Original Article

Adsorption rate of 198 reactive red dye from aqueous solutions by using activated red mud

Mohammad Ali Zazouli. [1] * **Davad Balarak**. [2]Yousef Mahdavi.[2] Masoumeh Ebrahimi.[3]

1-Department of Environmental Health Engineering, Health Sciences Research Center, Mazandaran Univrsity Of Medical Sciences, Sari, Iran.
2-MSc student of Environmental health, Mazandaran University Of Medical Sciences.
3- MSc student of Environmental health student, Tabriz University Of Medical Sciences

***dbalarak2@gmail.com**

Abstract

***Backgroud and purpose*:** Dye is one of the problems of industrial effluent such as textile industries. The dyes can be removed by various methods. Therefore, the aim of this study was the evaluation of adsorption rate of reactive red 198 from aqueous solution by activated red mud.

***Materials and methods*:** This research was a lab study. Activated red mud was used as an adsorbent to remove reactive red 198 dye. The effect of various parameters on performance of adsorbent was investigated and the isotherm of adsorption was determined. The dye concentration was measured in wavelength of 518 nm by spectrophotometer.

Results: The results indicated that the adsorption efficiency reduced by increasing of initial dye concentration. Increasing of contact time and adsorbent dose can lead to increasing of the removal efficiency. The maximum removal efficiency was occurred pH between 2 to 3. The data was best fitted on Frandlich and Temkin isotherms.

Conclusion: The red mud had a satisfactory quality in dye adsorption. It can be used as effective and inexpensive adsorbents for treatment of textile effluent.

[Zazouli MA. *Balarak D. Mahdavi Y. Ebrahimi M. ***Adsorption rate of 198 reactive red dye from aqueous solutions by using activated red mud. IJHS 2013; 1(1): 36-43]***
http://jhs.mazums.ac.ir

***Key words*:** Red mud, Azo dyes, RR198, Textile wastewater, Adsorption

1. Introduction

Dyes are organic aromatic compounds that absorb light in 350-700 wavelengths (1,2). Dyes are categorized into 20-30 groups based on chemical structure or chromophore. The most important of them include the Azo, anthraquinon, phthalocyanine and acidic, basic (1-6). At present, about 100,000 dyes are produced in the world and annual production rate is 0.7 to 1 billion tons (1, 4). Textile industries are one of the largest industries that produce colorful wastewater. It is estimated that about 50% of consumptive reactive dyes is converted to wastewater and their concentration in industrial effluent is 10-200mg/l (7-10). Reactive dyes are widely used in textile industries. They are usually used in coloring of strings, wool and polyamide fibers (10). Mainly, the dyes have one or more aromatic benzene which are toxic and low degradable, so if they released without treating, they have adverse effects on environment. These wastewaters should be treated before discharging to environment (3,4,11). Several methods are used for this purpose such as biologic methods, membrane processes and advanced oxidation processes(3,8,9).Conventional methods such as coagulation and precipitation are not suitable to dye removal due to water-solubility of dyes (10,12-17). The most of conducted studies in dye removal are based on advanced oxidation processes which despite its high efficiency in dye removal, there are some problems such as By-products formation and high costs (10). Adsorption is a common method to dye removal. Activated carbon is widely used as adsorbent. However, it is very expensive and is required to expert operator (1,15). Therefore, researchers are studying the performance of the cheaper and natural adsorbents as alternatives. Nowadays several researchers have been conducted on natural absorbents such as Chitosan, Oxihumolite, Fly ashes, the core of peach & olive and also charcoal for removal of the organic and inorganic pollutants (5,8,11). The red mud is an inexpensive adsorbent which is widely used to treat the effluents. It is the most important residue of alumina production process (5,11,17). Bauxite stone has a large amount of aluminum hydroxide (Al_2O_3), so it is used in alumina production in Bayer process. This process is based on sodium hydroxide's reaction with bauxite under pressure and heat and red mud is produced waste of this process (5,21). Red mud is the mixing of various oxides and hydroxides. It is estimated that 1 ton of alumina production can produce 1-2 tons of red mud. Red mud is used in various processes such as constructional and road building materials and ceramic production, but a large amount of red mud is still remaining (5). Therefore the aim of this study was to investigate the red mud performance as a cheap absorbent in Reactive red198 (RR198) removal from an aqueous solution.

2. Materials and Methods

2.1. The characteristics of dye:

The Reactive Red198 is a mono azo dye. The used dye was the analytical grade which were purchased from alvan sabet CO. it's molecular weight is 967.5 mg/mol. it's chemical fomula is $C_{27}H_{18}C_lN_7Na_4O_{15}S_5$. The chemical structure of RR198 is shown in Figure1.

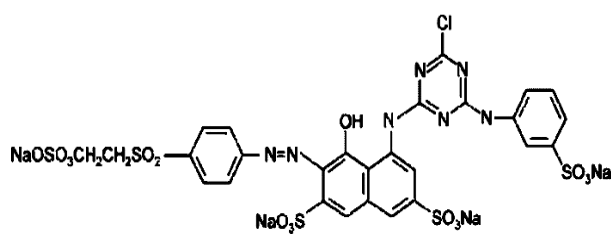


Figure 1. **Chemical structure of RR198 (9, 20)**

2.2. Adsorbent characterization:

The adsorbent is a waste By-product of alumina production process. It contains the oxygen, iron and calcium and etc with various contents. Elemental analysis was performed by electron microscope (SEM) using Oxford instrument (Stereo Scan S360) which is accomplished by Energy dispersive X-ray (EDX). The available surface has been estimated using Belsorp instrument (Data Analysis Software 5.3.3.0 Belsorp).

2.3 Preparation procedure of adsorbent

The first, the red mud was provided from Tabriz Aluminum Co. The each 10gr of red mud was activated by using of 20 ml Nitric acid for 24 h. Then, it was rinsed 3 times by the distilled water. It was dried in 103^{o}C for 6h. After that the red mud was grinded and sieving by using a 100 mesh sieve.

2.4. Analytical methods

The dye concentration was measured at a wavelength corresponding to the maximum absorbance (λ_{max}), 518nm, by a spectrophotometer (DR4000). To adjust pH before any process were used 1N HCL or NaOH solutions. All chemicals were purchased from Merck Co, Germany.

2.5. Batch adsorption experiments

Studies showed that the main effective parameters on adsorption efficiency are solution pH, adsorbent dose, contact time and dye concentration. The dye concentration in textile effluent is 10 to 100 mg/l. Therefore, initial dye concentration selected as 20, 40, 60, 80 and 100 m/l. The effect of pH (2-9), adsorbent dose (2-20g/l) and the contact time (5, 10, 20, 30, 45, 60, 90min) were investigated. The 250 ml E Mayer flask was used to batch experiments. In every experiment, a certain concentration of dye and specific dose of absorbent spilled into the Flask and completely mixed with magnetic stirrer at 3600 rpm for 60 minutes. Then the sample was centrifuged at 3600 rpm for 10 minutes.

3. Results

3.1. Adsorbent characterization

The adsorbent contains the oxygen, iron and calcium and etc with various contents. The Figures 2&3 show that red mud has a non-crystallize structure and has suitable porosity and surface to adsorption. The available surface has been estimated 30 m/gr using Belsorp instrument.

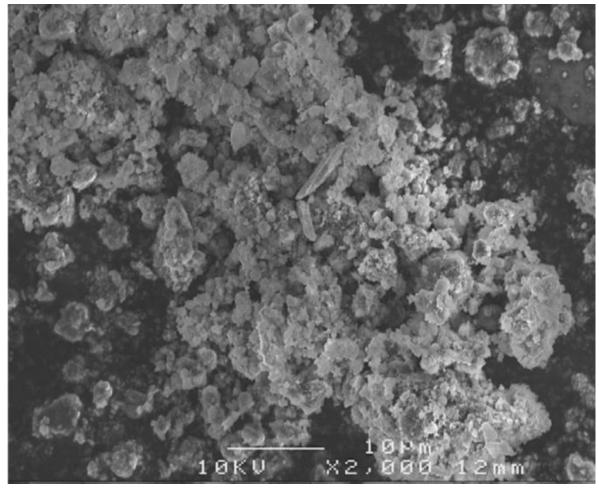


Figure2. SEM image of activated red mud

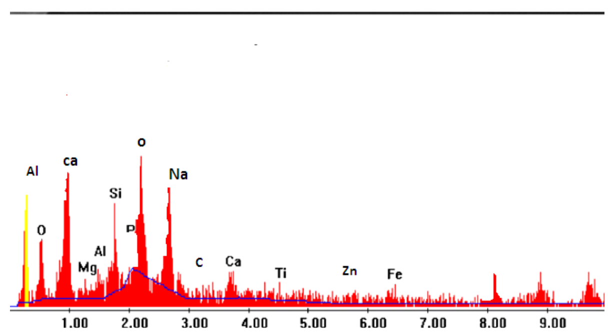


Figure 2. EDX image of red mud

3.2. Effect of pH

In order to investigate the optimum pH of dye removal, experiment was conducted by using 20mg/L dye concentration, adsorbent dose of 16g/l and contact time of 45 in pH between 2 to 12. The results of this experiment are illustrated in Figure3. Which, it shows that the adsorption efficiency increased by increasing of pH up to neutral pH. However, it decreased by increasing of pH more than 8. Therefore, the optimum pH was between 7 to 8.

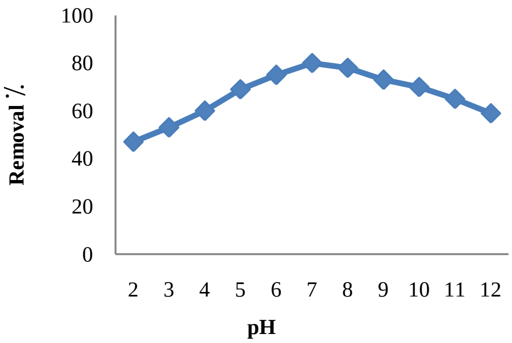


Figure3. Effect of pH on dye removal

3.3. Effect of dye concentration

In order to investigate the effect of dye concentration on dye removal efficiency, different initial concentrations (20, 40, 60, 80 and 100mg/l were tested. This experiment was conducted at pH=7, adsorbent dose=16 g/l and equilibrium time=45 min. The results of this experiment are shown in Figure 4. As shown, the dye removal efficiency reduced by increasing of dye concentration.

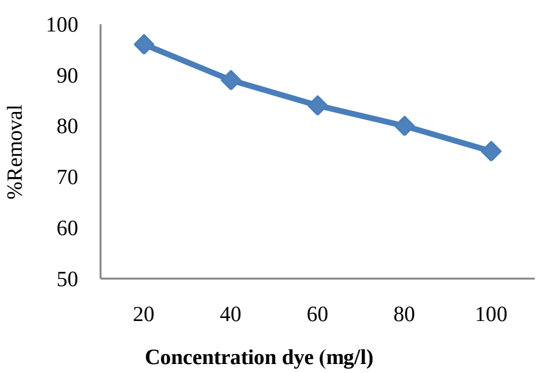


Figure4. The effect of initial dye concentration on removal efficiency

3.4 Effect of Adsorbent dose

Effect of initial adsorbent dose was investigated by varying the adsorbent dose from 2 to 20 mg/l. This experiment was conducted at pH=7, initial dye concentration= 20mg/l and balance time=45 min. Figure5 shows that increasing the adsorbent dose increased the dye removal. However, the dye removal reaches to balance in concentrations more than 16 mg/l.

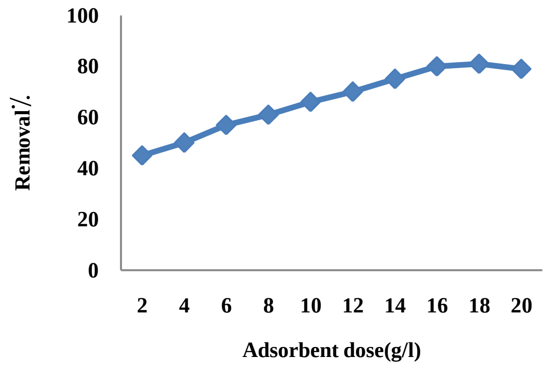


Figure5. The effect of adsorbent dose on removal efficiency

3.5. Effect of contact time

The influence of contact time on dye efficiency by varying of contact times (5 to 90 minutes) in pH=7, initial dye concentration=20gr/l and adsorbent dose=16g/l. the Figure6 indicates that the dye removal efficiency increased up to the contact time of 45 min. However, it reached to balance after this time. Therefore, the optimum contact time was 45 min.

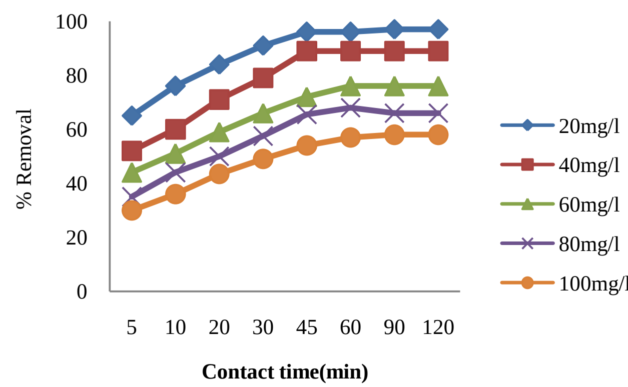


Figure6. The effect of contact time on removal efficiency

3.6. Determination of Adsorption isotherms

The equilibrium experiments of adsorption process will occur after determination of equilibrium time in order to evaluate the effect of adsorbent mass on dye removal to obtain the adsorption isotherms. The obtained data from equilibrium experiments is known as adsorption isotherms (19). The data is basic data which is used to design of adsorption system.

[DOI: 10.18869/acadpub.jhs.1.1.36]

The classical adsorption models including Langmuir, Freundlich, and Tekmin were used. These models will determine the equilibrium relationship between adsorbent and solution. Isotherms equations are shown in table 1 and results of these equations are shown in Figure 7.

Table 1. The equations of isotherms

Model	equation
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} C_e$
Freundlich	$\log q_e = \log k + \frac{1}{n} \log C_e$
Tekmin	$q_e = B_1 \ln(K_1) + B_1 \ln(C_e)$

The adsorption synthetic, adsorption isotherms and adsorption capacity were determined base on the results of batch adsorption experiments. The following equation was used to determine the adsorption capacity:

$$q_e = \frac{(C_0 - C_e)V}{M}$$

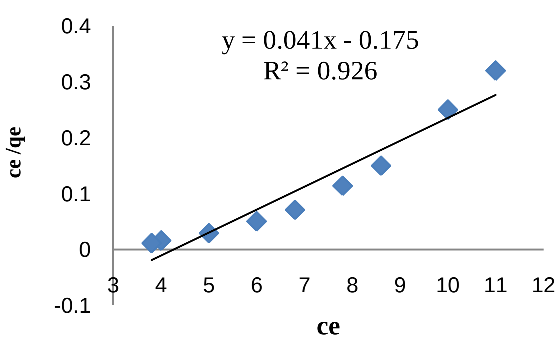
Where, q_e= adsorption capacity (mg/ gr adsorbent)

C_0= initial dye concentration (mg/l)

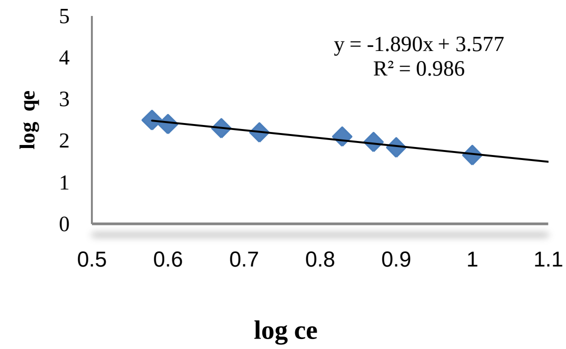
C_e= dye concentration in t time (mg/l)

M= adsorbent mass (gr)

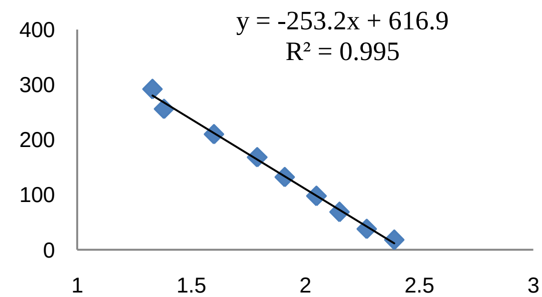
V= sample volume (l)



(a)



(b)



(c)

Figure7. The isotherm's models (a: Langmuir b: Freundlich c: Tekmin)

4. Discussion

4.1. Adsorbent characterization

The results of this study indicated that the main components of red mud were calcium and iron compounds which is agreed with other studies (5, 11). The effective surface of red mud for adsorption was 28 m^2/gr which is suitable and consistent to results of Samarghandi's study (32 m^2/gr). However, it is not agreed with Liu's study (14-20 m^2/gr). Red mud consists with many residue products from bauxite such as Goethite (a-FeOOH) and boehmite (c- AlOOH) which acts as agent groups Ractive dyes are one of azo dyes which has (N=N) band and the decolonization is occurred by breaking of the bands by released electron of red mud which it is consistent with other study (25).

4.2. Effect of pH

pH plays an important role in all process and adsorption capacity. It can influence on various aspects of adsorption including adsorbent surface charge, the degree of ionization, separation of functional groups on the adsorbent active sites and solution chemistry. Many researchers reported that pH plays a main role in electrostatic force between adsorbent and studied dye. In this study the maximum dye removal was obtained in neutral pH which is similar to Moussavi's study on dye removal by sludge (1). However, these findings were not in accordance with previous studies (3,26).

4.3. Effect of dye concentration

As shown Figure 4, the dye removal efficiencies increased when its concentration increased. The removal efficiency increased probably due to increased contact of adsorbate with available sites of adsorbent. In other words, the adsorbent sites decreases on the adsorbent. Therefore, when the initial dye concentration increases, the adsorbent sites filled earlier and the dye removal efficiency decreases. The result of present study is consistent with other studies such as Shokohi and et al, also Ghaneian research that was on dye removal by egg shell (3, 5); and the Mahvi's findings on dye removal by activated carbon (20). The concentration of dye in the treated sample was reduced, when the initial concentrations of the dye increased. Because the repulsion force increased by increasing the initial dye concentration and it could cause that the dye molecules repelled each other and the removal efficiency reduced (3).

4.4. Effect of adsorbent dose

As shown Figure5, the dye removal rate was increased with increasing of adsorbent dose up to reach to equilibrium in high doses. This finding is similar to Saghi's finding that was about the dye removal by biosorption and the study of Gok (16, 27). Although the dye removal increased by increasing of adsorbent dose; however the q_e decreased which it agreed with previous studies (8-10).

4.5. Effect of contact time

Fig.6 illustrates the effect of contact time on dye adsorption. It can be seen that the dye removal or adsorption rate was occurred at the initial stage of the contact (up to 30min), but it gradually slowed down until the equilibrium time (45-50min). The fast adsorption at the initial stage can be attributed to the fact that a large number of surface sites are available for adsorption. In other words, this could be due to filling of initial pore of adsorbent surface by dye. The present finding seems to be consistent with those reported by other researchers (11, 28, 29).

4.6. Adsorption isotherms

The results obtained by the adsorption of dye were analyzed by the well- known models of Langmuir, Freundlich and Tekmin. The results showed that RR198 dye on red mud fitted according to Tekmin isotherm model (R^2=0.995). Furthermore it agreed with Freundlich isotherm (R^2=0.986) that better than Langmuir (R2=0.926). The findings of the current study are consistent with studies of Samarghandi and Saghi (4, 27). However, these results are not similar to Asilian's study which follows Langmuir isotherm (1). According to the results red mud which is a waste product in aluminum industrial production can be an effective adsorbent to RR198 removal from textile effluent. The various parameter including the contact time, adsorbent dose, pH, initial dye concentration is affected on dye removal efficiency. The current adsorbent can remove the RR198 dye from aqueous solutions more than 90%. The Tekmin and Freundlich isotherm models fit with these results and could well describe the adsorption of these dyes onto red mud.

Acknowledgements

The authors would like to express their thanks to the laboratory staff of the Department of Environmental Health Engineering, Faculty of Health, for their collaboration and also to student research committee of Mazandaran University of Medical Sciences for the financial support of this study.

References

1.Asilian H, Moussavi GR, Mahmoudi M. Adsorption of Reactive Red 198 Azo Dye fromAqueous Solution onto the Waste Coagulation Sludge of the Water Treatment Plants. Iranian Journal of Health and Environment,2010;3(1):94-103.(persian)

2.Aos Santos AB, Cervantes FJ, van Lier JB. Review paper on current technologies for decolourisation of textile wastewaters: Perspectives for anaerobic biotechnology. Bioresource Technology,2007;98(12):2369-85.

3.Mahvi A, Heibati B. Removal Efficiency of Azo Dyes from Textile Effluent Using Activated Carbon Made from Walnut Wood and Determination of Isotherms of Acid Red18. Public Ardabil,2009;1(3):7-15.(persian)

4.Samarghandi MR, NooriSepehr M, Zarrabi M, Norouzi M, Amraie F. Mechanism and Removal Efficiency of C.I. Acid Black 1 by Pumice Stone Adsorbent. Iranian Journal of Health and Environment,2011;3(4):399-410.(persian)

5.Shokohi R, Jafari Z. Removal dye Acid Blue 113 from aqueous environment by adsorption on Activated red mud. medical kordestan,2011;16:55-65.(persian)

6.Ghaneian MT, Ehrampoush MH, Dehvary M, Jamshidi B, Amrollahi M. A Survey of the Efficacy of Cuttle Fish Bone Powder in the Removal of Reactive Red 198 dye from Aqueous Solution. Tolooe Behdasht,2011;10(3):127-38.(persian)

7.Nateghi R, Bonyadinejad GR, Amin MM. Nickel oxide nanoparticles application as an efficient adsorbent for dye removal from synthetic wastewater treatment. Health Systems Research, 2009; 6:1015-21.(persian)

8.Ghanizadeh G, Asgari G. Removal of Methylene Blue Dye from Synthetic Wastewater with Bone Char. Iranian Journal of Health and Environment,2009;2(2):102-12.(persian)

9.Ghaneian M, Ehrampoush M, Ganizadeh G, Shahi MA, Momtaz M. Application of Ozonation on the removal of Reactive Red 198 dye at alkaline Condition. Tolooe behdasht,2010;9(2):11-21.(persian)

10.Naddafi K, Nodehi RN, Jahangiri rad M. Removal of Reactive Blue 29 Dye fromWater by Single-Wall Carbon Nanotubes. Iranian Journal of Health and Environment,2011;3(4):359-68.(persian)

11.Jafari SJ, Shokouhi R, Zadeh EH, Taghavi M, Arezoumandi R, Ahadi H. Removal of Reactive Black 5 (RB5) dye from aqueous solution by using of adsorption onto activated red mud: kinetic and equilibrium study. Jundishapur Health Sciences,2012;4(1):57-67.(persian)

12.Yazdanbakhsh AR, Mohammadi AS, Sardar M, Mohammadi H, Zarabi M. Investigation of Iron Powder, Hydrogen Peroxide and Iron Hydrogen Peroxide for Removal of Acid Yellow Powder 36 Dye from Aqueous Solutions. Iranian Journal of Health and Environment,2010;2(4):295-302.(persian)

13.Ghaneian MT, Ehrampoush MH, Ghanizadeh G, Dehvary M, Abootoraby M, Jasemizad T. Application of Solar Irradiation / K2 S2 O8 Photochemical Oxidation Process for the Removal of Reactive Blue 19 Dye fromAqueous Solutions. Iranian Journal of Health and Environment,2010;3(2):165-75.(persian).

14.Rahmani AR, Samarghandi MR. Electrocoagulation Treatment of Color Solution Containing Colored Index Eriochrome Black T. Water and wastewater,2009(1):52-9.(persian)

15.Toor M, Jin B. Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chemical Engineering, 2011(187):79-88.

16.Gok o, Ozcan AS, Ozcan A. Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite. Applied Surface Science,2010(256):5439-43.

17.Shokohi R, Samarghandi MR, Pourfarzi F, Siboni MS, vahedi H. Removal of Reactive Black 5 (RB5) Dye fromAquatic Solution by Using of Adsorption onto Synthesized Sodium Alginate Magnetic Beads. Iranian Journal of Health and Environment,2011;4(1):1-10.(persian)

18.Shokouhi R, Hosseinzadeh E, Zare M, Torabi E. Sodium Alginate Magnetic Beads for Removal of Acid Cyanine 5R from aqueous solution. Hormozgan Medical Journal,2011;1(2):101-11.(persian)

19.Hadi M, Samarghandi MR, Azizian S, Samadi MT, Shokoohi R, Rahmani A. Using Thomas Model to Evaluate Dye Removal from Aqueous Solutions in Fixed-bed Columns of Activated Carbon.Journal of Water and wastewater,2011(1):23-34.(persian)

20.Ghaneian M, Ehrampoush MH, Ghanizadeh G, Momtaz M. Study of Eggshell Performance as a Natural Sorbent for the Removal of Reactive Red 198 Dye from Aqueous Solution. Tolooe Behdasht,2011;10(1):70-81.(persian)

21.Claudia B, Carlo C, Paolo M, Valentina P, Leonardo T. Reuse of a treated red mud bauxite waste: Studies on environmental compatibility. Journal of Hazardous Materials B117,2005:55-63.

22.Weiwei H, Shaobin W, Zhonghua Z, Li L, Xiangdong Y, Victor R, et al. Phosphate removal from wastewater using red mud. Journal of Hazardous Materials,2008;158: 35–42.

23.Liu Y, Naidu R, Ming H. Red mud as an amendment for pollutants in solid and liquid phases. Geoderma,2011;163:1-12.

24.Wang S, Ang HM, Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes. Chemosphere,2008;72(11):1621-35.

25.Satapanajaru T, Chompuchan C, Suntornchot P. Enhancing decolorization of Reactive Black 5 and Reactive Red 198 during nano zerovalent iron treatment. Desalination,2011;266:218-30.

26.Wang S, Boyjoo Y, Choueib A, Zhu ZH. Removal of dyes from aqueous solution using fly ash and red mud. Water Research,2005;39:129-38.

27.Saghi M, Allahabadi A, Sani A, Vazeiri T, Hekmatshoar R. Removal of Reactive Orange 3 dye from aqueous solution by biosorption technology. Journal of Sabzevar University of Medical Sciences,2012;19(2):127-35.(persian)

28.Yunus C, Ali TB, Gulsin Arslan, Mustafa Ersoz, Sait Gezgin. Removal of boron from aqueous solution by using neutralized red mu. Journal of Hazardous Materials,2007;1:412-417.

29.Yousefi Z, Mohseni A, Mohamadpour RA, Maleki A, Gharemani A. Removal performance of the GAC-SBR hybrid system to removal Reactive Yellow 3 and Disperse Yellow 3 dye of wastewater. Mazandaran University of Medical Sciences,2011;21(1):41-9.(persian)