly

reactive oxy radicals are one of the main reasons of oxidative DNA damage causing DNA strand breakage and bases modification [33]. Thus, the hydroxyl radical (OH) is able to replace hydrogen atoms from sugar residues preferably in the 4-carbon atom. The resulting radicals are unstable and, in most cases, converted into strand breaks by means of well-known mechanisms [34]. Therefore, the increased quantity of products of DNA damage is used as an indicator of oxidative stress caused by various xenobiotics to marine organisms, including bivalves [35-38]. Under exposure to cadmium, the level of oxidized deoxyguanosine in the bivalve *Perna perna* was also increased specifically in cells of the digestive gland and gills, but not in mantle. This was also true in case the mollusks were transferred to a polluted area [7]. Along with oxy radicals, intermediate products of lipid peroxidation can have a damaging effect on the DNA structure. These in particular are α,β -unsaturated aldehydes, which can react with DNA bases with the formation of etheno-adducts [33, 39].

The above examples suggest that the leading factor of cadmium genotoxicity is oxidative stress. Since the genome has an exclusive role in the functioning of biological systems, DNA damage is among the most important manifestations of cadmium toxicity. It should be emphasized that, irrespective of the specific mechanisms responsible for cadmium genotoxicity, all types of structural alterations and modifications that the DNA molecule undergoes are of great interest, no matter whether or not they lead to mutations and the disturbance of metabolism or to the cell death.

4. Conclusions

It can be noted in conclusion that the elucidation of the biochemical mechanisms underlying "hidden" pathological shifts is necessary for solving the problem of reliable scientific prognosis of ecological consequences of aquatic pollution. Therefore, the study of biochemical changes associated with metal accumulation in aquatic organisms can be regarded as

one of the main directions of research that provide a basis for ecological optimization of natural resources use. The investigations of Cd-genotoxicity in the marine scallop of different age groups will be the subject of future studies.

References

- [1] V.P. Chelomin, Ecotoxicological aspects of bioaccumulation of cadmium (illustrated by bivalve mollusks), Abstract of Doctoral (Biol.) Dissertation, Vladivostok, 1998.
- [2] J.M. Frazier, Bioaccumulation of cadmium in marine organisms, *Environ. Health Perspect* 28 (1979) 75-79.
- [3] S. Ray, Bioaccumulation of cadmium in marine organisms, *Experientia* 40 (1984) 14-23.
- [4] N.V. Dovzhenko, A.V. Kurilenko, N.N. Belcheva, V.P. Chelomin, Cadmium-induced oxidative stress in tissues of the bivalve *Modiolus modiolus*, *Biol. Morya* 5 (2005) 358-362.
- [5] V.P. Chelomin, N.N. Belcheva, M.V. Zakhartsev, Biochemical mechanisms of adaptation of the mussel *Mytilus trossulus* to cadmium and copper ions, *Biol. Morya* 5 (1998) 319-325.
- [6] V.P. Chelomin, N.N. Belcheva, The effect of heavy metals on processes of lipid peroxidation in microsomal membranes from the hepatopancreas of bivalve mollusks *Mizuhopecten yessoensis*, *Comp. Biochem. Physiol. C* 103 (1992) 419-422.
- [7] V.P. Chelomin, E.A. Bobkova, O.N. Lukyanova, N.M. Chekmasova, Cadmium-induced alterations in essential trace element homeostasis in the tissues of scallop *Mizuhopecten yessoensis*, *Comp. Biochem. Physiol. C* 3 (1995) 329-335.
- [8] M.V. Zakhartsev, V.P. Chelomin, N.N. Belcheva, The adaptation of mussels *Crenomytilus grayanus* to cadmium accumulation results in alterations in organization of microsomal enzyme-membrane complex (non-specific phosphatase), *Aquat. Toxicol.* 50 (2000) 39-49.
- [9] H. Sies, *Oxidative Stress: Oxidants and Antioxidants*, Academic Press, London, 1991.
- [10] P. Lopez-Ortal, V. Souza, L. Bucio, DNA damage produced by cadmium in a human fetal hepatic cell line, *Mutation Res.* 439 (1999) 301-306.
- [11] S.A. Mouron, C.D. Golijow, F.N. Dulout, DNA damage by cadmium and arsenic salts assessed by the single cell gel electrophoresis assay, *Mutation Res.* 498 (2001) 47-55.
- [12] V.A. Tronov, I.I. Pelevina, The comet assay for individual cells, principles and applications, *Tsitologiya* 4-5 (1996) 427-439.
- [13] V.A. Tronov, T.A. Nikolskaya, M.A. Konoplyanikov, DNA comets as a marker of cell death, *Biofizika* 2 (1999) 288-295.
- [14] A.R. Collins, V.L. Dobson, M. Dusinska, The comet assay: what can it really tell us? *Mutation Res.* 375 (1997) 183-193.
- [15] A.N. Jha, Ecotoxicological applications and significance of the comet assay, *Mutagenesis* 3 (2008) 207-221.
- [16] L.R. Shugart, DNA damage as a biomarker of exposure, *Ecotoxicology* 9 (2000) 329-340.
- [17] J.T. Wilson, P.L. Pascoe, J.M. Parry, D.R. Dixon, Evaluation of the comet assay as a method for the detection of DNA damage in the cells of a marine invertebrates, *Mytilus edulis* L. (Mollusca: Pelecypoda), *Mutation Res.* 399 (1998) 87-95.
- [18] N.P. Singh, M.T. McCoy, R.R. Tice, E.L. Scheider, A simple technique for quantification of low levels of DNA damage in individual cells, *Exp. Cell Res.* 237 (1988) 123-130.
- [19] C.L. Mitchelmore, C. Birmelin, D.R. Livingstone, J.K. Chipman, Detection of DNA strand breaks in isolated mussel (*Mytilus edulis* L.) digestive gland cells using the "comet" assay, *Ecotoxicol. Environ. Saf.* 41 (1998) 51-58.
- [20] A.R. Collins, A.G. Ma, S.J. Duthie, The kinetics of repair of oxidative DNA damage (strand breaks and oxidized pyrimidine) in human cells, *Mutation Res.* 336 (1995) 69-77.
- [21] V.A. Tronov, D.G. Tereshchenko, M.A. Konoplyanikov, Mechanism of irradiation-induced death of lymphocytes of the human peripheral blood assessed by the comet assay, *Biofizika* 1 (1998) 115-124.
- [22] C. Emmanouil, T.M.T. Sheehan, J.K. Chipman, Macromolecule oxidation and DNA repair in mussel (*Mytilus edulis* L.) gill following exposure to Cd and Cr (VI), *Aquat. Toxicol.* 82 (2007) 27-35.
- [23] L. Pan, H. Zhang, Metallothionein, antioxidant enzymes and DNA strand breaks as biomarkers of Cd exposure in a marine crab, *Charybdis japonica*, *Comp. Biochem. Physiol. C* 144 (2006) 67-75.
- [24] W.E.G. Muller, R. Batel, M. Lacorn, Accumulation of cadmium and Zinc in the marine sponge *Suberites domuncula* and its potential consequences on single-strand breaks and on expression of heat-shock protein: A natural field study, *Mar. Ecol. Prog. Ser.* 167 (1998) 127-135.
- [25] S.R. Desai, X.N. Verlecar, U. Goswami, Genotoxicity of cadmium in marine diatom *Chaetoceros tenuissimus* using the alkaline comet assay, *Ecotoxicology* 15 (2006) 359-363.
- [26] K.B. Jacobson, J.E. Turner, The interaction of cadmium and certain other metal ions with proteins and nucleic acids, *Toxicology* 16 (1980) 1-37.
- [27] N.T. Christie, M. Costa, In vitro assessment of the toxicity

of metal compounds. IV. disposition of metals in cells: Interactions with membranes, glutathione, metallothionein and DNA, *Biol. Trace Elem. Res.* 6 (1984) 139-158.

- [28] M. Hartmann, A. Hartwig, Disturbance of DNA damage recognition after UV-Irradiation by nickel(II) and cadmium(II) in mammalian cells, *Carcinogenesis* 4 (1998) 617-621.
- [29] A.M. Pruski, D.R. Dixon, Effects of cadmium on nuclear integrity and DNA repair efficiency in the gill cells of *mytilus edulis* L., *Aquat. Toxicol.* 57 (2002) 127-137.
- [30] J. Liu, S.Y. Qian, Q. Guo, Cadmium generates reactive oxygen- and carbon-centered radical species in rats: insight from in vivo spin-trapping studies, *Free Radic. Biol. Med.* 45 (2008) 475-481.
- [31] Y. Wang, J. Fang, S.S. Leonard, K.M.K. Rao, Cadmium inhibits the electron transfer chain and induces reactive oxygen species, *Free Radic. Biol. Med.* 36 (2004) 1434-1443.
- [32] S.J. Stohs, D. Bagchi, Oxidative mechanisms in the toxicity of metal ions, *Free Radic. Biol. Med.* 2 (1995) 312-336.
- [33] E.A. Almeida, A.C.D. Bainy, A.P.M. Loureiro, Oxidative stress in *perna perna* and other bivalves as indicators of environmental stress in the Brazilian marine environment: antioxidants, lipid peroxidation and DNA damage, *Comp. Biochem. Physiol.* 146 (2007) 588-600.
- [34] J. Cadet, M. Berger, T. Douki, J.L. Ravanat, Oxidative damage to DNA: Formation, measurement and biological significance, *Rev. Physiol. Biochem. Pharmacol.* 131 (1997) 1-87.
- [35] S. Canova, P. Degan, L.D. Peters, Tissue dose, DNA adducts, oxidative DNA damage and CYP1A-immunopositive proteins in mussels exposed to waterborne benzo[a]pyrene, *Mutation Res.* 399 (1998) 17-30.
- [36] J. Jebali, M. Banni, Oxidative DNA damage levels and catalase activity in the clam *ruditapes decussates* as pollution biomarkers of Tunisian marine environment, *Environ. Monit. Assess.* 124 (2007) 195-200.
- [37] D.R. Livingstone, Contaminant-stimulated reactive oxygen species production and oxidative damage in aquatic organisms, *Mar. Pollut. Bull.* 8 (2001) 656-666.
- [38] A. Rodrigues-Ariza, J. Alhama, F.M. Diaz-Mendez, J. Lopez-Barea, Content of 8-OxodG in chromosomal DNA of *sparatus* fish as biomarker of oxidative stress and environmental pollution, *Mutation Res.* 438 (1999) 97-107.
- [39] A.P.M. Loureiro, P. Di Mascio, O.F. Gomes, M.H.G. Medeiros, *trans, trans*-2,4-Decadienal-Induced 1,N²-Etheno-2'-Deoxyguanosine adduct formation, *Chem. Res. Toxicol.* 13 (2000) 601-609.

The Effect of Training and Community Based Management on Earthquake Impacts on Environmental Resources

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Abstract: Disasters have been defined as ecological disorders or emergencies, which lead to disease incidence, damage or injury and loss of property. Iran is located in a region prone to earthquake hazard and has faced several tragic earthquakes in its history which have led to mortalities and destruction of natural and socio-economic resources. Several researches have shown the positive effect of training in decreasing negative impacts of disasters. In societies where people are properly trained and obtain necessary information about how to react in case of earthquake or other natural disasters, the rate of fatalities would be significantly decreased. Earthquake is not a preventable natural disaster. So the only way to decrease its negative consequences would be effective preparedness. Public training is the main way of enhancing the awareness to the whole society and is the core of disaster planning. In this research, the aim is to evaluate the effect of training on the knowledge and practice of people vulnerable to earthquakes.

Key words: Earthquake, vulnerability, community-based management, training.

1. Introduction

Disasters have been defined as ecological disorders or emergencies that lead to disease incidence, damage or injury and loss of property. World Health Organization has also mentioned disaster as an unexpected ecological phenomenon, which needs beyond organizational contributions [1]. Disasters are categorized in two groups: natural and manufactured [2]. Humankind is facing the growing measures of natural disasters. On the other hand, lack of appropriate programs for prevention, reduction of demolishing effects and preparedness for disasters can confront a vulnerable society to a catastrophic event [3].

Huge natural disasters during two recent decades in the world have affected at least 800 million people.

Population congestion and poor condition settlement have increased the number of affected people in different regions, which is equal to more than 12800 people all over the world [4]. Natural disasters cause 87 billion dollars loss every year [5].

Tectonic studies indicate that the Iranian plateau has a very high density of active and recent faults. Thus, several regions are vulnerable to destructive earthquakes [6] and several tragic earthquakes have led to mortalities, homelessness, destruction of industrial facilities agricultural lands and damages to national resources [7]. Iran is the fourth country in Asia and the sixth in the world from the point of natural disaster incidents, leading to enormous social and economical costs [2]. During each year in the period of 1980-2000, about 1074 people lost their life because of the earthquake [1]. In a recent earthquake in Iran (Bam), more than 30,000 people died, and 10,000 were injured,

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while more than 10,000 became homeless and earthquake refugee [8].

Being a natural disaster, earthquake is not preventable. Therefore, the only way to decrease its negative consequences would be effective preparedness [7]. Public training is the main key to enhance the awareness of the whole society [9]. It is the core of disaster planning [10]. There is a positive relationship between the level of training and preparedness for earthquakes [11].

Several researches show the positive effects of training in decreasing negative impacts of disasters. In societies where people are properly trained and obtain necessary information about how to react in case of an earthquake or other natural disasters, the rate of fatalities would be significantly decreased [12].

Considering the importance of public level of knowledge, it should be mentioned that public training is the most important element when facing disasters in Iran [13]. Nateghi believes that reducing harm program should provide a safety culture in order to make public aware of the existing dangers. Public awareness can be gained through different ways such as short-term activities: radio, television, posters and long-term activities that can be achieved by public training [14]. Shivaco and Shav believed that family and society training are key factors to prepare people before disaster occurrence. Society training is dependent on its entity (city or village). Therefore, it is necessary to make disaster management as a part of society culture to provide the possibility of obtaining preparedness for people [15]. Disaster training is considered as an important part of disaster management. There is growing evidence to show that most top-down disaster risk management and responses programs fail to address specific local needs of vulnerable communities, ignore the potential of local resources and capacities and may in some cases even increase people's vulnerability [16]. All communities have some vitally important assets to deal with disasters. These may include knowledge of disaster warning signs, locally

safe and vulnerable areas, experience of past disasters, methods of survival and social relations that are often vitally important in coping with crisis [17].

International Strategy for Disaster Reduction (ISDR) believes that the risk reduction measures are most successful when they involve the direct participation of the people most likely exposed to hazards [18]. In this research, the aim is to evaluate the effect of training on the knowledge and practice of people vulnerable to earthquakes.

2. Materials and Methods

2.1 Study Area

The study area is located within 3 dehestans¹ that are Ghaleno, Kahrizak, and Ghani abad. Ghaleno dehestan contains 19 residential points that are all villages and two of which are being sample in this research. Kahrizak contains 44 residential points that are 2 cities: Baghershahr, Kahrizak and 42 villages that seven of which have been sampled. Finally, Ghani abad contains 7 residential points (all villages) one of which has been sampled for this research. Following in the Fig. 1, the location of study area is illustrated according to Iran and Tehran.

2.2 Vulnerability of the Study Area to Earthquake Disaster

Poor people who are mostly involved in low-income jobs in Tehran or Rey, and cannot afford for accommodation costs inhabit the study area. Poverty is considered as the most important consequence of disasters like earthquake [19]. Low economic level of rural livelihoods is one of the key factors that configure risk (such as earthquake) to hazards. High rate of poverty and population density along with old and timeworn residential buildings make the study area highly vulnerable to earthquake disaster.

The seismicity map of the study area shows the high vulnerability to the potential earthquake.

¹ A political division in Iran which consists of a number of residential areas.

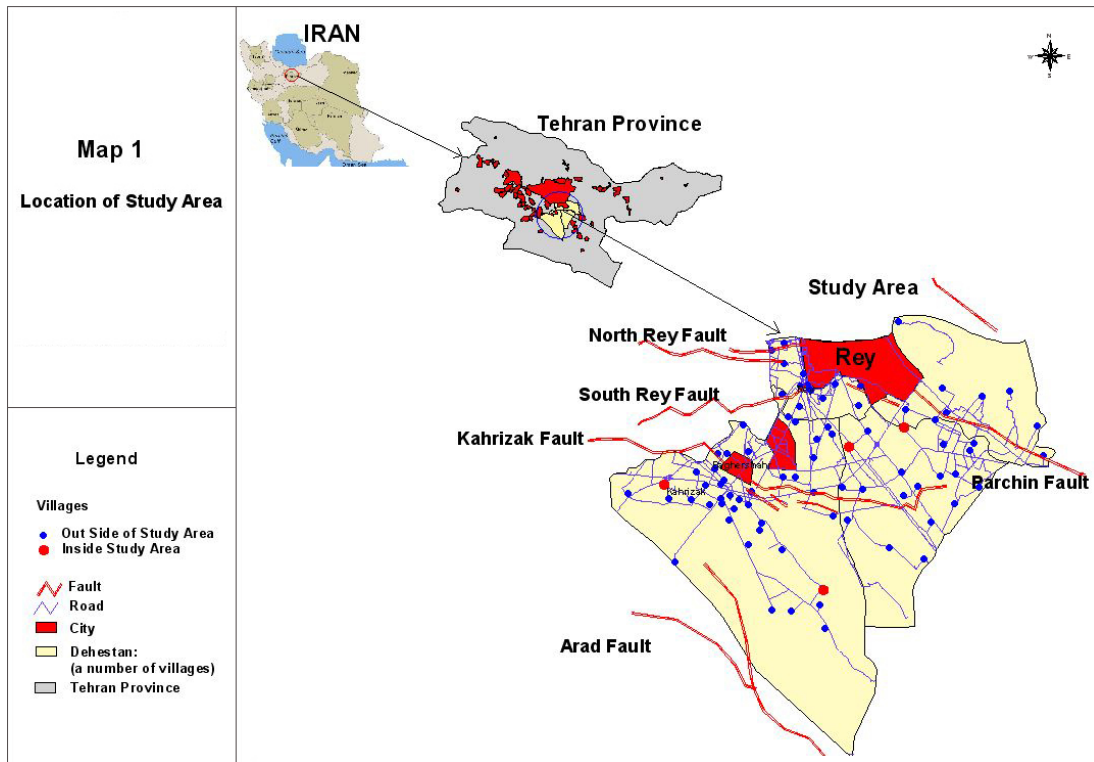


Fig. 1 Location of the study area.

As illustrated in Fig. 2, the sample villages are located very near to the faults and high earthquake prone areas.

2.3 Model Used for the Analysis

In this research, Village Disaster Taskforce (VDT) model has been used for the analysis. This model consists of a community-based program of the disaster risk management, in which the rural society is actively engaged in the identification, analysis, treatment, monitoring and evaluation of the disaster risks, in order to reduce the vulnerabilities and enhance its capacities. This model focuses on community participation, bottom-up approach and facilitation of warning dissemination and communication to grassroots [20].

The community activities are coordinated through a taskforce. The program follows the general structure, rules of Comprehensive Rescue Program, and is based on:

- people-centered bottom-up approach.
- community participation and efficient use of local

capacities with no or minimum cost to help the program sustainability.

- integration of current administrative programs at higher level than village; since a viable community-based disaster reduction depends on a favorable political environment that understands, promotes and supports this participation process.

2.4 Study Design

The study is designed as a before-after assessment of training effectiveness on raising the knowledge and practice of a rural community in the study area, focusing on preparedness and resiliency for possible earthquakes in the upcoming future. Measurement is done before and after the intervention. Households residing in 10 villages in the area were the target population, which were chosen randomly in such a way that they are relatively apart in terms of geographic distance, in order to minimize the ‘contaminating’ effect of the intervention on ‘non-intervention’ villages. The aim of such selection is to reduce transfer of the

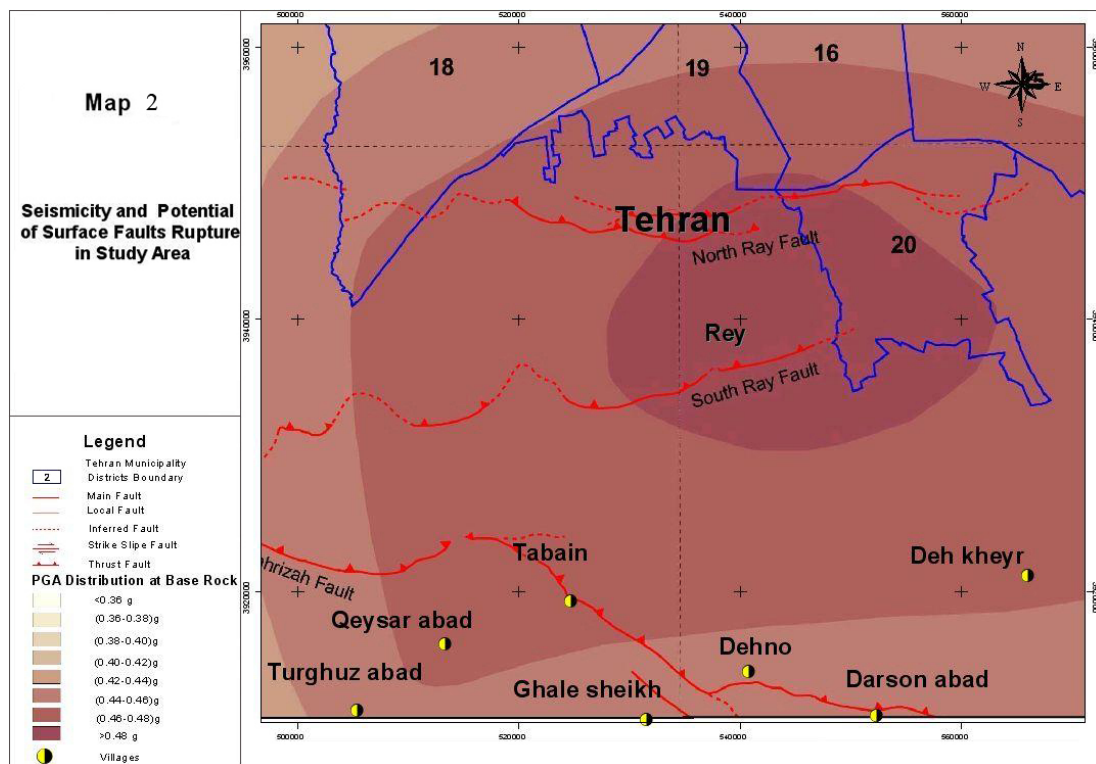


Fig. 2 Seismicity and potential of surface faults rupture in the study area.

training results from the households undergoing training to the households in the non-intervention villages. The intervention group was further divided into two subgroups of ‘group training’ and ‘face-to-face training’.

Twenty personnels, called as behvarz, were selected amongst 10 villages of the area under study, and were trained to gain knowledge about earthquake risks, different ways of risk reduction before, during and after the disaster occurrence, safer locations of the residence, emergency bag, identification card, ways of informing the next village after the earthquake and essential information about mental health. After completion of this period, they were ready to train the intervention group with the same discussion topics. Questionnaires were distributed amongst people for data collection purpose. Seven questions about knowledge and 10 questions about practice were asked from one respondent in each household, along with questions on 8 independent factors, i.e., demographics, socioeconomic status, and history of previous

earthquake experiences. Knowledge and practice variables were summarized as two main outcome variables of interest. Effectiveness of training in increasing the outcome variables in the intervention group was compared with any possible increase in the non-intervention group. Moreover, that adjusted for any difference of outcome variables. Level between the intervention and non-intervention groups before the intervention started, and for any possible difference of basic factors between the intervention and non-intervention group that could have a confounding effect, e.g., demographic and socioeconomic variables.

2.5 Analysis Method

Crude comparisons of outcome variables before and after the intervention were provided first. These comparisons were carried out in both the intervention and non-intervention groups. Two different types of intervention are included in these comparisons. To assess the degree to which the demographic and socioeconomic variables can distort the results of the

above-mentioned comparisons, they have also been compared between the different intervention groups. Regression model was used as adjusted analysis that takes into account the difference in the non-intervention group and the difference in confounding factors' distributions between the two intervention groups, and gives a pure estimation of the difference in the outcome variables in the intervention group before and after the intervention. Enter method was used for inclusion of variables in the regression model.

For construction of the summary knowledge variable, the original knowledge variables' values were recorded so that correct answers are represented with greater values than those for wrong answers. Three types of answers (and their values) were wrong (0), correct but incomplete (1), and correct and complete. The seven original knowledge variables have undergone the estimation of Cronbach's alpha coefficient as a measure of internal consistency reliability. Variables were dropped from calculation of alpha to increase the value of coefficient, until no further increase in alpha was attainable. Then the remaining original knowledge variables' values were summed to give a summary knowledge variable. The maximum possible score (of three) for each question to find the maximum attainable value for the latter summary knowledge variable multiplied the number of remaining original variable. Value of the latter summary measure of knowledge for each respondent was divided by the maximum attainable value to give a 0-100 summary knowledge variable that was used in further parts of analysis. The same procedure was performed for constructing the summary practice variable. For unadjusted analysis, independent t-test and one-way ANOVA were used for comparison of ratio variables between two and more than two groups respectively.

Chi square (or Fisher's exact test) was used for comparing nominal variables among multiple groups. Chi square for trend was used for comparing ordinal variables among multiple groups. Chi square (or Fisher's exact test) and odds ratio point and interval

estimates were used for comparing two-level nominal variables across two groups. For adjusted analysis, each of the 0-100 summary variables for knowledge and for practice were used separately as the outcome variable in a set of regression models.

3. Results and Discussion

In Fig. 3 the distribution of intervention groups and two phases of measurements are illustrated. As it shown, the total sample population is dividing into two categories: the intervention group, which is further divided into group and face-to-face training and the non-intervention group.

According to demographic variables, the average number of understudy families was 3.77 and the average age was 42.9 years old. In 91.4% of families, father was the head of household, in 7.5% mother, in 1.1% sibling and in 0.1%, another person had this responsibility. 10.9% of the participants were illiterate, 6.6% had university education. 3.1% were unemployed and 28.6% had business jobs. 36.4% did not have the earthquake experience before. Only 2.7% were under the coverage of rural insurance.

Table 1 shows the responses given to knowledge and practice questions. All questions were related to knowledge and most questions were related to practice, the complete correct questions have increased after training.

In unadjusted comparison, face-to-face training was less effective for increasing the knowledge of understudy participants than group training, and there was a higher increase in the knowledge of these two intervention groups than that of non-intervention, while there was only a minimal change for the latter (3.80 percent more or 1.08 times increase) (Table 1).

In unadjusted comparison, appropriate practice increased more intervention (training) group than that in non-intervention group, the latter with only minimal change (0.83 percent point or 1.11 times increase) (Table 2). In unadjusted comparison, face-to-face training was more effective in increasing appropriate

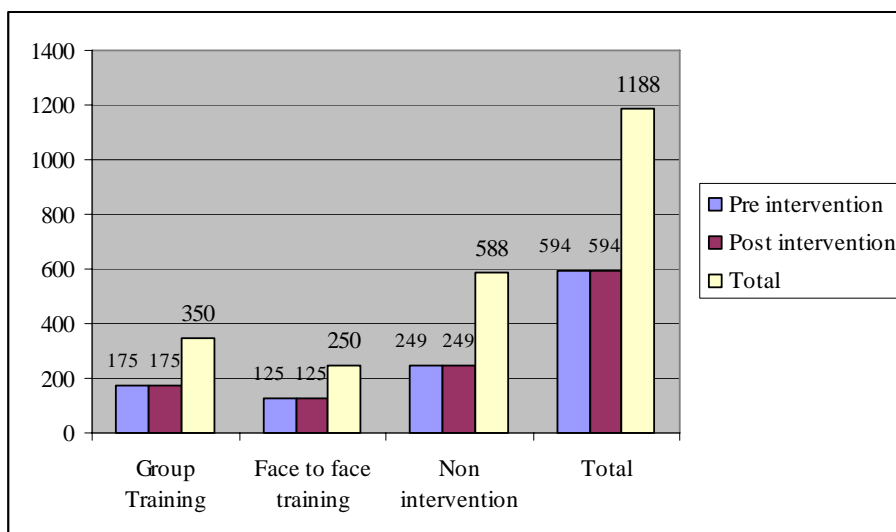


Fig. 3 Distribution of study subjects by three intervention groups and two measurement phases.

Table 1 Total score of knowledge questions in intervention and non-intervention group.

		Mean	Medium	S.D	Min	Max	Number
Group training	Pre intervention	41.40	41.67	24.87	0	100	125
	Post intervention	89.51	91.67	8.05	67	100	120
Face to face training	Pre intervention	33.24	33.33	26.88	0	100	175
	Post intervention	88.61	91.67	11.57	58	100	172
Non training group	Pre intervention	46.77	50.0	19.94	0	83	249
	Post intervention	50.57	50.0	19.12	0	83	292

practice of study participants than group training, and appropriate practice increased more in these two intervention groups than that of non-intervention group, the latter with only minimal change (0.83 percent point or 1.11 times increase).

According to Table 3, group training has more effect on increasing the knowledge scores compared to the face-to-face training. The difference in score obtained by intervention and non-intervention group was statistically significant ($p < 0.0001$), but there was no meaningful statistical difference between two training groups.

As shown in Table 4, the increase in practice score in

face-to-face training group was higher than that of group training. In this case, the difference in score increase, in all three groups was statistically meaningful ($p < 0.0001$).

Multi variable regression analysis has been utilized for modification of the results. Table 5 shows the results of regression analysis.

The mean value of knowledge summary variable increased from pre-intervention to post-intervention phase in the intervention group as compared to the non-intervention group. This increase was statistically significant when adjusted only for the pre-measurement levels of practice variable in the intervention and

Table 2 Total score of practice questions in intervention and non-intervention group.

		Mean	Medium	S.D	Min	Max	Number
Group training	Pre intervention	8.63	14.29	7.44	0	29	125
	Post intervention	45.28	50.0	22.14	7	79	121
Face to face training	Pre intervention	8.24	0.0	10.40	0	57	175
	Post intervention	31.40	28.57	13.80	0	57	172
Non training group	Pre intervention	7.68	0.0	8.95	0	57	249
	Post intervention	8.51	7.14	7.94	0	29	293

Table 3 The effect of training on knowledge improvement.

	Pre intervention	Post intervention	Difference	Ratio
Group training	32.24	88.61	55.37	2.67
Face to face training	41.40	89.51	48.11	2.16
Non training	46.77	50.57	3.80	1.08

Table 4 The effect of training on practice improvement.

	Pre intervention	Post intervention	Difference	Ratio
Group training	8.24	31.40	23.16	3.81
Face to face training	8.63	45.28	36.65	5.25
Non training	7.68	8.51	0.83	1.11

Table 5 The result of regression analysis of knowledge and practice variables.

Dependant variable	B	Beta	p-Value
Knowledge	-13.39	-0.251	0.0001
Practice	-14.58	0.427	0.0001

non-intervention groups (beta = -13.937 for moving from non-intervention to intervention group, $p < 0.001$). A similar situation existed for intervention as group training versus face-to-face training (beta = -6.638 for moving from group training to face-to-face training or from face-to-face training to non-intervention group, $p < 0.001$). The increases in mean value of practice summary variable from pre-intervention to post-intervention phase, in the intervention group, as seen in

unadjusted comparison, did not exist when adjusted for confounding effects of other explanatory variables. The mean value of practice summary variable increased from pre-intervention to post-intervention phase in the intervention group as compared to the non-intervention group and this increase was statistically significant when adjusted only for the pre-measurement levels of practice variable in the two groups of intervention and non-intervention (beta = -14.580 for moving from non-intervention to intervention group, $p < 0.001$). A similar situation existed for intervention as group training versus face-to-face training (beta = -6.565 for moving from group training to face-to-face training or from face-to-face training to non-intervention group, $p < 0.001$). The increases in mean value of practice summary variable from pre-intervention to post-intervention phase in the intervention group, as seen in unadjusted comparison, did not exist when adjusted for confounding effects of other explanatory variables.

4. Conclusions

Group training had stronger effect on participants' knowledge compared to the face-to-face training. Improvement in practice score through face-to-face training was more than improvement achieved by group training. It can be concluded that having direct

contact with people and training them individually has more effectiveness in people's practice and in this way we can expect that the possibility of behavior modification and useful training would be increased. For the reason that natural disaster occurrence is unavoidable, therefore, the only way is to decrease the dangerous effect which threaten people's life. Therefore, it is necessary to make people prepare to best encounter with disasters and also make them ready to show appropriate reaction for rescuing their lives. On the other hand, a proper action and adequate knowledge should exist when a disaster occurs. Useful trainings for the purpose of transferring knowledge and improving knowledge are necessary. Although training is an important factor for improvement in knowledge and practice, but it is apparent that direct training methods like face-to-face training are more effective in behavior modification and consequently, they increase the level of learning.

References

- [1] K. Jahangiri, J. Tayebi, Strategic planning in decreasing the harmful economical effects of natural disasters, *Payesh Journal* 4 (2007) 281-287.
- [2] R. Mohebbi Far, S. Asef Zadeh, Criticism to public structure of dealing with natural disasters in Iran: research in health care system, *Journal of Research in Medicine* 3 31 (2008) 195-199.
- [3] K. Jahangiri, J. Tayebi, Disaster management, *Payesh Journal* 3 (2004) 205-214.
- [4] D. Mayers, W. Mayers, F. David, *Disaster Mental Health Services*, Brunner-Rout Ledge Company, 2005.
- [5] K. Sharma, R. Sharma, *National Disaster*, APH Publishing Corporation, 2005.
- [6] B. Tavakoli, M. Ghafory-Ashtiany, *Seismic Hazard Assessment of Iran International Institute of Earthquake Engineering and Seismology (IIEES)*, 2008.
- [7] R. Shaw, K. Shiwaku, H. Kobayashi, M. Kobayashi, Linking experience, education, perception and earthquake preparedness, *Disaster Prevention and Management* 1 (2004) 39-49.
- [8] M. Khankeh, Health care management in natural disaster, *Rehabilitation Journal* 2 (2006) 123-134.
- [9] B. Abolshams Asgari, The generalities of unpredictable accident, in: the Second International Congress of Disaster Management and Health Proceeding, Shokravi Publication, Tehran, 2004.
- [10] M. Davoodi, Public education for preparedness in earthquake, in: the Second International Congress of Disaster Management and Health Proceeding, Shokravi Publication, Tehran, 2007.
- [11] H. Mahallati, Z. Kaveh, Measuring people attitudes earthquake in Tehran: focusing on training and ways of information distribution, in: the Second International Congress of Disaster Management and Health Proceeding, Shokravi Publication, Tehran, 2004.
- [12] *Disaster Preparedness and Mitigation, UNESCO's role, United Nations Educational, Scientific and Cultural Organization*, 2007.
- [13] R. Shaw, Linking experience, education, perception and earthquake preparedness, *Journal of disaster prevention and management* 1 (2004) 13.
- [14] N. Bamdad, The role of community knowledge in disaster management: the Bam earthquake lesson in Iran, in: *International Conference on Engaging Communities*, Australia, 2005.
- [15] F. Nateghi, Disaster mitigation strategies in Tehran, Iran, *Disaster Prevention and Management* 3 (2000) 205-211.
- [16] K. Shiwaku, R. Show, R. Chandra Kandel, S. Narayan Shresta, A. Mani Dixit, Future perspective of school disaster education in Nepal, *Disaster Prevention and Management* 4 (2007) 576-587.
- [17] Asian Disaster Preparedness Center, *Community-based disaster management for local authorities*, 2006.
- [18] M. Saghafinia, Treatment management in disaster: a review of the Bam earthquake experience, *Journal of Treatment Management in Disaster* 6 (2007).
- [19] S. Bakhtiari, Investigating the fire events as a consequence of earthquake in the world, *Journal of Farhang-e-Eamenei* 2 (2002) 54-61.
- A. Ardalan, Disaster health management: Iran's progress and challenges, *Iranian J. Publ. Health* 38 (2009) 93-97.

Farmers' Perceived Impact of Fair Trade: The Case of Costa Rica

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Abstract: The perceived usefulness of Fair Trade influences both its effectiveness and farmers' long-term participation. The aim of this paper is to measure the perceived economic, social and environmental impact of Fair Trade by farmers in Costa Rica. One hundred farmers were interviewed, and their perceived change in living and working conditions due to Fair Trade participation was measured through a t-test analysis. The sample characters' influence on the perceived change was also measured, adopting a regression model and a t-test. The results showed a positive perception of the impact of Fair Trade, with a particularly strong perceived improvement in the farmers' technical, economic and managerial skills. There was relatively less perceived change in the environmental, educational and sanitary conditions. The results showed the need for Fair Trade to better adjust its strategy to the expectations of the farmers' communities.

Key words: Fair Trade, impact, Costa Rica, technology acceptance model, small farmers.

1. Introduction

1.1 Background

The impact of Fair Trade on participating farmers has often been measured in terms of its economic, social and environmental consequences. Many researchers reported that entering Fair Trade contributed to protection from the world market price volatility, better access to credit and external funding, debt reduction, increased investments and employment, higher income, better access to food, health and education, increased labour skill and more sustainable agronomic practices [1, 2]. Others underlined Fair Trade's positive contributions to the self-esteem and cultural revival of rural communities [3]. The positive impact on rural communities' cultural and political empowerment was confirmed by other researchers who suggest that Fair Trade enhanced these communities' political influence [4] and self reliance [5]. Fair Trade

also has a positive effect on conflict prevention by reducing discrimination against indigenous people [6]. The same researchers investigated the role of gender and found a positive effect of Fair Trade on women's skills and on their participation in community activity, although negative aspects (related to excessive workload and relatively less access to managerial roles) emerged. These findings confirmed the results of previous research [7]. The positive environmental impact of Fair Trade is related to its connection to organic production practices [2, 5] and to agroecology principles [8].

In most of the literature examined, suggestions for further investigation focus on developing a more efficient relationship along the supply chain from the local community level to international distribution channels. One interesting suggestion concerns the necessity of increasing the supply volume by encouraging the producers' participation in Fair Trade networks [3]. The literature surveyed also explains the success of Fair Trade in terms of quantitative objective indicators like income, access to food, mortality, etc..

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The effect of Fair Trade participation on these indicators is not always easily separable from other joint initiatives such as improving supply chain management efficiency or granting easier access to credit [2].

The extent to which the expected changes in farmers' living conditions resulting from Fair Trade objectives are actually perceived by the farmers is an important aspect not considered in the literature. The likelihood of the farmers' increased participation in Fair Trade is related to their degree of satisfaction, which is based on subjective perception. This statement is supported by the theoretical approach defined in the Technology Acceptance Model (TAM) [9]. Following the assumptions of this model, and substituting the technological innovation (adoption of information systems) with a process innovation (adoption of Fair Trade), the positively perceived impact¹ should not only encourage the farmers to continue their participation in Fair Trade, but also enhance their efficiency and level of collaboration. This, in turn, could increase the neighbouring farmers' participation by word of mouth, a powerful communication tool in rural communities all over the world. The TAM also states that it is necessary to adapt the innovation to the company culture to motivate the personnel to actually and effectively use it.

1.2 Goal of the Paper

The goal of this paper is to contribute to a deeper knowledge of the factors influencing the sustainability of Fair Trade by analysing its impact in terms of perceived usefulness in a farming community. In particular, the aim is to measure how strongly the farmers perceived the impact of the different objectives of Fair Trade.

¹ In the TAM, two variables are seen as influencing the technology adoption: the perceived ease of use and the perceived usefulness of the technology. In our case, only the perceived usefulness is considered; that is, "the degree to which a person believes that using a particular system would enhance his or her job performance [or living conditions]" [9].

2. Materials and Methods

The perceived impact of Fair Trade was measured by interviewing a random sample of 100 farmers, members of the Asociación de Pequeños Productores y Productoras de Talamanca (APPTA) [10] cooperative, based in Talamanca, Costa Rica. The interviews and the other data collection took place in 2009 at the cooperative centre. The respondents were the farm owners.

The cooperative involves 1,200 associate farmers who produce, process and export organic and Fair Trade products. The total cultivated land is 2,000 ha and the average farm size is small (1.5 ha). The products (mainly cocoa and bananas) are traded to the North American and European markets following the Fair Trade Labelling Organisation (FLO) certification rules. The yearly production of cocoa amounts to 160-180 t; APPTA total turnover is US\$ 411,000.

The questionnaire contains 29 questions related to the perceived usefulness of Fair Trade participation measured in terms of perceived improvement of job performance and overall living conditions. The questions are grouped into five categories representing the main Fair Trade objectives:

- (1) Technical/economic development;
- (2) Economic/social development;
- (3) Social justice;
- (4) Improved market accessibility;
- (5) Environmental sustainability;

The variables were measured following a scale where 0=no change; 1= better; -1= worse².

A one-sample t- test against a value of 0 was adopted to test the significance of the difference in the community's social, economic and environmental conditions before and after the adoption of Fair Trade.

The influence of relevant social and structural

² The differences in the intervals are considered equally spaced (that is, the level of perceived improvement is equal to the perceived worsening); these variables can be considered interval variables, thus allowing for the use of quantitative descriptive and inferential statistics like means, standard deviation t-test and linear regressions.

characteristics of the farmers sample on the perceived level of satisfaction was also analyzed using different techniques:

(1) A multiple linear regression model

$$y = \alpha + \beta x_1 + \beta x_2 + \beta x_3 \quad (1)$$

Where, y = perceived change;

x_1 = duration of affiliation;

x_2 = cultivated area;

x_3 = age.

Education is not considered because of its very homogeneous distribution: with few exceptions, the farmers associated with APPTA have a primary level of education.

(2) A t-test for sample independence³ related to the following characters:

- Gender;
- access to drinking water;
- availability of electric power;
- availability of sanitary facilities;
- to assess the influence of the farmers' socio-economic conditions on the perceived change in the level of satisfaction.

3. Results and Discussion

The average values of the perceived change due to participating in Fair Trade have been divided into four categories: highly positive (from 0.96 to 0.70), positive (from 0.62 to 0.52), mildly positive (from 0.44 to 0.31) and very low non-perceived change (from 0.17 to 0).

The total sample analysis shows a highly positive perceived change, mainly for the variables belonging to the categories technical/economic development and improved market accessibility (see Table 1); the satisfaction for an higher income and the increase in social and environmental initiatives are the only variables belonging to social or environmental categories included in this interval. These variables, however, are either closely related to economic aspects or only indirectly related to improved social or

environmental conditions.

A positively perceived change is related to labour safety (0.56) and workers sanitary conditions (0.55). Other variables, not directly related to farming activity, show even lower positive values; the only exceptions are the environmental sustainability of community life (0.53) and the quality of food available for self-consumption (0.52). No change in the access to sanitary services was perceived; the values are very low, close to zero, and the t-test for independence did not give significant results, thus confirming the null hypothesis (Table 1). The non-perceived change could be influenced by the still-too-expensive sanitary system, which the increased income from Fair Trade could not compensate for.

The other characteristics (age, gender, cultivated area, duration of affiliation with the cooperative, access to drinking water, electricity and sanitary facilities) did not influence the perceived Fair Trade impact. Both the regression models and the t-test for independence very often showed non-significant values (see Tables 2 and 3). In the following (relatively few) cases significant relations emerged.

(1) A positive, even if not highly significative, relation between duration of affiliation to Fair Trade and the dependent variables workers sanitary conditions ($p=0.10$) and transparency in the relations with suppliers and clients ($p= 0.10$) suggests that in the long run, farmers' relationships with APPTA and Fair Trade lead them to perceive more clearly and/or obtain an improvement in their working conditions and market relations.

(2) Increasing farm size seems positively related with a better quality of food available for self-consumption, suggesting that more land available for organic production allowed for an higher share of better quality products for self-consumption.

(3) Farmers with drinking water availability show significantly higher means in the perceived improvement of timeliness in market access and environmental sustainability of the production than the

³ The t-test is two-tailed and considers different sample sizes; The different variance t-test was adopted on the basis of an F-test on the two-sample variance difference.

Table 1 Perceived impact of Fair Trade on APPTA cooperative members.

Fair Trade goals categories	Related variables	Average	prob. t	Values	Values	Values
				% (+)	% (-)	% (0)
IV	Timeliness in market access	0.96	***	96	0	4
I	Improved labour organisation	0.94	***	94	0	6
I	Improved production techniques	0.92	***	92	0	8
IV	Higher prices paid from APPTA	0.83	***	85	2	13
I	Increased technical skills	0.79	***	79	0	21
III	Degree of satisfaction perceived income	0.76	***	81	5	14
V	Social and environmental initiatives	0.75	***	75	0	25
I	Increase in quantity and quality of investments	0.74	***	74	0	26
I	Quality of the product at the farm	0.72	***	74	2	24
I	Yield/ha	0.70	***	69	0	31
IV	Selling time reduction	0.70	***	69	0	31
IV	Products bought from APPTA	0.62	***	66	4	30
IV	Reduction in the product waste	0.62	***	62	0	38
IV	Satisfaction in the relationship with APPTA	0.61	***	64	3	33
IV	Transparency in the relationship with suppliers/clients	0.57	***	59	2	39
III	Labour safety	0.56	***	58	2	40
III	Workers sanitary conditions	0.55	***	58	3	39
V	Environmental sustainability of the production	0.55	***	56	1	43
V	Environmental sustainability of community life	0.53	***	54	1	45
III	Quality of food available for self-consumption	0.52	***	55	3	42
III	Participation to community life	0.44	***	45	1	54
III	State of health of the farmer and his/her family	0.43	***	44	1	55
III	n. of working hours at the farm	0.36	***	43	7	50
V	Farm environmental impact	0.36	***	36	0	64
II	Quantity of food bought from the market	0.31	***	40	9	51
II	Quantity of food available for self-consumption	0.17	**	28	11	61
II	Quality of food bought from the market	0.04	*	4	0	96
II	Access to education	0.02	>0.1	2	0	98
II	Access to health services	0	>0.1	1	1	98

***p< 0.001, **p< 0.01, *p< 0.05.

farmers without availability of drinking water. Farmers with access to sanitary facilities more strongly perceived an improvement in the social and environmental initiatives. These findings suggest that farmers living in small villages or organised communities (where drinking water and sanitary services are available) show a slightly higher level of awareness of the positive impact of Fair Trade, probably due to their stricter relation with APPTA and other stakeholders promoting Fair Trade.

(4) Considering the gender influence on the perceived impact of Fair Trade, the only significant difference is

related to the improved labour organisation (p=0.085).

The variability of the characters associated with the perceived impact of Fair Trade is quite low. The absolute majority of values were either positive (+1) or null; in a few cases, poorer living conditions among farmers were perceived as a consequence of participation in Fair Trade (Table 1).

According to the TAM construct, the following question was asked to verify how the generally positive perception of Fair Trade encouraged the farmer's attitude towards its adoption: "Do you intend to continue the Fair Trade experience?" Positive answers

Table 2 Variables influencing on the perceived Fair Trade impact-regression models results.

Fair Trade goals categories	Dependent variables (y)	Duration of affiliation		Cultivated area	
		Regr. coeff.	prob. t	Regr. coeff.	prob. t
IV	Transparency in the relationship with suppliers/clients	1.652	0.101	-0.41	n.s.
III	Workers sanitary conditions	1.621	0.108	0.634	n.s.
III	Quality of food available for self-consumption	-0.256	n.s.	2.659	**

**p< 0.01.

Table 3 Variables influencing on the perceived Fair Trade impact - t-test of sample independence.

Fair Trade goals	Perceived impact of fair trade participation	Gender	Water	Electr	Sanitary
		prob. t	prob. t	prob. t	prob. t
IV	Timeliness in market access	n.s.	*	n.s.	n.s.
I	Improved labour organisation	*	n.s.	n.s.	n.s.
V	Social and environmental initiatives	n.s.	n.s.	n.s.	**
V	Environmental sustainability of the production	n.s.	**	0.103	n.s.

**p< 0.01, *p< 0.05.

came from 98 per cent of the respondents. The reasons for the farmers' answers were investigated by asking: "Why do you intend to continue participating in Fair Trade?" The answers confirmed the fundamental role of the technical-managerial and economic aspects in motivating the farmers' adoption of Fair Trade (Table 4): 34 per cent of the respondents indicated higher income, 24 per cent support from the cooperative, and 7 per cent change from traditional conventional farming activity. A significant 34 per cent of the respondents saw an overall improvement in working and living conditions (general improvement) as a reason to continue the Fair Trade experience.

With respect to the negative consequences of Fair Trade adoption (Table 5), 81 per cent of the farmers answered none, confirming the very low perceived negative impact of Fair Trade. The main problems stem from relations with conventional traders (12 per cent), an expected outcome; 5 per cent of the farmers reported problems with the cooperative management, while only 1 per cent had problems with other farmers not related to Fair Trade.

The expected changes related to Fair Trade were also analysed (Table 6). An increase in income and production quantity and quality was by far the most important aspect (67 per cent of respondents). Only 7

Table 4 The farmers' answers of question Why do you intend to continue participating in Fair Trade.

Higher income	34%
No answer	1%
Support from buyer (CONAPI)	24%
General improvement	33%
Change from tradition	7%
Easy relation with one buyer (CONAPI)	1%
Total	100%

Table 5 Problems related to the participation to Fair Trade.

Relations with conventional traders	12.0%
Relations with other farmers	1.0%
Relations with APPTA	5.0%
None	81.0%
Relations with local institutions	1.0%
Total	100.0%

Table 6 Expectations related to the participation to Fair Trade.

Increased quality, quantity & income	67.0%
Better support from APPTA	16.0%
Better market relations	4.0%
No changes	5.0%
General improvement	7%
Better living conditions	1%
Total	100.0%

per cent expected a general improvement, and just 1 per cent explicitly indicated an improvement in their living conditions.

4. Conclusions

This relatively simple analytical approach allows for monitoring the Fair Trade impact perception in rural communities. It also provides a starting point for a more effective harmonisation of Fair Trade with the producers' ideas on welfare, equity and sustainability issues; this, in turn, contributes to a greater acceptance of Fair Trade among farmers and rural communities. The results indicate that entering Fair Trade projects led to a perceived improvement of the farmers' working and living conditions. In particular, an improvement in their technical, economic and managerial skills emerged (better product quality, higher yields, better access to market, increased quantity and quality of investments, etc.⁴). These improvements also seem important to the farmers, according to the analysis of their expectations upon entering Fair Trade. The results do not seem to be strongly influenced by the farmer's gender, farm size, duration of their relation with Fair Trade or by other structural characteristics related to their access to more modern infrastructures and/or services. Nevertheless, a positive relation between farm size and access to quality food for self-consumption emerged. It is possible that farmers with less available land are more likely to sell a larger share of their products to the market. This hypothesis should be further investigated to provide indications of the necessity of increasing smaller farmers' access to locally produced, good quality food. Another interesting outcome is the relatively weak perception of ethical, environmental or social improvements for the whole of the community.

This outcome should not be considered as the result of an ineffective Fair Trade impact. The extremely large share of farmers willing to continue their experience with Fair Trade shows the opposite, confirming part of the TAM assumption: a positive perception of the usefulness related to the adoption of

⁴ Even though objective measurements are out of the scope of the paper, in many cases the above-mentioned variables are easily measurable by the farmers, thus reducing the level of subjectivity of the results obtained.

an innovation encourages continuation of its use. If the other part of the assumption ("it also increases the efficiency and level of collaboration"⁵) holds, it will be possible for the farmers to develop Fair Trade related projects more in line with the locally desired ethical, social, sanitary and environmental improvements, as a consequence of increased technical and managerial skills. This could reduce the risk of stimulating a passive attitude among local communities towards superimposed development models and consequent opportunistic, and thus less effective and more volatile, farmers' participation in Fair Trade. Further research should therefore measure the Fair Trade project's impact by considering the improvement of the indicators that are considered important locally. This implies an analysis of how the Fair Trade stakeholders (cooperative management, processors, importers, retailers, NGOs and Fair Trade labelling organisations) effectively interact with the local farmers to discuss, define, implement and verify the Fair Trade goals. A full-length supply chain analysis, from the farmers in developing countries to consumers in wealthy countries, should be performed. Differences in cultural and/or ethical approaches should be included, as they strongly influence the organisation and performance of the entire Fair Trade supply chain [11].

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⁵ Different authors confirm that Fair Trade contributes to the improvement of farmers' skills and other non-material aspects like self-esteem, family stability, and employment opportunities [6]. In turn, this encourages more effective collaboration with other Fair Trade stakeholders.

References

- [1] D. Jaffee, *Brewing Justice: Fair Trade Coffee, Sustainability, and Survival*, University of California Press Ltd, London, England, 2007.
- [2] L. Becchetti, M. Costantino, *The effects of fair trade on marginalized producers: an impact analysis on Kenyan farmers*, Working Paper CEIS 220, Rome, Italy, 2006.
- [3] D. Murray, L. Raynolds, P. Taylor, *One cup at a time: poverty alleviation and fair trade coffee in Latin America*, Fair Trade Research Group Report, Colorado State University, 2003.
- [4] N. Eberhart, *Etude d'impact du commerce équitable sur les organisations et familles paysannes et leurs territoires dans la filière café des Yungas de Bolivie*, Agronomes et Vétérinaires sans frontières (VSF-CICDA), France, 2006, available online at: http://www.ruralter.org/index.php?option=com_flexicontent&view=items&cid=17%3Abase-de-datos&id=72%3Adispositif-de-mesure-dimpact-du-commerce-equitable-metodologica&Itemid=100002&lang=fr.
- [5] C. Bacon, *Confronting the Coffee Crisis: Can Fair Trade, Organic, and Specialty Coffees Reduce Small-Scale Farmer Vulnerability in Northern Nicaragua?* World Development, Elsevier Ltd., Great Britain, 2008, pp. 497-511.
- [6] S. Imhof, A. Lee, *Assessing the Potential of Fair Trade for Poverty Reduction and Conflict Prevention: A Case Study of Bolivian Coffee Producers*, 2007, available online at: http://www.swisspeace.ch/typo3/fileadmin/user_upload/pdf/Assessing_the_Potential_of_Fair_Trade_for_Poverty_Reduction_and_Conflict_Prevention.pdf.
- [7] L. Mayoux, *Impact Assessment of Fair Trade and Ethical Enterprise Development*, 2001, available online at: <http://www.enterprise-impact.org.uk/pdf/IAofFairTrade.pdf>.
- [8] C. Zanasi, P. Venturi, M. Setti, C. Rota, *Participative organic certification, trust and local rural communities development: the case of Rede Ecovida*, *New Medit* 2 (2009) 56-64.
- [9] F.D. Davis, *Perceived usefulness, perceived ease of use, and user acceptance of information technology*, *MIS Quarterly* 3 (1989) 319-339.
- [10] APPTA Website, 2009, available online at: <http://www.appta.org/>.
- [11] C. Zanasi, L. Paluan, *Value propositions and fair trade supply chain organisation and performance: the case of Italian Alternative Trade Organisations (ATO's)*, in: M. Canavari, N. Cantore, A. Castellini, E. Pignatti, R. Spadoni, (Eds.), *International Marketing and Trade of Quality Food Products*, Wageningen Academic Publishers, The Netherlands, 2009, pp. 223-238.