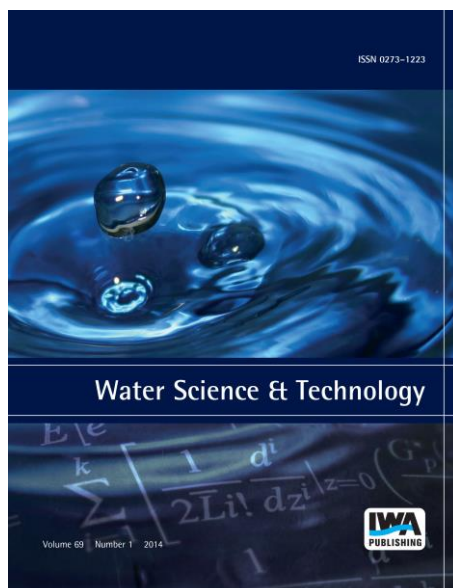


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Adsorption of methylene blue using modified adsorbents from drinking water treatment sludge

M. Nageeb Rashed, M. A. El-Daim El Taher and Somaya M. M. Fadlalla

ABSTRACT

This study aims to explore the preparation and application of alum sludge (AS) and mud sludge (MS) from a drinking water treatment plant to remove methylene blue (MB) dye from aqueous solution. The sludge (MS and AS) was treated by chemical and physical activation to obtain new adsorbents. The adsorption experiments were carried out under different conditions of initial dye concentration (50–100 mg/L) adsorbent dosage (0.05–0.25 g), solution pH (3–9), temperature (20–60 °C) and contact time (20–90 min). Scanning electron microscopy (SEM) and X-ray diffraction instruments were used for characterization of the developed adsorbents. The results show that sludge activated by nitric acid (0.25 M HNO₃) and pyrolysis at 700 °C were the best chemically and physically activated adsorbents. The optimum adsorption conditions for the adsorption of MB are 100 ppm initial dye concentration, 1 hour contact time, 250 °C solution temperature, pH 7 and 0.25 g adsorbent dosage. Application of the Langmuir and Freundlich Isotherm models showed that adsorbents fitted the Langmuir model well. SEM studies indicated the porous structural aspects of sludge suitable for removing MB dye.

Key words | adsorption, environment, methylene blue, pollution, sludge, water treatment

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INTRODUCTION

Drinking-water treatment sludge is a by-product generated during the production of drinking water, where an aluminum based salt is used as a coagulant to remove colour, turbidity and humic substances. Wastewater treatment is carried out to remove dyes, pigments, heavy metals, organic pollutants and other biological impurities. Coagulation, filtration, iron exchange, ozonation, photo-catalytic degradation, biosorption and adsorption are used as suitable technologies for wastewater treatment (Rafatullah *et al.* 2010).

Several studies have reported the application of different adsorbents for methylene dye removal, which include rice husk, globe artichoke leaves, Neem leaf powder, wheat shells, dead *Posidonia Oceanica* leaves, cotton stalk, hazelnut shell, spent coffee grounds, swede rape straw, oil palm fiber, Indian rosewood sawdust, cedar sawdust, garlic peel, rattan sawdust, lotus leaf, coir pith carbon, rejected tea, jute fibers, peanut husk, sugar beet pulp, and pineapple leaf powder (Bulut & Aydin 2006; Han *et al.* 2011; Garg *et al.* 2004; Bhattacharyya & Sharma 2005; Senthilkumaar *et al.* 2005; Hamdaoui 2006; Hameed *et al.* 2007; Kavitha &

Namasivayam 2007; Dogan *et al.* 2009; Franca *et al.* 2009; Hameed & Ahmad 2009; Benadjemia *et al.* 2011; Cavas *et al.* 2011; Deng *et al.* 2011; Foo & Hameed 2011; Nasuha & Hameed 2011; Song *et al.* 2011; Vargas *et al.* 2011; Feng *et al.* 2012; Vucurovic *et al.* 2012; Adam *et al.* 2013). There are different varieties of synthetic dye, acidic and basic. It is estimated that more than 100,000 commercially available dyes, with over 7×10^5 tonnes of dyestuff, are produced annually worldwide (Owamah *et al.* 2013). The colour is the first contaminant to be recognized in waste water. The presence of even a very small amount of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable (Banat *et al.* 1996). Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk. It can cause eye burns, which may be responsible for permanent injury to the eyes of human and animals. MB is widely used in coloring paper, dyeing cottons and wools, and as a coating for paper stocks. It is not strongly hazardous, but it can cause some harmful effects such as a cute exposure to shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans (Kumar *et al.* 2005).

Different dye treatment processes have been applied, such as photocatalytic degradation (Sohrabi & Ghavami 2008), biological treatment (Alinsafi *et al.* 2006), chemical coagulation (Selcuk 2005), cation exchange membranes (Wu *et al.* 2008), electrochemical degradation (Fan *et al.* 2008), adsorption (Zhu *et al.* 2007; Hameed & Daud 2008; Wu & Tseng 2008), and integrated chemical-biological degradation (Sudarjanto *et al.* 2006). As dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of dyes has been considered to be a simple and economical method for their removal from wastewater. Adsorption has been found to be superior to other techniques for wastewater in terms of flexibility and simplicity of design, low cost, ease of operation and lack of sensitivity to toxic pollutants (Rafatullah *et al.* 2009).

Drinking water treatment sludge (DWTS) is an effective adsorbent. Some authors have reported the adsorption of dyes on drinking water sludge. Sadri Moghaddama *et al.* (2010) reported the performance of a water treatment works sludge (ferric chloride sludge, FCS) for the removal of acid red 119 dye from aqueous solutions. The optimum initial pH, FCS dosage and initial dye concentration were found to be 3.5, 236.68 mg dried FCS/L and 65.91 mg/L, respectively. Al-Fatlawi & Neamah (2015) studied phosphate removal by using DWTS. Zhou & Haynes (2010) showed that water treatment sludge was an effective adsorbent for Pb(II), Cr(III) and Cr(VI). The phosphate adsorption potential of three types of water treatment sludge, namely alum sludge (AS), lime sludge and lime-iron sludge was exhibited, of which lime-iron sludge showed the highest adsorption capacity, which was 34 and 52% higher than that for lime sludge and AS (Chittoo & Sutherland 2014). Makris *et al.* (2006) studied the use of aluminum-based drinking-water treatment residuals as a novel sorbent for perchlorate removal.

The present work aims to investigate the adsorption of MB dye from polluted water by developed adsorbents from DWTS, and extending to study the effect of various operating parameters (initial dye concentration, adsorption dose, pH, temperature of the solution and contact time) on dye adsorption.

MATERIALS AND METHODS

Sample collection

Sludge from the two drinking water treatment plants (DWTS) used in this study has advantages, due to its low cost, as well as environmental benefits in terms of reuse of solid wastes.

Sludges from drinking water treatment plants were used as the raw material to prepare different types of activated adsorbents.

Sludge samples (mud sludge, MS) were obtained from the sedimentation tanks of the Gabal Takok drinking water treatment plant in Aswan city (which abstracts clean river water and so has no need to use alum), and alum sludge (AS) from the Fatera drinking water treatment plant in Kom Ombo city, Aswan governorate, Egypt. The chemical properties of AS and MS are presented in Table 1.

The sludge samples were air dried in a clean place and crushed to a uniform 0.2 mm size, and then oven dried at 105 °C for 24 h. After cooling, the samples were kept in the desiccators until use.

Preparation of sludge adsorbents

Two methods (physical and chemical activation) were used in the current study to prepare the sludge adsorbents.

Physical activation of AS and MS

A portion of 10 g of dry sludge was pyrolyzed at 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C for one hour. The products are labeled AS400, AS500, AS600, AS700, AS800, and AS900 for AS adsorbents and MS400, MS500, MS600, MS700, MS800, and MS900 for MS adsorbents.

Chemical activation of AS and MS

Activation with acetic acid: two procedures were used for activation with acetic acid (AA):

Table 1 | Chemical composition of AS and MS

Sample	SiO ₂ %	LOI%	Fe ₂ O ₃ %	Al ₂ O ₃ %	Cd ppm	Zn ppm	Pb ppm	Cu ppm
AS	54.72	9.66	10.32	12.1	12.70	0.482	UD	UD
Mud sludge	55.92	11.23	13.43	11.1	7.71	0.601	UD	UD

UD = under detection limit.

- (a) Activation of the sludge only using different concentrations of AA.
(b) The same as procedure (a) but with pyrolysis.

For procedure (a), 10 g of dry sludge was mixed with 100 ml of each AA concentration (0.1, 0.5, 1, 2 and 3 M), stirred at 60 °C for four hours, filtered, washed with deionized water, and dried at 120 °C for 12 hours. The dried residue was pyrolyzed in the oven at 500 °C for two hours, and left in the desiccators for further use. The developed AS adsorbents were labeled AS1 (0.1 M AA), AS1(0.5 M AA), AS1(1 M AA), AS1(2 M AA) and AS1(3M AA) for treatment with 0.1, 0.5, 1, 2 and 3 M AA, respectively. The developed mud sludge adsorbents labeled MS1 (0.1 M AA), MS1(0.5 M AA), MS1(1 M AA), MS1(2 M AA) and MS1 (3M AA) for treatment with 0.1, 0.5, 1, 2 and 3 M AA, respectively.

For procedure (b), a sludge sample was mixed with water to yield a moisture content of 20%. The sludge pellet form was made by cutting it to a uniform size of 2–2.5 mm. Pellets were heated in an oven at 500 °C for 2 hours. Pellets (10 g) were mixed with 100 ml of each AA concentration of (0.1, 0.5, 1, 2, and 3 M) and stirred at 60 °C for 4 h. The sample was dried at 120 °C for 12 hours and left in a desiccator. The developed AS adsorbents labeled AS2 (0.1 M AA), AS2(0.5 M AA), AS2(1 M AA), AS2(2 M AA) and AS2 (3M AA) for treatment with 0.1, 0.5, 1, 2 and 3 M AA, respectively. The developed MS adsorbents labeled MS2 (0.1 M AA), MS2(0.5 M AA), MS2(1 M AA), MS2(2 M AA) and MS2 (3M AA) for treatment with 0.1, 0.5, 1, 2 and 3 M AA, respectively. The developed adsorbents were labeled AS2 (0.1 M of AA at 20%) and MS2 (0.5 M of AA at 20%)

Activation with nitric acid: The dried sludge sample (10 g) was mixed with 50 ml of each HNO₃ concentration (0.25, 0.5, 1, and 2 M), filtered and left for 24 hours. After that it was washed with deionized water, dried at 60 °C in an oven for 24 h and left in desiccators for further use. The developed AS adsorbents were labeled AS3 (0.25 M NA), AS3(0.5 M NA), AS3(1 M NA) and AS3(2 M NA) for treatment with 0.1, 0.5, 1, 2 and 3 M AA, respectively. The developed MS adsorbents were labeled MS3 (0.1 M NA), MS3(0.5 M NA), MS3(1 M NA) and MS3(2 M NA) for treatment with 0.1, 0.5, 1 and 2 M HNO₃, respectively.

All the developed adsorbents were ground in an agate mortar and sieved to 63 µm.

Preparation of adsorbate (MB dye)

MB used in this study was of commercial purity (FW, 319.86; MF, C₁₆H₁₈N₃SCL). A stock solution of MB

(1,000 ppm) was prepared by dissolving the required quantity of the dye in distilled water. The working dye solution was prepared by diluting the stock solution with a suitable volume of distilled water to the desired concentration. The pH of the solution was maintained at a desired value by adding 0.1 M of NaOH or HCl.

Batch adsorption experiments

Batch adsorption experiments were carried out by batch process. Batch adsorption experiments examined the effect of solution pH, initial MB concentration, temperature, adsorbent dosage, and contact time on the MB dye adsorption. The experiments were carried out in a 250 ml Erlenmeyer flask and the total volume of the reaction mixture was kept at 100 ml.

Effect of initial dye concentration

Here, 0.25 g of adsorbent was placed in an Erlenmeyer flask with 100 ml volume of MB solution. The initial concentrations of the dye solution were 50, 60, 75 and 100 mg/L. The mixture was agitated and filtered through a Goch funnel, then the concentrations of MB were analyzed using a spectrophotometer.

Effect of temperature

0.25 g of adsorbent was added to a 100 ml volume of 100 mg/L MB solution. The experiments were carried out at 25, 40, and 60 °C for 1 hour contact time at pH 7. After filtration, the concentration of MB was measured.

Effect of pH

The effect of initial pH was investigated at various pH (3, 5, 7, and 9). 0.25 g of adsorbent was added to 100 ml volume of MB aqueous solution (initial concentration 100 mg/L) and stirred for a constant sorption time of 1 hour. The sample was taken and filtrated, and the equilibrium concentration of MB was then measured by spectrophotometer.

Effect of contact time

0.25 g of adsorbent was added to 100 ml of 100 mg/L MB solution for various contact times (20, 40, 60 and 90 hours) at a constant pH 7 and temperature of 25 °C. After the specified time, the sample was filtered and the equilibrium MB concentration was measured by spectrophotometer.

Effect of dosage adsorbent

A 100 ml volume of MB solution (100 mg/L) was mixed with various dosages of adsorbent (0.05, 0.1, 0.25 g) at a contact time of 1 hour, 25 °C and pH 7. After filtration, the concentration of MB was measured by spectrophotometer.

The amount of MB adsorbed at equilibrium per unit mass of adsorbent q_e (mg/g) was determined according to the following equation:

$$q_e = V(C_o - C_e)/m \quad (1)$$

where C_o is the initial concentration of MB (mg/L), C_e is the equilibrium concentration of MB (mg/L), V is the volume of MB solution (L), m is the mass of adsorbent (g) and q_e is the MB quantity adsorbed at equilibrium (mg/g).

The percentage removal of MB dye was calculated as follows:

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Analytical technique

The equilibrium concentration of the MB dye solution before and after adsorption was analyzed using a UV-Vis spectrophotometer (model Thermo Scientific Nicolet evolution 100). The standard calibration curve of MB was prepared by recording the absorbance values of various concentrations of MB dye at the maximum absorbance wavelength (668 nm). The instruments used were a pH meter (Jenway 3510) and magnetic stirrer.

Morphological features

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) instruments were used for characterization of the developed adsorbents before and after physical and chemical activation. The micromorphology and chemical composition of raw sludge and treated sludge (adsorbent) AS3 and MS3 were examined with a scanning electron microscopy dispersive (SEM-EDX), JEOL, JSM-5500LV electron microscopy instrument operating at five kV specimens on which a thin layer of gold or carbon had been evaporated. XRD of the adsorbents were obtained using a Philips X-ray diffraction instrument with filtered Cu K α radiation ($n = 1.5418 \text{ \AA}$) and operated at 40 kV and 40 mA. The XRD pattern was recorded from 1.5 to 50 ° 2 θ with a scanning speed of 0.02 ° 2 θ per second.

RESULTS AND DISCUSSION

XRD of the developed adsorbents

For determining the structural changes in the developed adsorbent samples before and after activation, XRD analysis was done for adsorbents AS3 and MS3 before and after activation. Figures 1 and 2 confirmed that both adsorbents before and after activation contained Apatite as a major mineral (Hydroxyapatite and Francolite). The presence of Apatite's peaks (Hydroxyapatite and Francolite) indicates the stability of these compounds with activation. The AS3 adsorbent before and after activation showed that the S-Q for Quartz were 23.3 and 12.7%, respectively, while for Microcline they were 76.7 and 45.8%, respectively. The MS3 adsorbent before and after activation show that the S-Q for Quartz were 30.9 and 21.7%, respectively, while for Albite they were 69.1 and 78.3%, respectively. The majority of clay minerals have layered silicate structures with a marked basal cleavage and plating habit.

SEM images of the developed adsorbents

The surface structure of the developed adsorbents (AS3 and MS3) before and after chemical activation is monitored by SEM and presented in Figure 3. The figure shows the SEM images of the AS3 and MS3 adsorbents before and after activation, and reveals the presence of the cylindrical-like shape, mesosize pores, and similar amorphous structures. Both the morphological structure, pore size and the pore shape remain unchanged during activation.

Activation processes of AS and MS

Chemical activation of AS and MS with AA and ignition at 500 °C (Table 2) revealed that the removal percent of MB, with AA and ignition at 500 °C was best at 3 M AA (56%) for alum sludge (AS1) and 79.9% for mud sludge (MS1) at 0.1 M AA.

Chemical activation with AA only revealed that the removal percent of MB was highest (73.7%) for alum sludge (AS2) at 0.1 M AA and 81.9% for mud sludge (MS2) at 0.5 M AA (Table 2).

Chemical activation with nitric acid (Table 3) shows that the removal percent of MB was best (82.12%) for alum sludge (AS3) and best (93.6%) for mud sludge (MS3) at 0.25 M nitric acid.

Physical activation (Table 4) revealed that the MB removal percent by ignition at 400, 500, 600, 700, 800,

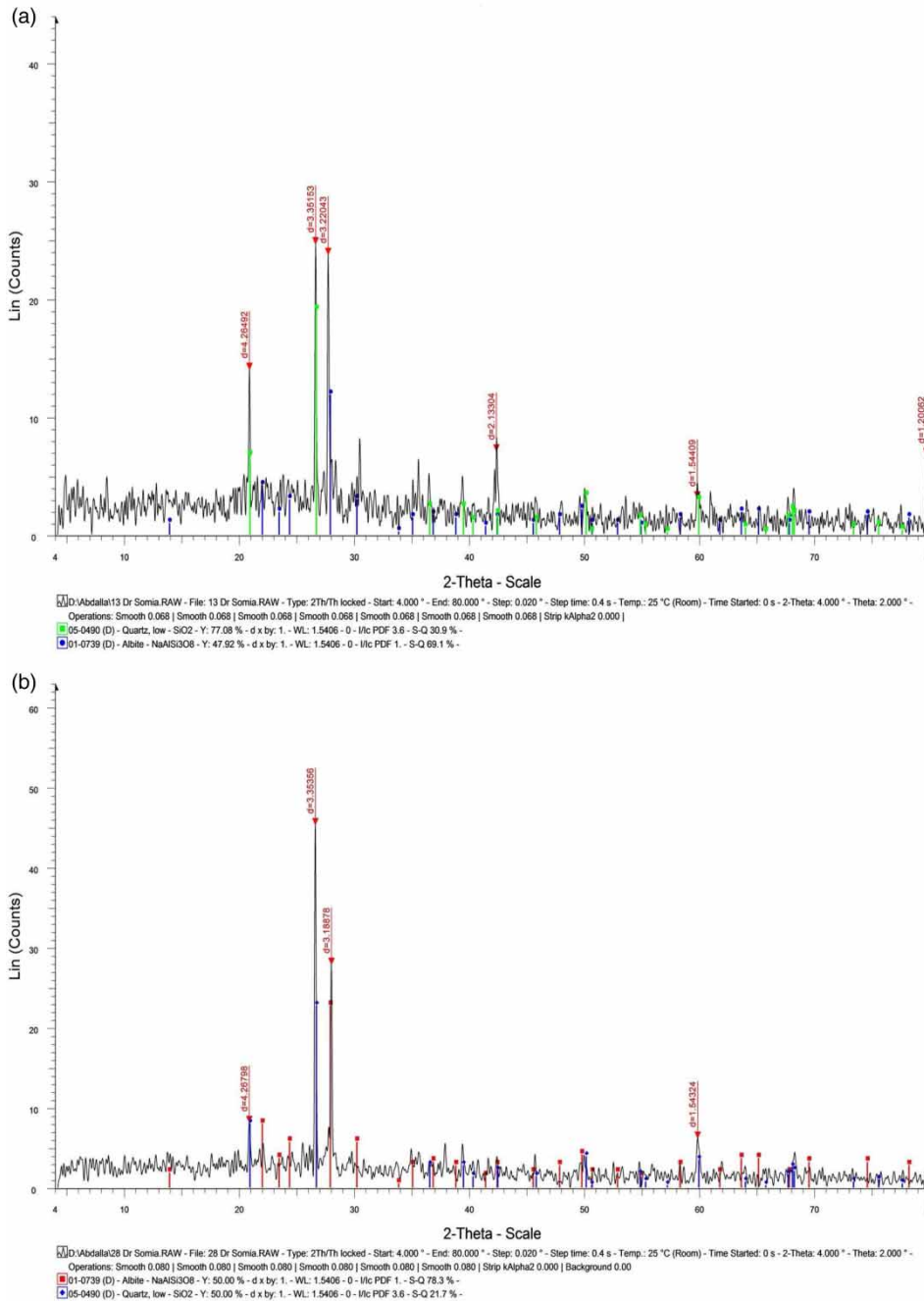


Figure 1 | XRD patterns for alum sludge (AS3) (a) before and (b) after activation.

900 °C was highest at 700 °C (75.7%) for alum sludge (AS700), and 72.6% for mud sludge (MS700).

The adsorbents AS1, AS2, AS3, MS1, MS2, and MS3 were selected as the best chemically activated sludge adsorbents, while AS700 and MS700 adsorbents were selected as the best physically activated sludge adsorbents.

Batch adsorption

Effect of initial dye concentration on adsorption

The adsorption data for the removal of MB by AS and MS adsorbents at different MB concentrations (50, 60, 75 and 100 mg/L) with fixed experimental conditions (adsorbent

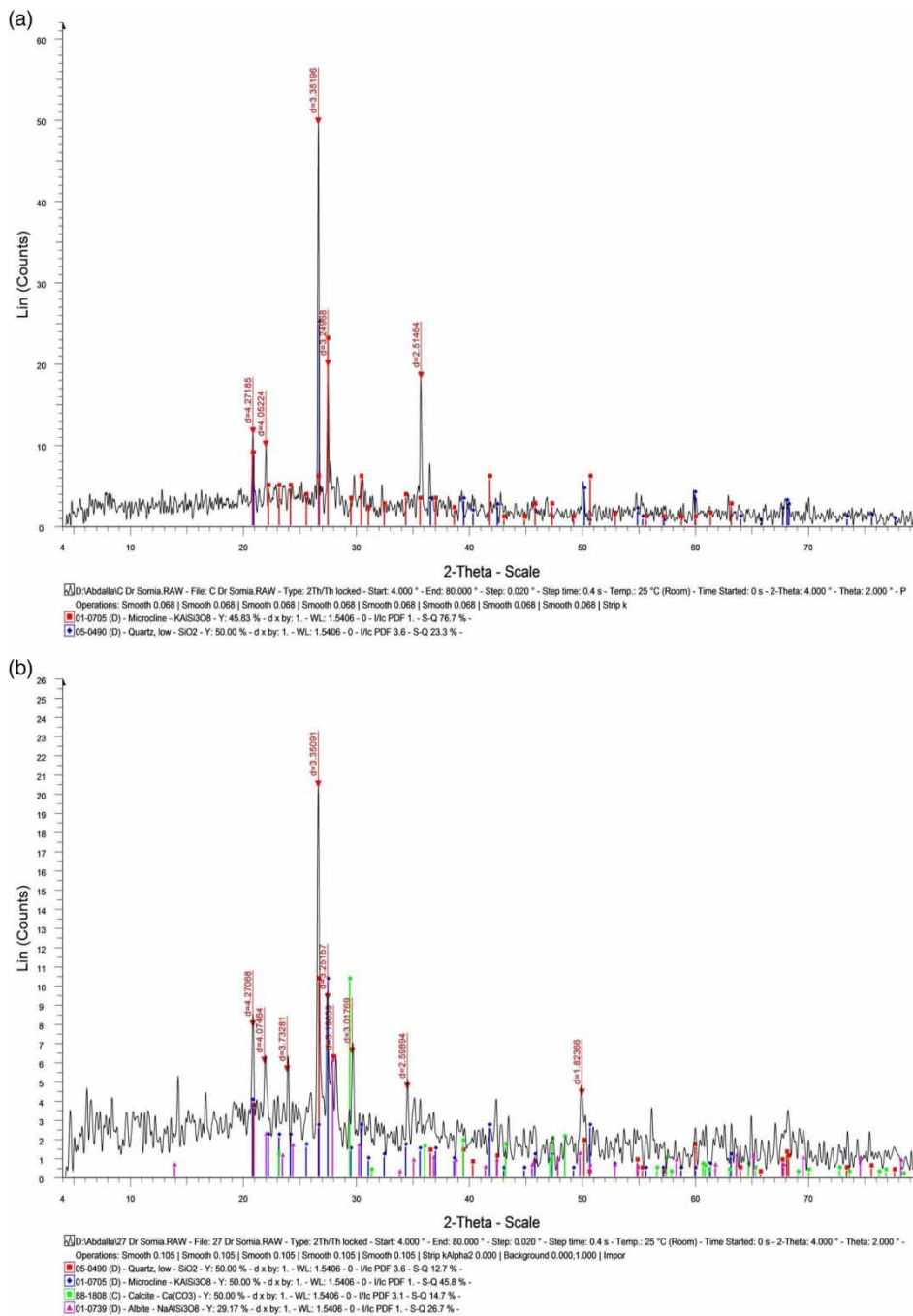


Figure 2 | XRD patterns for mud sludge (MS3) before (a) activation and (b) after activation.

dose 0.25 g/100 ml; contact time 60 min; solution temperature 25 °C and pH 7) are represented in Figures 4 and 5.

The adsorption data in Figures 4 and 5 revealed that with an increase in the initial MB concentration from 50 to 100 mg/L, the removal percent of MB by AS1, AS 2, AS 3 and AS 700 adsorbents increased from 24.92% to

69.88%, 21.86% to 81.92%, 35.41% to 93.55% and 15.48% to 75.68%, respectively. The MB removal percent of MS 1, MS 2, MS 3, and MS 700 increased from 14.46% to 56.16%, 11.45% to 73.69%, 33.73% to 82.12% and 13.86% to 72.62%, respectively. So the adsorption capacity of MB on the AS adsorbent surface increases with an increase in MB concentration. With the increase in the initial

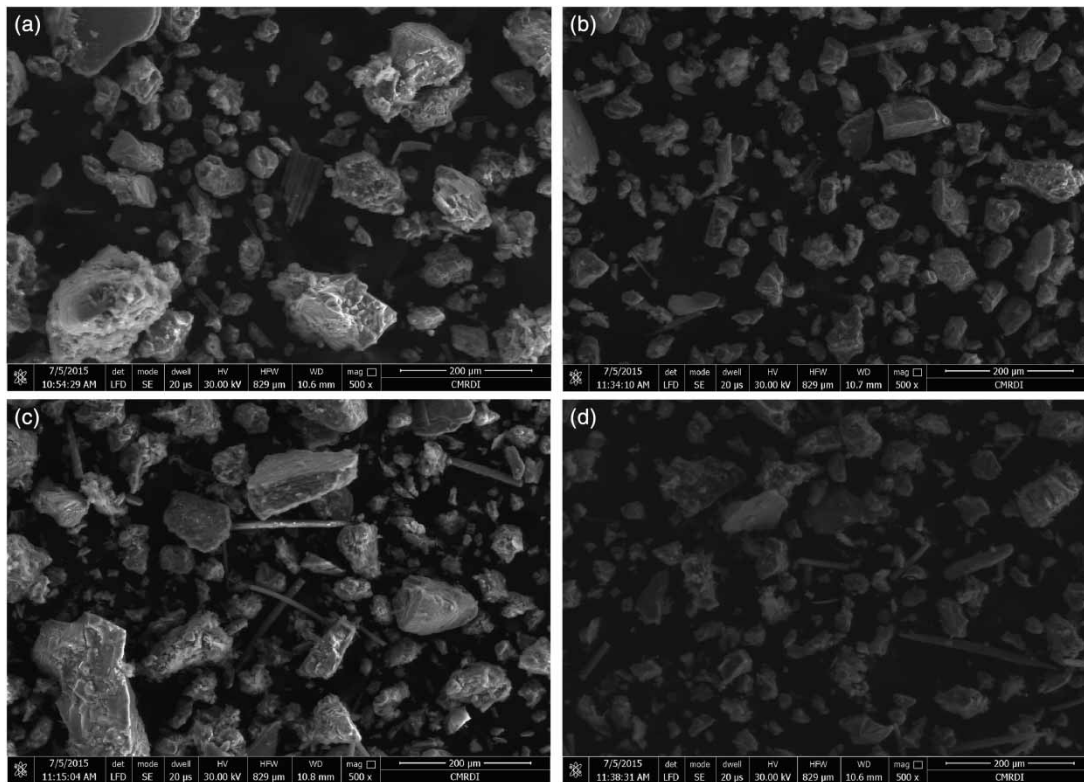


Figure 3 | SEM images of alum sludge (AS3) (a) before and (b) after activation, mud sludge (MS3) (c) before and (d) after activation.

Table 2 | Removal percent of MB by chemically activated sludge with AA and AA/pyrolysis at 500 °C

Activation by AA and pyrolysis			Activation by AA	
AA concentration (M)	AS removal (%)	MS removal (%)	AS removal (%)	MS removal (%)
0.1	32.9	79.9	73.7	75.7
0.5	30.6	52.6	49.2	81.9
1	37.8	49.6	60.8	79.2
2	55.2	51.3	57.0	66.8
3	56.1	52.6	36.9	40.5

Table 3 | Removal percent of MB by chemically activated sludge with nitric acid

Activation by nitric acid (NA)		
NA concentration (M)	AS removal (%)	MS removal (%)
0.25	82.1	93.6
0.5	74.2	76.3
1	72.8	79.6
2	67.0	54.2

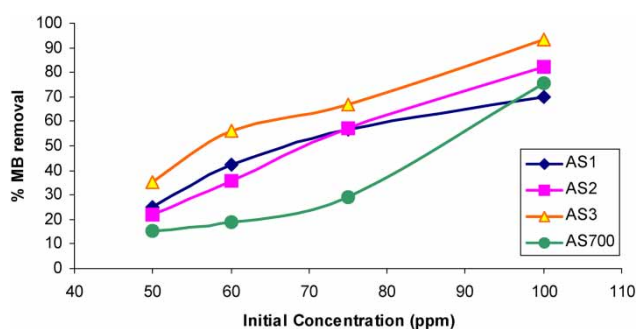
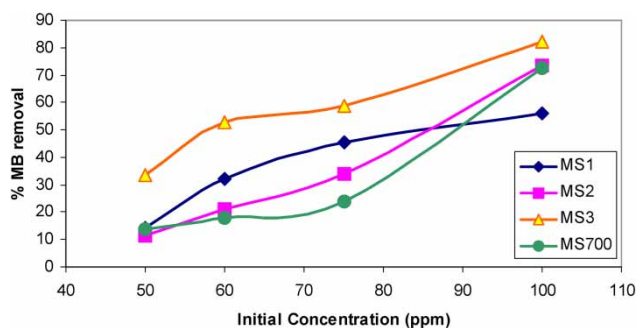
concentration of MB from 50, 60, 75 and 100 mg/L, the loading capacity of MB by AS1, AS2, AS3 and AS700 increased from 4.98 to 27.95, 4.37 to 32.79, 7.08 to 37.42 and 3.09 to 30.27 mg/g, respectively, while the loading capacity of MB by MS1, MS2, MS3, and MS700 increased from 2.89 to 22.46, 2.29 to 29.47, 6.74 to 32.84 and 2.77 to 29.04 mg/g, respectively.

Thus, the initial dye concentration slightly influenced the adsorption process efficiency. However, at a fixed adsorbent dosage, the percentage of dye removal decreased with increasing dye concentration. This could be ascribed to the accompanying increase in dye aggregation and/or depletion of accessible hydrolysis products of the coagulant.

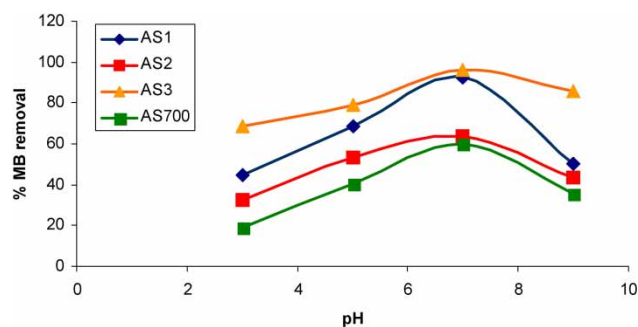
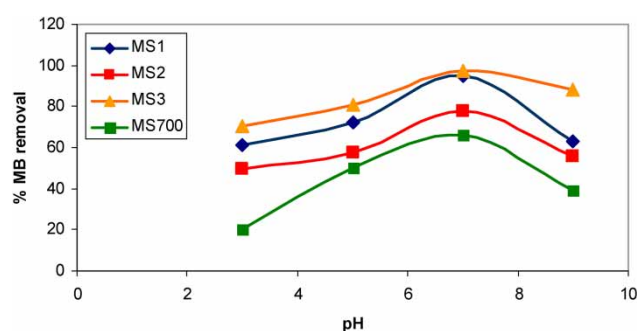
Gurses *et al.* (2006) reported that the adsorption capacity of MB dye on surface clay increased from 9.2 to 58.3 mg/g with an increase in initial dye concentration from 10 to 100 mg/L. This indicates that the initial dye concentration plays an important role in the adsorption capacity of dye. Neumann *et al.* (2002) showed that dye molecules can migrate from the external surface to the interlamellar region, resulting in de-aggregation of the aggregates and restoration of the monomers.

Table 4 | Removal percent of MB by physically activated sludge**Physically activated sludge (pyrolysis)**

Pyrolysis temperature (°C)	AS removal (%)	MS removal (%)
400	45.8	58.6
500	39.9	29.8
600	46.3	40.3
700	75.7	72.6
800	22.8	20.9
900	44.4	39.3

**Figure 4** | Effect of MB initial concentration on adsorption with AS adsorbents.**Figure 5** | Effect of MB initial concentration on adsorption with mud sludge adsorbents.**Effect of pH on dye adsorption**

It was observed from the results that pH significantly influence the adsorption process. The adsorption data for removal of MB by AS1, AS2, AS3, AS700, MS1, MS2, MS3 and MS700 adsorbents at various pH (3, 5, 7 and 9) under fixed experimental conditions (adsorbent dose, 0.25 g/100 ml, contact time 1 h, solution temperature 25 °C, and initial concentration 100 mg/L) are represented in Figures 6 and 7.

**Figure 6** | Effect of pH on removal efficiency of MB on AS adsorbents.**Figure 7** | Effect of pH on removal efficiency of MB on MS adsorbents.

The results presented in Figures 6 and 7 showed that the removal percent of MB by AS1, AS2, AS3, AS700, MS1, MS2, MS3 and MS700 adsorbents increased with an increase in pH from 3 to 7. The removal of MB by AS1, AS2, AS3 and AS 700 adsorbents increased from 44.75 to 92.41%, from 32.5 to 63.6%, from 68.75 to 96.23% and from 18.9 to 60.29%, respectively, with increasing pH. The removal of MB by MS1, MS2, MS3 and MS700 adsorbents increased from 61.11 to 94.95%, from 49.32 to 77.62%, from 70.2 to 97.56% and from 20.28 to 65.95%, respectively with increasing pH. So, the maximum uptake of MB dye was observed at pH 7. This result is in agreement with that reported for the adsorption of MB on wood shavings, spent tea leaves, and sunflower seed hull (Hameed 2008; Janos et al. 2009; Dakhil 2013). Yasin et al. (2007) found that the amount of MB removal onto treated activated carbon increased with an increase in solution pH.

MB is a cationic dye, which exists in aqueous solution in the form of positively charged ions. The low adsorption of MB at an acidic pH was suggested to be due to the presence of excess H⁺ ions that compete with the dye cation for adsorption sites. The number of positively charged sites decreases, while the number of negatively charged sites increases, which favours the adsorption of MB due to electrostatic

attraction. As the pH value increased from 7–9, the efficiency of the dye removal decreased. At higher solution pH, the decrease in the adsorption rate is due to the formation of a hydroxyl complex between the adsorbent and the dye.

Effect of adsorbent dose on dye adsorption

The adsorption data for removal of MB by AS1, AS2, AS3, AS700, MS1, MS2, MS3 and MS700 adsorbents at different dosages (0.05, 0.1 and 0.25 g/L) with fixed conditions (initial dye concentration 100 mg/L, contact time 1 h, solution temperature 25 °C and pH 7) are represented in Figures 8 and 9.

It appears from Figures 8 and 9 that by increasing the adsorbent dose from 0.05 to 0.25 g/L the removal percent of MB by AS1, AS2, AS3, and AS700 adsorbents increased from 20.69 to 69.88%, from 29.4 to 81.98%, from 33.78 to 93.6 and from 24.8 to 75.68%, respectively. The removal percent of MB by MS1, MS2, MS3 and MS700 increased from 14.5 to 56.2%, from 23.9 to 73.7%, from 25.5 to 82.1% and from 22.7 to 72.6%, respectively. So the effective adsorbent dose for the highest MB removal was 0.25 g/L.

Dakhil (2013) found that the removal percentage of MB increased from 36.4% to 95.2% with an increase in the adsorbent dose of spent tea leaves from 0.05 to 0.43 g; this

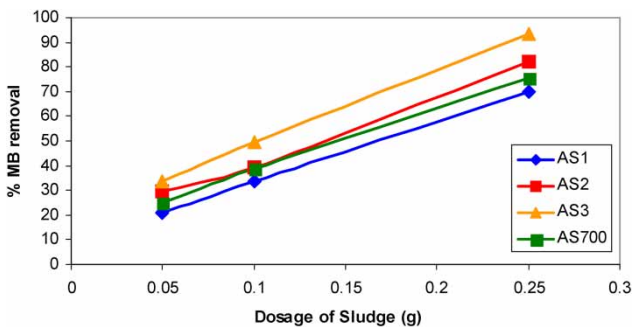


Figure 8 | Effect of AS adsorbents dosage on MB removal.

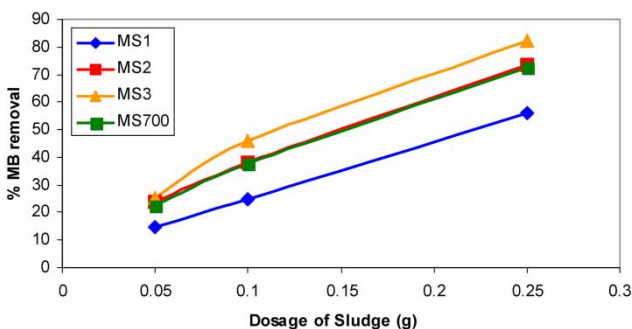


Figure 9 | Effect of mud sludge adsorbents dosage on MB removal.

can be attributed to the increase in adsorbent surface area and the availability of more adsorption sites resulting from the increase dosage of adsorbent.

A similar observation was reported for removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon (Mall *et al.* 2005), and removal of Brilliant green on treated sawdust (Venkat & Vijay Babu (2011). Gurses *et al.* (2006) found that with an increase in sorbent dosage (clay) from 0.1 to 0.3 g, the MB adsorption capacity increased (from 57.1 to 66.1 mg/g). Increasing the adsorbent dosage at a fixed MB concentration provided more available adsorption sites for MB on the adsorbent, and thus increased the extent of MB removal. Reham & Mahmud (2013) found that the maximum adsorption (94%) of MB occurred with 0.4 g adsorbent dose of Ricinus Communis stem powder. Saiful Azhar *et al.* (2005) found the percentage of dye removal was increased with the increase of absorbance dosage (powdered activated carbon). For the adsorbent dosage of 1 g, it was found that the amount of dye being adsorbed was nearly 100%. Yasin *et al.* (2007) found that the amount of MB removal increased with the increase in the amount of adsorbent used (activated carbon).

Effect of contact time on dye adsorption

The adsorption data for removal of MB by AS and MS adsorbents at different contact times (30, 60, 90 and 120 min) with fixed experimental conditions (initial dye concentration 100 mg/l, adsorbent dosage 0.25 g/100 ml, solution temperature 25 °C, and pH 7) are represented in Figures 10 and 11.

The results from Figures 10 and 11 show that the removal efficiency of MB on the adsorbents (AS1, AS2, AS3, AS700, MS1, MS2, MS3 and MS700) increased with increasing time from 20 to 60 min and remain constant up to 90 min. So one hours' contact time was enough to achieve maximum adsorption of MB on the surface of AS and MS

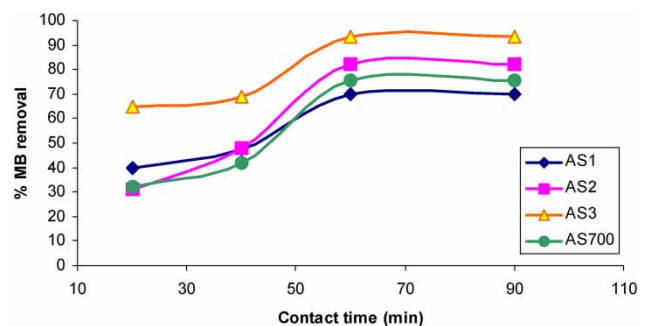


Figure 10 | Effect of contact time on MB removal using AS adsorbents.

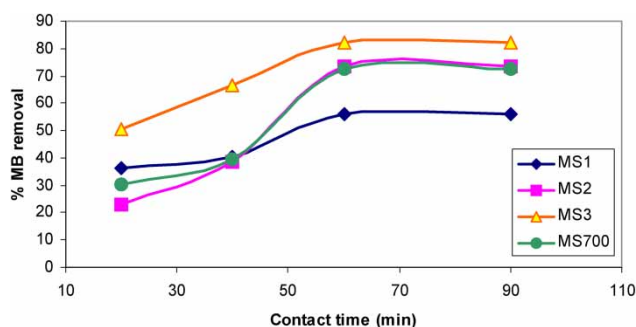


Figure 11 | Effect of contact time on MB removal using mud sludge adsorbents.

adsorbents. It can be concluded that MB was adsorbed into AS and MS adsorbents very rapidly within 20–60 minutes; the fast adsorption in the initial stage may be due to the higher driving force creating a fast transfer of MB dye to the surface of the adsorbent particles and the availability of the uncovered surface area and active sites on the adsorbent; with increasing time the availability of uncovered surface area and the remaining active sites decreased.

Yasin *et al.* (2007) reported that the amount of MB removal onto treated activated carbon increased with an increase in contact time. Gurses *et al.* (2006) reported that the adsorption of MB on clay adsorbent tends to attain equilibrium at nearly 60 min. Reham & Mahmud (2013) found that maximum adsorption of MB (76%) on *Ricinus Communis* stem powder attained equilibrium at 65 min. Makris *et al.* (2006) reported that the greatest amount (65%) of perchlorate removed by the aluminum-based drinking water treatment residuals (Al-WTR) was observed with the lowest initial perchlorate concentration (10 mg L^{-1}) after only 2 hours' contact time.

Effect of solution temperature

The adsorption data for removal of MB by AS and MS adsorbents (AS1, AS2, AS3, AS700, MS1, MS2, MS3 and MS700) at different solution temperatures (25, 40 and 60°C) with fixed experimental conditions (initial MB concentration 100 mg/L , adsorption dosage 0.25 g/100 ml , contact time 1 hour and pH 7) are represented in Figures 12 and 13.

The results from Figures 12 and 13 show that with the increase in solution temperature from 25°C to 60°C the removal percent of MB by AS and MS adsorbents decreased. The decrease in adsorption with the rise in temperature may be due to the weakening of the adsorptive forces between the active sites of the adsorbents and the adsorbate species. So the most suitable temperature for high MB removal was

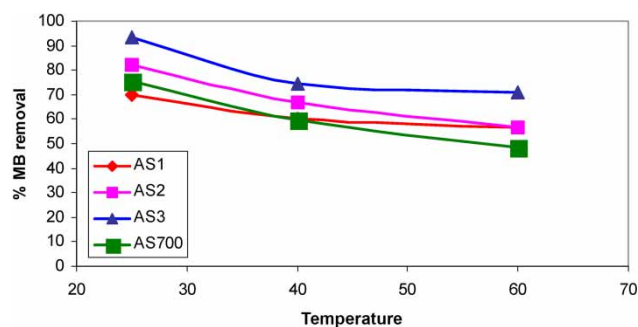


Figure 12 | Effect of temperature on MB removal using AS adsorbents.

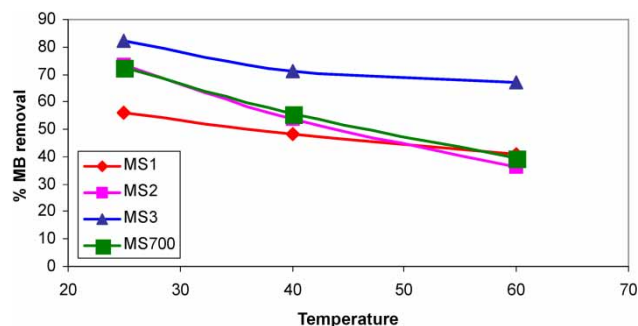


Figure 13 | Effect of temperature on MB removal using mud sludge adsorbents.

25°C . Gurses *et al.* (2006) reported that the adsorption of MB onto clay increases with decreasing temperature. Reham & Mahmud (2013) found at higher temperature a decrease in the movement of the solution, which results in a decrease in adsorption. Maximum adsorption of MB with *Ricinus Communis* stem powder was 73%, which occurred at 40°C .

Adsorption isotherms

Isotherms give an equilibrium relationship between the amounts of adsorbent adsorbed on the adsorbent surface and its concentration in the solution at a constant temperature. In this study, the data were fitted using Langmuir and Freundlich models. Each of these models makes use of a parameter q_e (i.e. the adsorption capacity per unit mass of the adsorbent at equilibrium) in mg/g .

$$q_e = (C - C_e) \frac{v \text{ mg}}{x \text{ g}} \quad (3)$$

where C is the initial concentration of the solution (mg/L), C_e is the equilibrium concentration of the solution (mg/L), v is the volume of solution (L), and x is the amount of adsorbent used (g).

Langmuir isotherm model

The linear form of Langmuir expression:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{bQ_0} \quad (4)$$

where C_e is the equilibrium concentration of dye solution (mg/L), q_e is the equilibrium capacity of dye on adsorbent (mg/g), Q_0 is the monolayer adsorption capacity of the adsorbent (mg/g), and b is the Langmuir adsorption constant (L/mg).

The Langmuir model fitted well to the experimental data as shown in Table 5. From the Langmuir parameters, the maximum adsorption for MB dye by alum sludge adsorbent (AS) AS1, AS2, AS3 and AS700 is 70.4, 65.79, 45.87 and 68.97 mg/g, respectively. Thus, the AS1 adsorbent exhibited higher maximum adsorption of MB (q_e) (70.4 mg/g) than that of AS2, AS3 and AS700. The AS700 adsorbent showed high q_e (68.97 mg/g). The maximum adsorption of MB dye by MS adsorbent (MS1, MS2, MS3 and MS700) is 64.1, 64.52, 64.52 and 65.79 mg/g, respectively. Therefore, MS adsorbents (MS1, MS2 and MS2) were in the near ranges of q_e , while the MS700 adsorbent showed a higher q_e (65.79 mg/g) than those of MS1, MS2 and MS3.

The values of R^2 for MB adsorption on AS adsorbents were 0.997 for AS1, 0.999 for AS2, 0.996 for AS3 and 0.999 for AS700. The values of R^2 for adsorption of MB on MS adsorbent were 0.996, 0.997, 0.997, and 0.998 for MS1, MS2, MS3 and MS700 (Table 5). The results show that the Langmuir isotherm is the most appropriate for MB dye adsorption on the developed adsorbents, indicating that the monolayer of dye molecules covers the adsorbent sludge surface.

Table 5 | The values of parameters for each isotherm model in the current study

Adsorbent	Langmuir isotherm model			Freundlich isotherm model		
	q_e (mg/g)	b	R^2	k_f	$1/n$	R^2
AS1	70.4	0.024	0.997	3.49	0.5	0.949
AS2	65.79	0.027	0.999	3.47	0.507	0.933
AS3	45.87	0.057	0.996	1.35	0.726	0.931
AS700	68.97	0.025	0.999	1.7	0.657	0.963
MS1	64.1	0.029	0.996	1.11	0.730	0.948
MS2	64.52	0.028	0.997	1.07	0.738	0.963
MS3	64.52	0.028	0.997	1.46	0.7	0.942
MS700	65.79	0.027	0.998	2.32	0.564	0.954

Freundlich isotherm model

The Freundlich model is based on the assumption that metal ions are adsorbed on a heterogeneous surface and are not restricted to the formation of a monomolecular layer.

The linear form can be written as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (5)$$

where k_f and n are the Freundlich adsorption isotherm constants. This indicates the capacity and intensity of the adsorption, respectively.

The Freundlich model was fitted to the experimental data, as shown in Table 5. From the Freundlich constants, the values of $1/n$ for adsorption on the AS adsorbent were 0.5 for AS1, 0.507 for AS2, 0.726 for AS3, and 0.657 for AS700. The values for adsorption on the MS adsorbent were 0.73 for MS1, 0.738 for MS2, 0.7 for MS3 and 0.564 for MS700 (Table 5). The previous values of $1/n$ were between 0–1, which revealed the heterogeneity of alum and mud adsorbent surfaces.

The values of R^2 for Langmuir and Freundlich isotherms given in Table 5 indicated that the adsorption data for MB dye on alum and mud adsorbents fitted better to the Langmuir model than the Freundlich model, but the closeness of these values indicated that both of them are almost equally obeyed. It can be concluded that probably the surface of the sludge contains heterogeneous moieties that are uniformly distributed on the surface, which accounts for both Langmuir and Freundlich adsorption isotherms.

Kinetic models

Several models can be used to express the mechanism of solute sorption onto adsorbent. In order to investigate the mechanism of sorption, the constants of sorption and intra-particle diffusion of dye were determined using the pseudo-first order equation of Lagergren (1898), and pseudo-second order mechanism (Weber & Morris 1963).

Pseudo-first order model

The sorption kinetics may be described by the pseudo-first order. The differential equation is the following:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (6)$$

Integrating Equation (1) for the boundary conditions $t = 0$ to $t = t$, and $q_t = 0$ to $q_t = qt$ gives:

$$\text{Log} \frac{q_e}{q_e - q_t} = \frac{k_1}{2.303} t \quad (7)$$

which is the integrated rate law for a pseudo-first order reaction where q_e is the amount of dye sorbed at equilibrium (mg g^{-1}), q_t is the amount of dye sorbed at time t (mg g^{-1}), and k_1 is the equilibrium rate constant of pseudo-first sorption (min^{-1}).

Equation (2) can be rearranged to obtain a linear form:

$$\text{Log}(q_e - q_t) = \log(q_e) - k_1/2.303t \quad (8)$$

In order to obtain the rate constant, the straight line plot of $\log(q_e - q_t)$ against t , the rate constant, k_1 , and correlation coefficients, R^2 , values of the dye were calculated from these plots.

Pseudo-second order model

The sorption kinetics may be described by a pseudo-second order equation. The differential equation is as follows:

$$\frac{dq_e}{dt} = k(q_e - q_t)^2 \quad (9)$$

Integrating Equation (4) for the boundary conditions $t = 0$ to $t = t$ and $qt = 0$ to $qt = t$, gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e + k t} \quad (10)$$

which is the integrated rate law for a pseudo-second order reaction, where q_e is the amount of dye sorbed at equilibrium (mg g^{-1}) and k is the equilibrium rate constant of pseudo-second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$).

Equation (5) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{1}{q_e} t \quad (11)$$

The straight line plots of t/q_t against t have also been tested to obtain rate parameters. The k , q_e and correlation coefficients (R^2) values of MB dye under different conditions were calculated from these plots.

Additionally, the relative rate constants and parameters were shown in Table 6.

Table 6 | Pseudo-first order rate and pseudo-second order rate for adsorption of MB onto the AS and MS adsorbents

Adsorbent	Pseudo-first order model			Pseudo-second order model		
	q_{e1} (mg/g)	K_1 (min^{-1})	R^2	q_{e2} (mg/g)	K (g/mg^{-1})	R^2
AS1	57.11	0.062	0.839	20.62	0.0094	0.994
AS2	56.1	0.075	0.867	34.72	0.0008	0.991
AS3	57.98	0.063	0.887	26.46	0.0204	0.978
AS700	94.78	0.069	0.794	28.33	0.0014	0.991
MS1	58.44	0.063	0.884	15.38	0.0127	0.992
MS2	55.7	0.074	0.835	42.55	0.0003	0.999
MS3	53.7	0.063	0.94	47.85	0.0007	0.985
MS700	92.6	0.069	0.81	26.11	0.0017	0.974

It can be seen that the experimental data fit better with pseudo-second order model with detrimental coefficient R^2 of 0.994 for AS1, 0.991 for AS2, 0.978 for AS3, 0.991 for AS700, 0.992 for MS1, 0.999 for MS2, 0.985 for MS3 and 0.974 for MS700, compared with R^2 of the first order model 0.839 for AS1, 0.867 for AS2, 0.887 for AS3, 0.794 for AS700, 0.884 for MS1, 0.835 for MS2, 0.94 for MS3 and 0.81 for MS700. The high determination coefficient R^2 implies the good applicability of the second order kinetics equation for MB dye adsorption using AS and MS.

CONCLUSION

The activated sludge adsorbents developed by physical activation at 700°C from drinking water treatment AS and MS are suitable adsorbents to remove MB dye from polluted water. The activation of AS and MS by AA and nitric acid showed that they were effective as chemical activation reagents to remove MB dye from polluted water. The adsorbents developed by activation of AS and MS with nitric acid are considered as a more effective means of MB removal than the others.

The optimum parameters for high removal of MB on the developed adsorbents were: initial dye concentration 100 mg/L , pH 7, adsorbent dosage 0.25 g , contact time 1 hour, and solution temperature 25°C . The adsorption data of MB dye on AS and MS adsorbents fitted well with the Langmuir model. The activated sludge adsorbent which derived from the Fatera drinking water treatment plant (AS) was more effective than that derived from the Gabal Takok drinking water treatment plant (MS).

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