

## Use of aluminium-coagulated water treatment residue in the treatment of dye containing wastewater

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### ABSTRACT

In this study, the possibility of the use of alum sludge as an adsorbent in reactive dye (Remazol Blue RR) removal from wastewater was investigated. The effects of adsorbent dose, initial dye concentration, initial solution pH and salt concentration on reactive dye adsorption were investigated by batch studies. The equilibrium data were analyzed using Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. The Freundlich isotherm model was found to be better fitted than the Langmuir and D-R isotherm models, and the monolayer adsorption capacity for Remazol Blue RR (RB) onto alum sludge was 0.453 mg/g. The results indicated that the alum sludge, aluminium-coagulated water treatment residue, is suitable as an adsorbent material for removing reactive dye from aqueous solution.

*Keywords:* Adsorption; Reactive dye; Remazol blue RR; Removal; Alum sludge

### 1. Introduction

Aluminum salts are one of the most commonly used coagulants in the water treatment industry. In potable water treatment plants where aluminum salts are used as the primary coagulating-flocculating agents, huge amounts of alum sludge are generated every day. The proper collection, transport and disposal cost to landfilling of the sludge is one of the most significant problems for the potable water treatment plants. Therefore, attention has been focused on research towards its reuse. Up to now, several researchers have investigated the suitability of alum sludge taken from drinking water treatment works for the removal of lead [1,2], chromium [2], arsenic [3,4], phosphate [4] and phosphorus [5–7] from aqueous solution.

When different research works were reviewed, it was seen that no study on dye adsorption on alum sludge (aluminium-coagulated water treatment residue) from aqueous solutions is available in the literature. Therefore, the purpose of this study was to evaluate the use of alum sludge

for the removal of reactive dye (Remazol Blue RR) from aqueous media.

Reactive dyes have advantages such as bright colours and ease of application. Therefore, they are commonly used in textile dyeing industries [8]. They are generally used for cotton and other cellulose. They are also used to a small extent on wool and nylon. Reactive dyes make a covalent bond with the fiber and contain chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Their chemical structures are simpler, absorption spectra show narrower absorption bands, and the dyeings are brighter, making them advantageous over direct dyes [9].

In the experimental studies, the dewatered alum sludge was used without any physical or chemical pre-treatment. The effects of adsorbent dose, initial dye concentration, initial solution pH and salt concentration on the adsorption efficiency of the Remazol Blue RR from aqueous solutions by alum sludge was reported in the present study. Equilibrium data was fitted to Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherm models. In this study, the alum sludge was characterized using surface area analyzer, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

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## 2. Materials and methods

### 2.1. Adsorbent and adsorbate

Dewatered alum sludge was obtained from Kagithane Water Treatment Plant in Istanbul, Turkey. In the experimental studies, the dewatered alum sludge was used without any physical or chemical pre-treatment. Remazol Blue RR (RB) was supplied from a textile factory in Istanbul, Turkey. The properties of the RB are shown in Table 1.

A stock solution of 1000 mg/L was prepared by dissolving an appropriate quantity of RB in a liter of deionised water. The stock solution was diluted to the required initial concentration.

The FT-IR spectrum of the alum sludge before and after adsorption was obtained by the use of a Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer Precisely Spectrum One FTIR). The surface morphology of the alum sludge before and after the adsorption of RB was observed by using a FEI Quanta FEG 450 scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) analysis. Analyses of the surface area of the alum sludge were carried out in the METU Central Laboratory-Training Centre in Ankara, Turkey.

### 2.2. Batch adsorption studies

Adsorption experiments were conducted at room temperature and batch mode. A fixed amount of adsorbent was added to a series of 250 mL Erlenmeyer flasks containing 100 mL of dye solution and shaken at 150 rpm using a temperature-controlled water bath with shaker (Zhcfeng ZHWY-211B). The flask contents were centrifuged at 2000 rpm for 10 min. Then the residual concentration of the RB dye was analyzed using UV-Visible spectrophotometer (DR 5000 Hach Lange) at a wavelength of 600 nm.

pH was adjusted by the addition of dilute (0.01 M) aqueous solution HCl or NaOH. The effect of salt concentration on the RB adsorption by alum sludge was studied using NaCl at different concentrations (4–40 mg/L).

The percent removal (R%) of the RB dye is defined as:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

The amount of the RB dye adsorbed ( $q$ ) was calculated from the following equations:

$$q = \frac{(C_0 - C) \times V}{m} \quad (2)$$

where  $C_0$  and  $C$  are the initial and equilibrium concentrations of the RB in the solution, respectively,  $V$  is the vol-

ume of dye solution (L), and  $m$  is the amount of adsorbent used (g).

Duplicate experiments were carried out, and the mean values are reported. The average deviation is found to vary as  $\pm 5\%$ .

### 2.3. Theory-equilibrium isotherms

Langmuir model (Eq. (3)) [10] and Freundlich model (Eq. (4)) [11] are expressed in linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where  $C_e$  is the equilibrium dye concentration (mg/L),  $q_e$  is the amount of dye uptake per unit weight of the adsorbent (mg/g),  $q_{\max}$  is the maximum adsorption capacity of the adsorbent (mg/g),  $b$  is the Langmuir isotherm constant (L/mg), and  $K_F$  (mg/g) and  $1/n$  are the Freundlich constants representing the adsorption capacity and adsorption intensity, respectively.

Dubinin-Radushkevich (D-R) isotherm model [12]:

$$\ln q_e = \ln q_m - B\epsilon^2 \quad (5)$$

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

where  $q_e$  is the amount of dye uptake per unit weight of the adsorbent (mg/g),  $q_m$  is the maximum adsorption capacity (mg/g),  $B$  is a constant related to the adsorption energy ( $\text{mol}^2/\text{kJ}^2$ ),  $\epsilon$  is the Polanyi potential,  $R$  is the gas constant ( $\text{kJ/mol K}$ ) and  $T$  is the absolute temperature (K).

## 3. Results and discussion

### 3.1. Characterization of the alum sludge

In this study, the alum sludge was characterized according to the surface area, surface morphology, and available functional groups. The specific surface area obtained by BET analysis for the alum sludge was  $71.43 \text{ m}^2/\text{g}$ .

The FT-IR spectrum of the alum sludge before and after adsorption is shown in Fig. 1. The peak in the region of  $3400\text{--}3500 \text{ cm}^{-1}$  can be assigned to  $\text{HO-OH}_2$  and  $\text{H}_2\text{O-OH}_2$  vibrations. The bands in the  $450\text{--}650 \text{ cm}^{-1}$  region may be related to the characteristic vibrations of metal oxides ( $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ ), which make it a good potential adsorbent for the treatment of wastewater [13]. It is thought that the bands in  $1065$  and  $1071 \text{ cm}^{-1}$  may be due to  $\text{S=O}$  stretching of sulfonate group ( $\text{SO}_3^-$ ) of RB dye [14].

Scanning electron microscopic (SEM) images of the alum sludge before and after RB adsorption is shown in Fig. 2a and b. The results obtained by EDS are presented in Fig. 3a and b. The EDS results showed that the raw alum sludge consists of oxygen, aluminum, carbon, silicon, sulphur, and calcium with atomic percentages of 56.57%, 21.19%, 17.81%, 3.57%, 0.52% and 0.34%. From the quali-

Table 1  
Properties of Remazol Blue RR (VS: vinyl sulphone)

Structure	Bifunctional
Reactive group	VS/VS
Reactivity	Medium
Substantivity	Medium

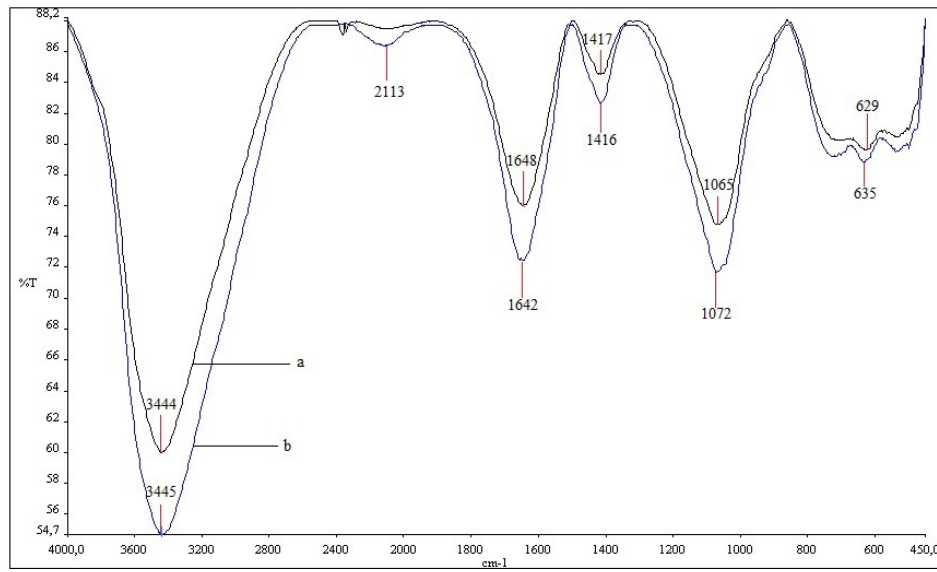
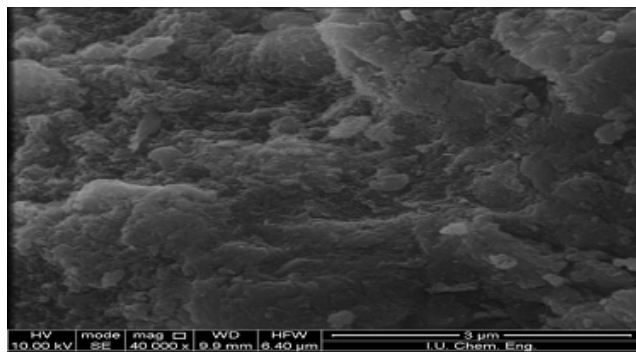
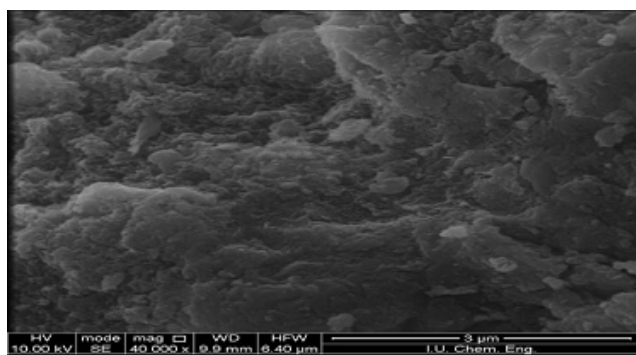


Fig. 1. FTIR spectra of the alum sludge before (a) and after (b) dye adsorption.



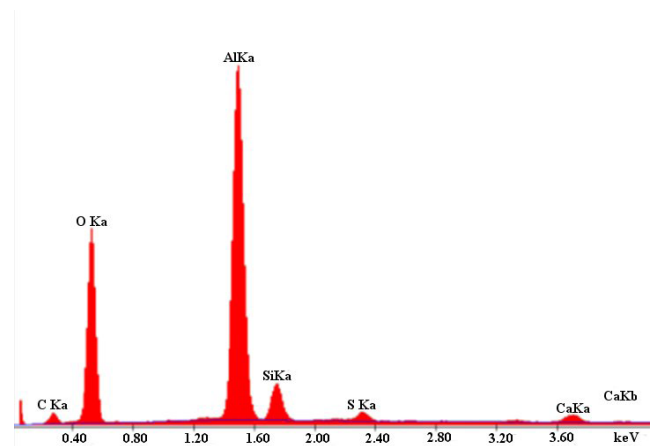
(a)



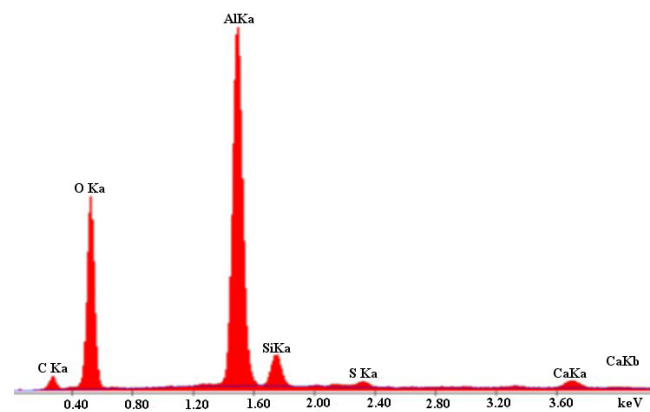
(b)

Fig. 2. SEM images of the alum sludge before (a) and after (b) dye adsorption.

tative EDX spectra for dye loaded alum sludge, it was seen that the atomic percentages of oxygen, aluminum, carbon, silisium, sulphur, and calcium are 54.99%, 20.61%, 20.71%, 3.01%, 0.34% and 0.34%, respectively. After RB dye adsorption, the percentage of the carbon on the surface of the alum sludge was increased from 17.81% to 20.71%.



(a)



(b)

Fig. 3. Spectra of EDS of the alum sludge before (a) and after (b) dye adsorption.

### 3.2. Adsorbent dosage

In the present study, the dye removal efficiency of alum sludge was examined with different adsorbent dosages (5–100 g/L) and shown in Fig. 4. The RB removal (%) increased with the increase in dosage of the alum sludge. This is due to the availability of more active sites [15]. As can be seen from Fig. 4, the RB uptake,  $q$  (mg/g) decreased by increasing the alum sludge due to a reduction in the adsorbate/adsorbent ratio [16].

### 3.3. Initial dye concentration

The effect of the initial dye concentration on the capacity of the alum sludge for adsorbing dye from aqueous solution was studied in the range 5–30 mg/L. As can be seen in Fig. 5, the RB adsorption increases with the increase of the initial concentration of the RB. This is probably due to a high-mass transfer driving force. It can be said that the initial dye concentration provides an important driving force to overcome the resistances to the mass transfer of dye molecules between the aqueous and solid phases [15]. This means that the interaction between the RB and the alum sludge enhances as the initial concentration of the RB increases.

Similar observations have been reported for the adsorption of reactive red 189 on chemical cross-linked chitosan

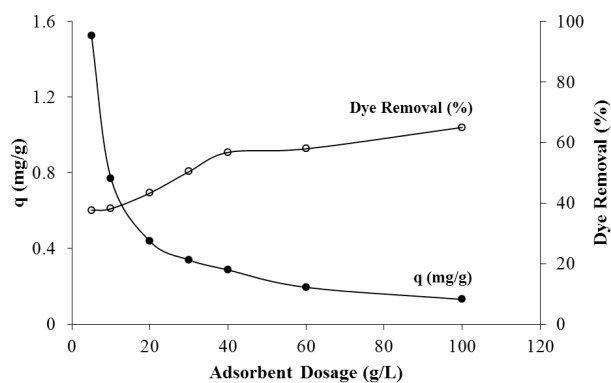


Fig. 4. The effect of adsorbent dosage ( $C_0$ : 20 mg/L, pH: 6.4,  $t$ : 60 min).

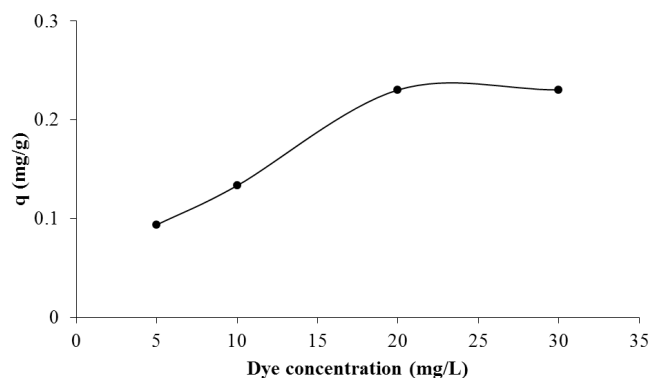


Fig. 5. The effect of initial dye concentration (pH: 6.4,  $m$ : 30 g/L,  $t$ : 90 min).

beads [17], adsorption of C.I. reactive black 5 on activated carbon derived from solid waste [18], and the adsorption of acid red 14 and acid red 18 on soy meal hull activated carbon [19].

### 3.4. Adsorption isotherm

The equilibrium data were analyzed using Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. The plot of  $q_e$  vs.  $C_e$  is shown in Fig. 6. The equilibrium isotherm constants for the adsorption of RB on the alum sludge are given in Table 2. The equilibrium data suggest that the Freundlich model provided better fitting than the Langmuir and Dubinin-Radushkevich isotherm model. The order of the best-fit isotherm models was found to be Freundlich (R: 0.9794) > Dubinin-Radushkevich (R: 0.9402) > Langmuir (R: 0.8845).

Confirmation of the experimental data with the Freundlich isotherm model indicates equilibrium on heterogeneous surfaces and thus does not suggest monolayer capacity [20]. It is well known that an  $n > 1$  indicates that the adsorbate is favorably adsorbed onto an adsorbent [21]. As can be seen from Table 1, the  $n$  value (1.139) was greater than one, suggesting favorable adsorption.

The Freundlich constant  $n$  is also a measure of the deviation from linearity of the adsorption. When  $n = 1$ , the adsorption is linear. If  $n < 1$ , this implies that the adsorption process is chemical. If  $n > 1$  or becomes larger ( $n \gg 1$ ), the adsorption bond becomes weak, and adsorption is a physical process [22]. In the present work, the  $n$  value of the alum sludge is above unity. This suggests that the physical adsorption is dominant when it is used for adsorbing the RB.

It is known that the mean free energy ( $E$ ) of adsorption from the Dubinin-Radushkevich isotherm could be used to estimate the adsorption mechanism as a chemical ion-exchange. When the value of  $E$  is between 8 and 16 kJ/mol, the adsorption process is followed by chemical ion-exchange. When  $E$  is < 8 kJ/mol, the adsorption process is of a physical nature. The  $E$  value of 0.20 kJ/mol for the adsorption of RB suggested that the adsorption of this dye onto the alum sludge might occur via physical interactions [23,24].

### 3.5. Initial solution pH

The influence of the initial solution pH on the dye adsorption on alum sludge was studied. The adsorption of the RB

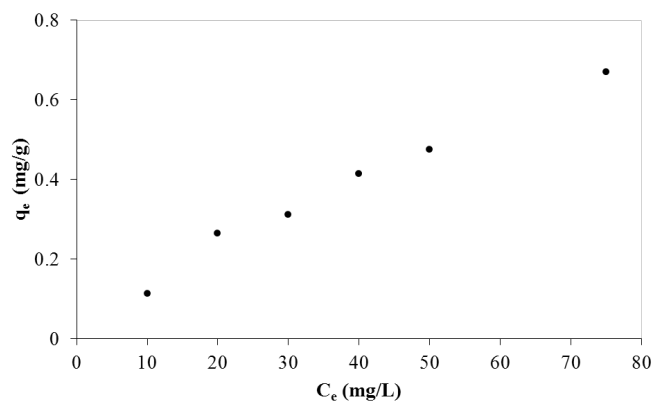


Fig. 6. The plot of  $q_e$  versus  $C_e$ .



Table 2  
The Freundlich, Langmuir and D-R constants for RB adsorption on alum sludge

Langmuir			Freundlich			D-R		
$q_m$ (mg/g)	$b$ (L/mg)	R	$K$ (mg/g)	$n$	R	$\beta$ (mol <sup>2</sup> /kJ <sup>2</sup> )	$q_m$ (mg/g)	R
1.54	0.013	0.8845	0.029	1.27	0.9794	12.43	0.48	0.9402

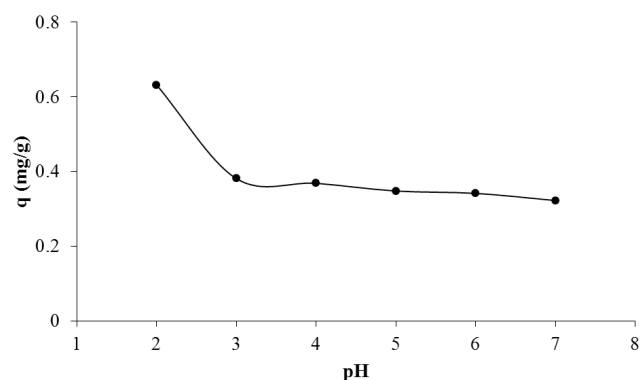


Fig. 7. The effect of pH ( $C_0$ : 20 mg/L,  $t$ : 90 min,  $m$ : 30 g/L).

decreased with an increase in the pH (Fig. 7). High dye removal at acidic pH is due to the fact that at acidic pH, the number of positively charged sites increases and the number of negatively charged sites decreases. Due to electrostatic attraction, a positive charged surface site on the adsorbent does favor the adsorption of anionic dye. At low pH, a strong electrostatic attraction occurs between the positively charged surface of the adsorbent and anionic dye molecule.

The maximum adsorption of the RB was at pH 2. The adsorption of the RB was not affected by pH except minor variations in the pH range of 3–7. Higher adsorption of the RB at pH 2 is due to the higher strong electrostatic attraction which is caused by the increased number of positively charged sites. Similar adsorption behavior with variation in the initial solution pH has been reported for the adsorption of reactive gray BF-2R [16], reactive blue 29 [20], C.I. reactive red 194 [25], reactive red 198 [26], reactive black 5 and reactive yellow K-4G [27], and direct blue-71 [28] in the literature.

### 3.6. Initial salt concentration

As stated by Aksu and Balibek [29], real textile dye effluents contain both dyes and salts. In addition to pH, ionic strength is also one of the important factors that affect the equilibrium uptake. The ionic strength of aqueous solution is directly proportional to the salt concentration.

The effect of salt concentration on the dye adsorption on alum sludge is shown in Fig. 8. As can be seen from Fig. 8, increasing the salinity does not lead to a dramatic decrease in the amount of the dye removed from the aqueous solution. The effect of the salt concentration on the dye adsorption seems to be negligible, especially within the range of salt concentration of 10–40 mg/L. Accordingly, it can be said that  $Cl^-$  ions do not significantly compete with the sulfonate group of the RB molecules for the active sites of the

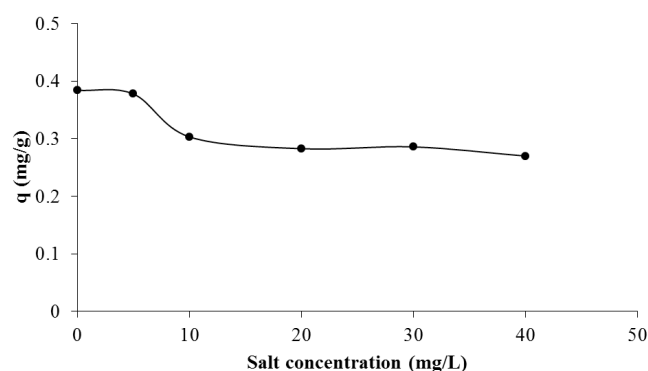


Fig. 8. The effect of salt concentration ( $C_0$ : 20 mg/L,  $t$ : 90 min,  $m$ : 30 g/L, pH: 6.4).

adsorbent [27,30]. A similar trend was observed for adsorption of reactive red 4 on coke waste [30], and reactive black 5 and reactive yellow K-4G on a solid waste product from food processing, crayfish carapace [27].

## 4. Conclusions

The adsorption of the reactive dye (Remazol Blue RR) was carried out through alum sludge. Based on the present results, it can be said that the Freundlich isotherm was the most appropriate isotherm to describe the equilibrium data for dye adsorption. The maximum adsorption capacity,  $q_{max}$  was found to be 1.54 mg/g. Adsorption was pH dependent and the maximum dye removal was observed at pH 2.0. The effect of the salt concentration on the dye adsorption was negligible. In the light of the results obtained from the present study, the evaluation of the use of alum sludge as an efficient adsorbent for the reactive dye removal showed that the alum sludge could be used as a low-cost material for reactive dye removal from an aqueous system.

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## References

- [1] W. Chu, Lead metal removal by recycled alum sludge, *Water Res.*, 33(13) (1999) 3019–3025.

- [2] Y.F. Zhou, R.J. Haynes, Removal of Pb(II), Cr(III) and Cr(VI) from aqueous solutions using alum-derived water treatment sludge, *J. Water, Air Soil Pollut.*, 215 (2011) 631–643.
- [3] R. Nagar, D. Sarkar, K.C. Makris, R. Datta, Effect of solution chemistry on arsenic sorption by Fe- and Al-based drinking-water treatment residuals, *Chemosphere*, 78 (2010) 1028–1035.
- [4] M.K. Gibbons, G.A. Gagnon, Understanding removal of phosphate or arsenate onto water treatment residual solids, *J. Hazard. Mater.*, 186 (2011) 1916–1923.
- [5] A.O. Babatunde, Y.Q. Zhao, Y. Yang, P. Kearney, Reuse of dewatered aluminium-coagulated water treatment residual to immobilize phosphorus: Batch and column trials using a condensed phosphate, *Chem. Eng. J.*, 136 (2008) 108–115.
- [6] Y. Yang, Y.Q. Zhao, A.O. Babatunde, P. Kearney, Two strategies for phosphorus removal from reject water of municipal wastewater treatment plant using alum sludge, *Water Sci. Technol.*, 60(12) (2009) 3181–3188.
- [7] A.O. Babatunde, Y.Q. Zhao, Equilibrium and kinetic analysis of phosphorus adsorption from aqueous solution using waste alum sludge, *J. Hazard. Mater.*, 184(1–3) (2010) 746–752.
- [8] P. Cooper, *Colour in Dyehouse Effluent*, Alden Press, Oxford, 1995.
- [9] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal-A review, *J. Environ. Manage.*, 90 (2009) 2313–2342.
- [10] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Society*, 40 (1918) 1361–1403.
- [11] H.M.F. Freundlich, Über die adsorption in lösungen, *Z. Phys. Chem.*, 57 (1906) 385–470.
- [12] M.M. Dubinin, L.V. Radushkevich, The equation of the characteristic curve of the activated charcoal, *Proc. Acad. Sci. USSR Phys. Chem. Sect.*, 55 (1947) 331–333.
- [13] G. Zhang, X. Li, Y. Li, T. Wu, D. Sun, F. Lu, Removal of anionic dyes from aqueous solution by leaching solutions of white mud, *Desalination*, 274 (2011) 255–261.
- [14] P.C.S. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed., Springer-Verlag, New York, 1983.
- [15] S.M.H. Gardazi, T.A. Butt, N. Rashid, A. Pervez, Q. Mahmood, M.M. Shah, M. Bilal, Effective adsorption of cationic dye from aqueous solution using low-cost corncob in batch and column studies, *Desal. Water Treat.*, 57 (2016) 28981–28998.
- [16] G.E. Nascimento, M.M.M. Bezerra Duarte, N.F. Campos, C.M. Bezerra de Menezes Barbosa, V.L. Silva, Adsorption of the reactive gray BF-2R dye on orange peel: kinetics and equilibrium studies, *Desal. Water Treat.*, 52 (2014) 1578–1588.
- [17] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, *Chemosphere*, 50 (2003) 1095–1105.
- [18] A.A. Ahmad, A. Idris, B.H. Hameed, Organic dye adsorption on activated carbon derived from solid waste, *Desal. Water Treat.*, 51 (2013) 2554–2563.
- [19] A. Haji, N.M. Mahmoodi, Soy meal hull activated carbon: preparation, characterization and dye adsorption properties, *Desal. Water Treat.*, 44 (2012) 237–244.
- [20] M.H. Dehghani, A. Naghizadeh, A. Rashidi, E. Derakhshani, Adsorption of reactive blue 29 dye from aqueous solution by multiwall carbon nanotubes, *Desal. Water Treat.*, 51 (2013) 7655–7662.
- [21] M.-C. Shih, Kinetics of the batch adsorption of methylene blue from aqueous solutions onto rice husk: effect of acid-modified process and dye concentration, *Desal. Water Treat.*, 37 (2012) 200–214.
- [22] J.-Q. Jiang, C. Cooper, S. Ouki, Comparison of modified montmorillonite adsorbents Part I: preparation, characterization and phenol adsorption, *Chemosphere*, 47 (2002) 711–716.
- [23] M.S. Onyango, Y. Kojima, O. Aoyi, E.C. Bernardo, H. Matsuda, Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, *J. Colloid Interface Sci.*, 279 (2004) 341–350.
- [24] S.S. Tahir, N. Rauf, Removal of cationic dye from aqueous solutions by adsorption onto bentonite clay, *Chemosphere*, 63 (2006) 1842–1848.
- [25] N.F. Cardoso, E.C. Lima, I.S. Pinto, C.V. Amavisca, B. Royer, R.B. Pinto, W.S. Alencar, S.F.P. Pereira, Application of Cupuassu shell as biosorbent for the removal of textile dyes from aqueous solution, *J. Environ. Manage.*, 92 (2011) 1237–1247.
- [26] A. Esmaili, M. Kalantari, Bioremoval of an azo textile dye, Reactive Red 198, by *Rhizopus oryzae*, *Desal. Water Treat.*, 57 (2016) 6401–6410.
- [27] Y. Wang, S. Wang, J. Lei, H. Sun, W. Jin, T. Ye, B. Li, L. Wang, Removal of reactive dyes by a solid waste product from food processing: *crayfish carapace*, *Desal. Water Treat.*, 52 (2014) 5541–5552.
- [28] M.H. Beyki, H. Alijani, M.H. Ghasemi, Melamine-anchored magnetic multiwall carbon nanotubes: tailoring functional groups reactivity for efficient adsorption of anionic dye, *Desal. Water Treat.*, 57 (2016) 20565–20573.
- [29] Z. Aksu, E. Balibek, Effect of salinity on metal-complex dye biosorption by *Rhizopus arrhizus*, *J. Environ. Manage.*, 91 (2010) 1546–1555.
- [30] S.W. Won, G. Wu, H. Ma, Q. Liu, Y. Yan, L. Cui, C. Liu, Y.-S. Yun, Adsorption performance and mechanism in binding of Reactive Red 4 by coke waste, *J. Hazard. Mater.*, B138 (2006) 370–377.