USING CEMENT KILN DUST TO TREAT TANNERY WASTEWAER EFFLUENTS

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ABSTRACT

Heavy metals are well recognized as potential health hazards as they can neither be degraded nor biologically detoxified. Discharge of heavy metals such as Chromium, copper, cadmium, lead, … etc. in wastewater can be toxic to aquatic life and render natural waters as they become unsuitable for human consumption due to their tendency to accumulate in living organisms. Chromium compounds present at high concentrations in wastewater discharged from industrial sites such as tanneries can be lethal to marine species. This paper focuses the light on the potential use of cement kiln dust (CKD) collected from Al-Mergheb Portland Cement Factory at Al-Khoms, Libya, as an adsorbent to remove chromium [Cr (III)] from tanning wastewater, collected from two local tanneries, under kinetic and equilibrium conditions. Adsorption capacity of CKD is evaluated according to different adsorbent doses and temperatures of the tested wastewater samples. Two samples of 2336 and 4320 mg/l of Cr (III) initial concentrations were investigated by batch process. Collected data were tested against three mathematical models, Simple first order model, Lagergren's model and Ritchie's model. Though the preliminary testing was achieved at ambient temperature, the effect of temperature on adsorption capacity was conducted experimentally as the best fit model was identified and presented as a relationship between temperature and equilibrium rate constant.

The study concludes that CKD is an effective adsorbent to remove Cr (III) from tannery wastewater and the percentage removal of Cr(III) depends on the adsorbent dose, such that optimum removal of Cr (III) occurs at ambient temperature, 1200 rpm agitation rate, 60 min. contact time and a pH value of 0.5. Ritchie's kinetic model offers the best fit of the kinetic behavior of the system. A linear relationship between the equilibrium rate constant of Ritchie's model and the system temperature suggests that the adsorption process is controlled by an endothermic reaction; however, an efficient Cr (III) removal can be achieved at ambient temperature.

The present study reveals a feasible practical use of Portland Cement Kiln Dust as a low cost adsorbent to remove Cr(III) from wastewater.

KEYWORDS: Chromium adsorption, Portland Cement Kin Dust, Tannery wastewater treatment.

1. INTRODUCTION

Heavy metals are well recognized as potential health hazards. Chromium, copper, cadmium, lead … etc can neither be degraded nor biologically detoxified and have tendency to accumulate in living organisms. Discharge of heavy metals in wastewater can be toxic to aquatic life and render natural waters as they become unsuitable for human consumption (Khan and Mohamad, 2007). Chromium compounds present at high concentrations in wastewater discharged from industrial sites such as tanneries can be lethal to marine species.

Current treatment techniques deployed to remove chromium from wastewater include solvent extraction, micro-filtration, precipitation and ion exchanges. These methods are rather costly; therefore, there is a need to develop low cost and easily available materials that can effectively remove chromium.

Adsorption by far is the most effective and widely used technique to remove toxic heavy metals from wastewater (Selvi *et al.*, 2001). In recent years, research has been directed towards the use of industrial wastes as adsorbent materials in an attempt to minimize processing costs, protect the environment and public health. Therefore, this study is dedicated to investigate the potential use of cement kiln dust (CKD), an air pollutant solid waste, as an adsorbent to remove chromium [Cr (III)] from tanning wastewater under kinetic and equilibrium conditions. The effects of various parameters such as adsorbent dose, agitation rate, contact time and temperature change on the adsorption process have been studied. This study was conducted to evaluate the adsorptive capacity of CKD.

2. MATERIALS AND METHODS

2.1. Materials

The experiments were carried out to remove Cr(III) from tanning wastewater effluents by using CKD collected from Al-Mergheb Portland Cement Factory at Al-Khoms, Libya, as an adsorbent.

X-ray fluorescence analyses of CKD samples are presented in Table 1.

Table 1. Results of the X-ray analyses of Portland CKD

Constituents	SiO_2	Al_2O_3	Fe_2O_3	*CaO*	*MgO*	K_2O	SO_3	*Cl*	Na_2O	*Other residues*
Composition* (wt.%)	19.58	3.6	2.97	54.89	2.12	2.32	0.83	0.54	0.109	13.041

** Average values for four different samples .*

Two wastewater samples collected from two local tanneries effluents were filtered to remove any suspended organic materials and treated further for Cr (III) removal.

2.2. Experimental Procedures

Collected samples from tannery effluents containing chromium were dominated by Cr(III) and small content of Cr(VI) that was converted to Cr(III) as applied by Ibrahim and Abushina, (2008). The samples were investigated by batch process and Cr(III) concentrations were determined using UV visible spectrophotometer (Unicam 8700) in accordance with a standard method, (Greenberg *et al*., 1992). The initial concentrations of Cr (III) in the samples were 2336 and 4320 mg/l.

Each sample was transferred to a conical flask and agitated at 1200 rpm for 60 minutes, as minimum time duration to reach equilibrium, and a pH value of 0.5 to achieve optimum adsorption conditions as concluded by Ibrahim and Abushina, (2008). The resulting effects from variations in adsorbent dose on pH values and the adsorption efficiencies were investigated. The equilibrium isotherms were evaluated on basis of experimental results obtained at ambient temperature (25 ± 2 ^oC) and the activation energy was assessed on temperature change of the system up to 90 ^oC.

3. RESULTS AND DISCUSSION

Changes in Cr(III) removal was investigated against changes in CKD doses, the initial concentration of Cr(III) ions and pH level. The equilibrium isotherms were also determined for the adsorption of chromium ions on CKD to determine the adsorption capacity of CKD. The effects of these parameters on the adsorption efficiency are detailed as follows:

3.1. Adsorbent Dose Effect

The effect of adsorbent doses on removal of Cr(III) for both samples is shown in figure 1. All experiments were primarily conducted under the conditions (25±2 °C, 1200 rpm and 60 minutes contact time). The results shown in the figure indicate that the percentage removal of Cr(III) increases with an increase in adsorbent dose. This is due to increase in the surface area of CKD and hence more active sites are available for the adsorption of the metal ions. It is also evident from the figure that an adsorbent dose of 20 g/l of tanning solution of the first sample results in a complete removal of Cr(III) from the solution, while a complete removal of Cr(III) of the second sample corresponds to 22 g/l occurring under the same operating conditions.

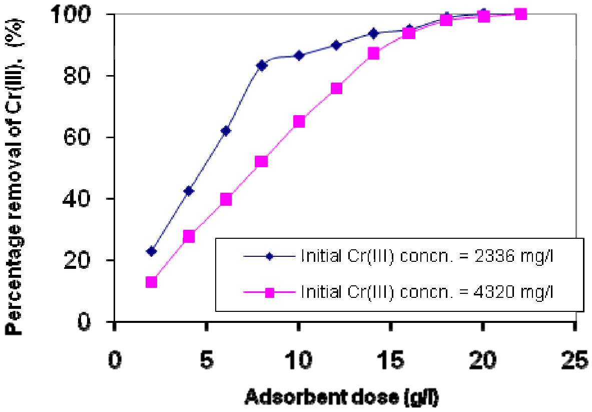

Figure 1. Variation of Cr(III) removal versus adsorbent dose for both samples, at (25±2 °C, 1200 rpm and contact time is 60 minutes)

As the adsorbent dose reaches 16 g of CKD per l liter of tanning solution, the Cr(III) removal for both samples converges at relatively high percentages of 95.11% and 93.72%.

The measurements reveal that increased CKD amount in both samples lead to higher pH values and the effect of higher pH corresponds to increased removal of Cr(III). Since the sample of the lower initial concentration (2336 mg/l) represent a diluted sample of the higher initial concentration sample (4320mg/l), the higher initial concentration sample is presented by the way of example.

The sample of 4320 mg/l Cr(III) initial concentration and pH 3.11 was treated by gradually adding CKD that resulted in a gradual increase of pH values as shown in figure 2. The gradual increase of pH was accompanied by proportional increase in precipitation of Cr(III) ions yielding $Cr(OH)_3$ under the effect of soluble alkalis and CaO present in CKD. Furthermore, figure (2) reveals that a pH of 7.94 corresponds to 99% removal where further increase up to 9.38 yields a complete removal of Cr(III) from the sample as an indication that Cr(III) removal is attributed to the amount of added adsorbent rather than the rise in the pH of the product solution.

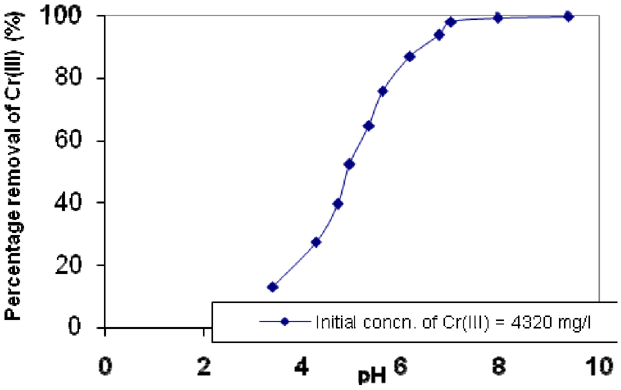

Figure 2. Effect of pH on the removal percentage of Cr(III), at (25 ± 2 ^oC, 1200 rpm and contact time is 60 minutes)

3.2. Adsorption Rate

The amount of Cr(III) adsorbed, q_t (mg/g), was computed as follows:

$$q_t = \frac{(C_o - C_t)V}{m_s} \tag{1}$$

Where C_o and C_t are the concentrations of Cr(III) in the solution at *t*=0 and *t*=*t*, (mg/l) respectively, V is the volume of the solution (l) and m_s is the mass of CKD (g). Each experiment was performed twice under identical conditions and the reproducibility of the measurements was within 2%.

It was observed that the concentration of Cr(III) decreases during the first 50 minutes and equilibrium was well established at 60 minutes. The initial adsorption rates, calculated according to Eq. (2), increase with the increase in the initial concentration of Cr(III) as shown in Table 2.

$$\left.\frac{dq_t}{dt}\right|_{t=0} = -\frac{V}{m_s}\left.\frac{dC_t}{dt}\right|_{t=0} \tag{2}$$

Table 2. The effect of initial concentration of Cr(III) on the initial rate of adsorption on CKD

Initial concentration (mg/l)	Initial adsorption rate. (mg/g)
2336	194.6667
4320	360.01

In order to describe the kinetic behavior of the system mathematically the experimental results were tested against three models:

3.2.1. Simple first order model

In an attempt to test a simple first order equation to model the experimental results, equation (3) was applied (Hossain *et al.*, 2005).

$$\log C_t = \frac{k_1}{2.303}t + \log C_o \tag{3}$$

Where C_t and C_o are the concentrations of chromium at time *t* and initially (mg/l), respectively, and k_1 is the first order rate constant (1/min.).

The experimental results in figure 3 show that the log C_t versus *t* for both samples deviate considerably from the theoretical model. A comparison of the results with the correlation coefficient shown in Table 3 indicates a failure in expressing this adsorption process by the simple first order kinetics. Sparks (1989) proposes that simple kinetic models such as first and second order rate equations are not applicable to adsorption systems with solid surfaces that are rarely homogeneous such as CKD, as the effect of transport phenomena and chemical reactions are often experimentally inseparable. A similar finding is proposed by Hossain *et al.* (2005).

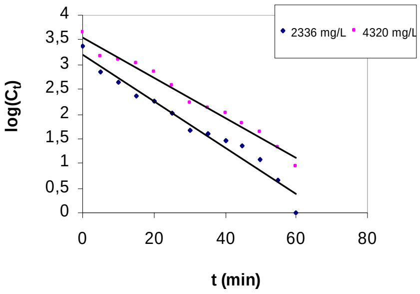

Figure 3. Plot of the simple first order adsorption kinetics of Cr(III) on CKD for both samples

3.2.2. Lagergren's model

The adsorption kinetics may also be described by a linear Lagergren's equation (Hossain *et al*., 2005; Özacar, 2003), as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (4)$$

Where q_e and q_t are amounts of adsorbed Cr(III) at equilibrium and at any other time t (mg/g), respectively, and k_1 is the equilibrium rate constant of Lagergren's model adsorption (1/min).

Lagergren's model constant k_1 and the equilibrium adsorption density q_e can be determined from the slopes and intercepts of the linearized plots shown in figure (4).

The figure shows that the experimental data present a considerable deviation from the theoretical plots. The correlation coefficients of Lagergren's model, r^2, Table (3) are relatively low with respect to the other tested models. Furthermore, q_e values of Lagergren's model do not agree with the experimental values. This suggests that the Lagergren's model is not the best representation of the adsorption system. Hossain *et al*., (2005) suggests that Lagergren's equation is rather suitable for homogeneous surfaces, where the CKD particles are nonhomogeneous surfaces.

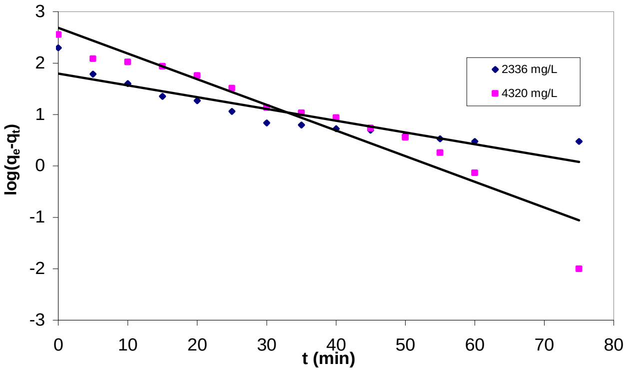

Figure 4. Plot of the Lagergren's adsorption kinetics of Cr(III) on CKD for both samples

3.2.3. Ritchie's model

The adsorption kinetics may also be described by a linear Ritchie's model equation (Chiou and Li, 2002), as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (5)$$

Where k_2 is the equilibrium rate constant of Ritchie's adsorption model (g/mg.min).

The slopes and intercepts of both plots t/q_t versus t as straight lines in figure (5) were used to calculate k_2 and q_e. The figure shows a good agreement between the experimental data and Ritchie's model for both initial Cr(III) concentrations. A summary of results listed in Table (3) indicate that the correlation coefficients of Ritchie's model are greater than 0.998 for both samples and the calculated q_e values tend to agree very well with the experimental data. Therefore, it is evident that the adsorption system belongs to Ritchie's model. Similar previous studies support this finding such as adsorption of dye RR189 on cross-linked chitosan beads (Chiou and Li, 2002), adsorption of Cr(IV) on used black tea leaves (Hossain *et al*., 2005) and adsorption of Cr(III) on by-pass cement kiln dust (Al-Meshragi *et al.*, 2008).

Table 3. Comparison of the simple first order, Lagergren's and Ritchie's adsorption constants, and calculated q_e values for both samples.

Experimental		**1st order**		**Lagergren's Model**			**Ritchie'sModel**		
C_o *(mg/L)*	$q_{e\ exp.}$ *(mg/g)*	k_1 *(1/min)*	r^2	k_1 *(1/min)*	$q_{e\ cal.}$ *(mg/g)*	r^2	k_2 *(g/mg.min)*	$q_{e\ cal.}$ *(mg/g)*	r^2
2336	194.6667	0.09925	0.976	0.05297	63.1865	0.848	2.12×10^{-3}	204.08	0.999
4320	360.01	0.0935	0.982	0.11492	483.931	0.914	5.87×10^{-3}	384.615	0.998

r^2 is a regression coefficient

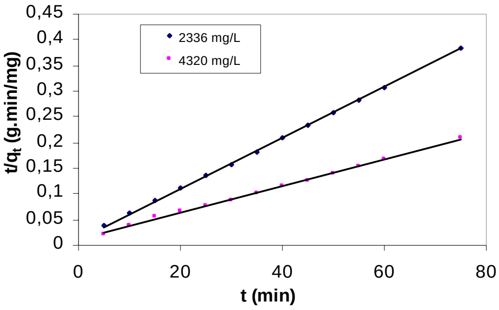

Figure 5. Plot of the Ritchie's adsorption kinetics of Cr(III) on CKD for both samples

3.3. Effect of Temperature

The primary testing was conducted at ambient temperature as a low cost approach, where the effect of temperature change on removal rate was tested against changes in rate constant of Ritchie's model. The effect of processing temperature on the adsorption rate constant is essential to determine the values of the thermodynamic parameters in order to predict the adsorption behavior. Batch experiments were carried out at different temperatures within 298 to 363 K range with a constant initial concentration of Cr(III), 4320 mg/l and a constant CKD dose of 16 g/l. Figure (6) shows that the rate constant increases almost linearity with an increase in temperature. This suggests that the adsorption process is controlled by chemical reactions. The activation energy of adsorption calculated from the Arrhenius' plot of the data is 1.867 kJmol^{-1} indicating that the activation energy is endothermic.

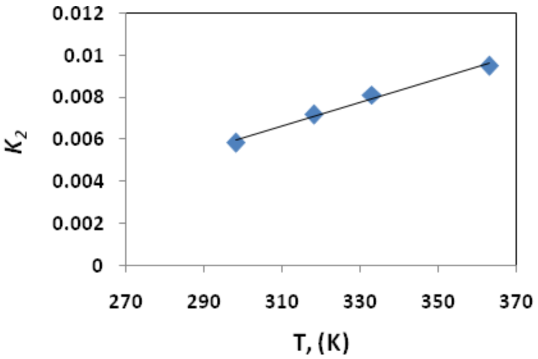

Figure 6. The effect of temperature on Ritchie's rate constant (C_o=4320 mg/l and m_s=16 g/l).

4. CONCLUSIONS

The present study concludes that Portland Cement Kiln Dust (CKD) has a great potential to remove Cr(III) from tannery wastewater. The percentage removal of Cr(III) depends on adsorbent dose. The optimum conditions for chromium removal operation from wastewater are 60 minutes contact time and 1200 rpm agitation rate in presence of 16 g of adsorbent per one liter of chromium tanning wastewater.

The adsorption of Cr(III) on the cement kiln dust is best represented by the Ritchie's kinetics model. The experimental results indicate that the adsorption rate increases at higher initial concentrations of Cr(III). The rate constant increases linearly with an increase in temperature, an indication of endothermic processes are involved. The Arrhenius' plot of the rate constants yields a small value of activation energy indicating that Cr(III) is easily adsorbed on the CKD particles. Therefore, removal at temperatures above ambient is rather cost ineffective.

The present study shows a feasible practical use of Portland Cement Kiln Dust as a low cost adsorbent to remove Cr(III) from wastewater.

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