Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2018, 5(12):84-89**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Adsorption kinetic studies for removal of Reactive Red 120 using Bentonite Clay

Davoud Balarak[1*], Mohadeseh Dashtizadeh[2], Atefeh Namvar[2]

[1]Department of Environmental Health, Health Promotion Research Center, School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran
[2]Department of Environmental Health, Student Research Committee, Zahedan University of Medical Sciences, Zahedan, Iran
*Corresponding Author: dbalarak2@gmail.com

Abstract The studies of the kinetics and isotherms adsorption of the Reactive Red 120 (RR120) onto bentonite clay were explored in a batch study in a laboratory. The mechanisms and characteristic parameters of the adsorption process were analyzed using five parameter isotherm models which revealed the following order (based on the coefficient of determination): Langmuir (0.998)> Freundlich (0.964) and Halsey (0.931)>Harkin-Jura (0.912)> Temkin (0.894)>Dubinin–Radushkevich (0.891). Kinetic parameters were tested using the pseudo-first order, pseudo-second order, and intraparticle and film diffusion models. The presence of film diffusion mechanism was found to play a major role in the adsorption process. The results indicated the potential of bentonite as a low-cost and eco-friendly adsorbent for the removal of dye ions from aqua media.

Keywords Adsorption, Reactive Red 120, Thermodynamics, Kinetics

Introduction

Color is an important part of the human world. A few decades earlier, the selection, application and use of dyes were not seriously considered regarding their environmental impacts; even the chemical compositions of dyes were unknown [1-3]. Dyes are widely used in the industries of dyestuffs, paper, plastics, textile, leather, cosmetics and food, which generate appreciable amount of wastewater [4]. The textile industry is the largest consumer of dyestuffs [5]. It has been reported that there is a large amount of residual dyes remaining in wastewater in the dyeing process, especially for reactive dyes [6, 7].

It is estimated that an average of 30% of applied reactive dyes end up in effluent in the alkaline dye bath because their hydrolyzed form has no affinity for textile fabrics [8, 9]. Reactive dyes cause major problems with respect to color. Dyes have been considered harmful organic compounds for environment, and most of the residual dyes are resistant to biodegradation processes and toxic, which caused water unfit [10-12].

Dyes can have adverse and toxic effects to humans, such as skin irritation and cancer. Untreated dyes cause biological and chemical changes in aquatic system by reducing light penetration, thereby affecting photosynthetic activities [13, 14]. Therefore, there is a need to treat the effluent before discharge and comply with the environmental regulations [15].

Several methods involved biological, physical, chemical and associated technologies have been reported for dyes removal [16]. The adsorption process is one of the most effective methods for the removal of dyes from wastewater [17]. The process of adsorption has an advantage over the other methods due to its cost-effectiveness and sludge free clean operation [18, 19]. Adsorbents that are commercially available, e.g., commercially activated carbon, are very effective but expensive. Therefore, research is currently focused on adsorbents that remove dyes from wastewater at a low cost [20, 21].

In the last decade, bentonite clay has been successfully applied for the adsorption of dyes [22, 23]. Bentonite clay has been considered as a potential adsorbent for the removal of pollutants from water [23, 24]. In the

present research study, the adsorption capacity of bentonite clay was investigated for removing Reactive Red 120 dye from an aqueous solution.

Materials and Methods

Adsorbate: One commercial dye, namely, Reactive Red 120 (RR120) (Figure 1), having a Number 61951-82-4; EC Number 263-351-0, molecular weight of 1469.98 g, Chemical Formula = $C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$ and maximum wavelength λ_{max} = 660 nm (Sigma-Aldrich), was selected as the adsorbate.

Adsorption Equilibrium Studies: Various dye solutions with different initial concentration, in the range of 20-200 mg/L, were prepared by diluting a stock dye solution. A sufficient amount of bentonite, 1.5 g/L, was brought into contact with known volumes (100 mL) of dye solutions. The bottles were sealed and agitated in a thermostatic shaker at a desired temperature, normally at 30 °C unless otherwise stated, for 1 h, which was found to be sufficient to reach equilibrium. After equilibrium was reached, each sample withdrawn was filtrated through a 0.45 μm membrane filter to remove any particles. The residual dye concentration of RR120 was then determined. The amount of MB adsorbed at equilibrium, q_e (mg/g) was obtained as follows [25, 26]:

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

Where C_O (mg/L) is the initial RR120 concentration, C_e (mg L) the RR120 concentration at equilibrium, V (L) the volume of the solution, and M (g) is the mass of the adsorbent.

Adsorption Kinetics: Adsorption kinetics study was carried out in order to test the relationship between contact time and RR120 dye uptake. Dye solutions (1000 mL) with different initial concentrations were prepared and maintained at 30 °C, prior to the experiment. Bentonite was then added into the dye solution while being constantly stirred. Samples were withdrawn at different time intervals.

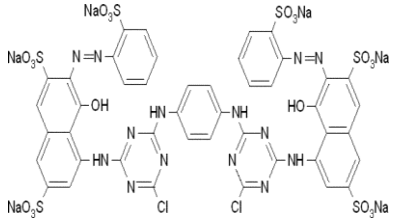

Figure 1: Molecular structure of RR120

Results and Discussion

Effect of Temperature: The effect of temperature on adsorption capacity was investigated by measuring the adsorption isotherms at various temperatures, namely, 10, 20, 30, 40 and 50 °C. The corresponding isotherm parameters obtained by fitting the experimental data are listed in Table 1. As can be seen with the increase of temperature from 10 to 30 °C, the adsorption capacity increases slightly from 128.5 to 144.2 mg/g. This observation reveals that the adsorption process is slightly endothermic. This may be caused by the increased tendency of adsorbate ions to be adsorbed from the solution into the dye clay interface. The adsorption capacity does not change as much when the temperature increases from 30 to 50 °C, suggesting the adsorption behavior is insensitive to the changes of temperature in this range. The overall temperature influence is weak for the adsorption of RR120, which probably indicates the low activation energy in the predominantly ionic system [27, 28].

Table 1: Langmuir Adsorption Isotherm Constants

Temperature (°C)	q_{max}	K	R^2
10	128.5	1.98	0.994
20	137.4	2.48	0. 992
30	144.2	2.74	0.996
40	139.7	2.65	0.998
50	138.8	2.59	0.997

Adsorption Kinetics

Adsorption kinetics governs the rate of reaction, which determines the residence time and is one of the important characteristics defining the efficiency of an adsorbent. The kinetics of dye sorption can be controlled by several independent processes which could act in series or in parallel, such as bulk diffusion, film diffusion,

chemisorptions and intraparticle diffusion [27, 28]. In the quest to investigate the mechanism of adsorption of RR120 ions unto bentonite and the potential rate controlling steps. The pseudo first order, pseudo second order, intraparticle and liquid film diffusion kinetic models were applied to the experimental data and their kinetic parameters are presented in Table 2.

The Lagergren pseudo first order model considers that the rate of occupation of adsorption sites is proportional to the number of the unoccupied sites and the linear form of this model equation is given as [29, 30]:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1}{2.303}t$$

Where K_1 is the Lagergren rate constant of adsorption (min^{-1}), q_e and q_t are the amounts of RR120 ions adsorbed (mg/g) at equilibrium and time t respectively. The slope and intercept of the plots of log (q_e-q_t) versus t were used to determine the pseudo first order rate constant K_1 and the equilibrium adsorption capacity q_e.

The pseudo second order model is based on the assumption that adsorption follows a second order mechanism. So the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The linear form of the pseudo second order equation is expressed as [4, 31]:

$$\frac{t}{q_t} = \frac{1}{k_2 q e^2} + \frac{t}{qe}$$

Where K_2 (g/mg.min) is the equilibrium constant of pseudo second order adsorption. The initial sorption rate (h) can be calculated from the equation [9]:

$$h = K_2 qe^2$$

The applicability of the pseudo second order model was tested by a linear plot of t/q_t versus t with a slope of $1/q_e$, the value of K_2 was calculated from the intercept of the plot (Fig 2).

The diffusion mechanism was determined by the intraparticle diffusion model. This is due to the fact that dye ions are transported from the aqueous phase to the surface of the adsorbent and subsequently they can diffuse into the interior of the particles if they are porous. The intraparticle diffusion equation is given as [32, 33]:

$$q_t = K_d t^{0.5} + C$$

Where C is the intercept and K_d (mg/g. $min^{1/2}$) is the intra-particle diffusion rate constant. Intraparticle diffusion is the sole rate determining step if the plot of q_t versus $t^{1/2}$ is linear and passes through the origin (C=0). Values of q_t and C were obtained from the slope and intercept of the plot and are shown in Table 2.

When the transport of the adsorbate from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the liquid film diffusion model can be applied [34]:

$$\text{Ln } (1\text{-}F) = K_f t$$

Where F is the fractional attainment of equilibrium ($F=q_t/q_e$) and K_f is the adsorption rate constant (mg/g.min). A linear plot of Ln (1-F) versus t with zero intercept would suggest that the kinetics of adsorption is controlled by diffusion through the liquid film surrounding the solid adsorbent. The constant K_f was obtained from the slope of the plot. A comparison of the correlation coefficient results (Table 2) showed that both the pseudo-first order and pseudo second order models gave good fits to the experimental data. However, the R^2 values presented by the Pseudo second order model were better than that of the Pseudo- first order model, which indicates greater conformity of the adsorption process to the former. However, the calculated q_e values ($q_{e\ cal}$) obtained from both models showed a great discrepancy with the experimental qe value ($q_{e\ exp}$) for the sorption of RR120 ions.

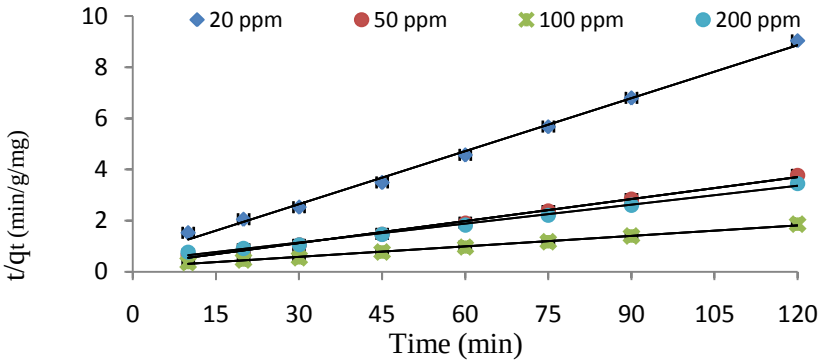

Figure 2: Pseudo- second-order kinetics of RR120 dye adsorption onto bentonite

Table 3: The results of kinetic model studies related to the RR120 adsorption onto bentonite

MB Concentration (mg/L)	$(q_e)_{exp}$	Liquid film Diffusion	Intraparticle diffusion model			Pseudo-first order			Pseudo-second order		
		R^2	K_d	C	R^2	$(q_e)_{cal}$	K	R^2	$(q_e)_{cal}$	K	R^2
20	13.21	0.911	0.681	4.172	0.811	4.172	0.954	0.925	12.79	0.0027	0.998
50	35.45	0.894	1.352	6.454	0.825	14.25	0.714	0.927	33.84	0.0049	0.997
100	66.38	0.885	2.418	8.591	0.798	31.76	0.649	0.938	61.52	0.0081	0.996
200	112.8	0.902	3.748	11.64	0.801	74.39	0.511	0.951	110.2	0.0095	0.999

Conclusion

A low-cost and easily obtainable bentonite was utilized for the removal of RR120 dye from a binary system. The bentonite was used without chemical modification in order to keep the process cost low. The scatchard plot analysis revealed the homogeneous nature of bentonite confirmed by the Langmuir isotherm which provided the best fit to the experimental data.

Acknowledgement

The authors are grateful from Student research committee of Zahedan University of Medical Sciences because of supporting of this research.

References

[1]. Jin X, Jiang M, Shan X, Pei Z, Chen Z. Adsorption of methylene blue and orange II onto unmodified and surfactant-modified Zeolite. J. Colloid Interf. Sci. 2008; 328; 243–247.

[2]. Gök O, Özcan AS, Özcan A. Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite, Appl. Surf. Sci. 2010; 256; 5439–5443.

[3]. Balarak D, Mahdavi Y, Kord Mostafapour F, Azarpira H. Using of Lemna Minor for adsorption of Acid Green 3 dye (AG3) from aqueous solution: Isotherm and kinetic study . Journal of Chemistry and Materials Research. 2016; 5 (5), 92-98.

[4]. Garg VK, Gupta R, Yadav AB, Kumar R. Dye removal from aqueous solution by adsorption on treated sawdust. Bioresource Technology.2003; 89(2); 121-124.

[5]. Balarak D, Mahdavi Y, Bazrafshan E, Mahvi AH. Kinetic, isotherms and thermodynamic modeling for adsorption of acid blue 92 from aqueous solution by modified azolla filiculoides. Fresenius Environmental Bulletin.2016; 25(5); 1321-30.

[6]. Garg VK, Rakesh Kumar R, Gupta R. Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of Prosopis cineraria. Dyes and Pigments.2004; 62(1); 1-10.

[7]. Kumar PS, Ramalingam S, Senthamarai C, Niranjanaa M. Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions.Desalination:2010: 261;52–60.

[8]. Kale RD, Kane BP. Colour removal using nanoparticles. Textiles Clothing Sustain. 2016; 2 (1):1-7

[9]. Balarak D, Mahdavi Y. Experimental and Kinetic Studies on Acid Red 88 Dye (AR88) Adsorption by Azolla filiculoides. Biochem Physiol. 2016;5:190-198.7

[10]. Nazari Sh, Yari AR, Mahmodian MH, Tanhaye Reshvanloo M, Alizadeh Matboo S, Majidi G. Application of H_2O_2 and H_2O2/Fe^0 in removal of Acid Red 18 dye from aqueous solutions. Arch Hyg Sci. 2013; 2(3); 110-114.

[11]. Ahmet Z, Gulbeyi D. Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon. J Hazard Mater. 2007; 146(1):262-9.

[12]. Pavan FA, Mazzocato AC, Gushikem Y. Removal of methylene blue dye from aqueous solution by adsorption using yellow passion fruit peel as adsorbent. Bioresour Technol 2008; 99(8): 3162-65 .

[13]. Sobhanardakani S, Zandipak R. Removal of Anionic Dyes (Direct Blue 106 and Acid Green 25) from Aqueous Solutions Using Oxidized Multi-Walled Carbon Nanotubes. Iranian J Health Sci 2015; 3(3):48-57.
[14]. Zazouli MA, Yousefi Z, Yazdani-Charati J ,Mahdavi Y. Application of Azolla Filiculoides Biomass in Acid Black 1 Adsorption from Aqueous Solution .Iranian J Health Sci 2014; 2(3):24-32.
[15]. Jafari Mansoorian H, Jonidi Jafari A, Yari AR , Mahvi AH, Alizadeh M, Sahebian H. Application of Acaciatortilis Shuck as of Low-cost Adsorbent to Removal of Azo Dyes Reactive Red 198 and Blue 19 from Aqueous Solution. Arch Hyg Sci 2014; 3(1):1-11.
[16]. Dehghani MH, Norozi Z, Nikfar E, Vosoghi M, Oskoei V. Investigation of Nano Alumina Efficiency for Removal of Acid Red 18 Dye from Aqueous Solutions .Alborz Univ Med J. 2013; 2(3):167-174.
[17]. Chiou CS, Chang CY, Shie JL. Decoloration of reactive black 5 in aqueous solution by electro-fenton reaction. J Environ Eng Manag J 2006; 16(4):243-248
[18]. Yagub MT, Sen TK, Afroze S, Ang HM. Dye and its removal from aqueous solution by adsorption: A review. Adv Colloid Interface Sci 2014; 209:172-184.
[19]. Blackburn RS. Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment. Environ Sci Technol 2004; 38(18):4905–09.
[20]. Crini G, Peindy HN, Gimbert F, Robert C. Removal of C.I. Basic Green 4 (malachite green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies. Sep Purif Technol. 2007; 53(1):97–110.
[21]. Mahmoodi NM, Abdi J, Bastani D. Direct dyes removal using modified magnetic ferrite nanoparticle. J Environ Health Sci Eng 2014; 12:96-102.
[22]. Tahir H, Hammed U, Sultan M, Jahanzeb Q. Batch adsorption technique for the removal of malachite green and fast green dyes by using montmorillonite clay as adsorbent. Afr. J. Biotechnol . 2010; 9; 8206-214.
[23]. Tahir SS, Rauf, N. Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. Chemosphere 2006, 63, 1842–1848.
[24]. Akpomie KG, Dawodu FA. Potential of a low-cost bentonite for heavy metal abstraction from binary component system, Beni-Suef Uni J Basic Applied Sci. 2015; 4(1), 1-13.
[25]. Mohammadi AS, Sardar M, Mohammadi A, Azimi F, Nurieh N. Equilibrium and Kinetic Studies on the Adsorption of Acid Yellow 36 Dye by Pinecone. Arch Hyg Sci. 2013; 2(4):158-164.
[26]. Asadi F, Dargahi A, Almasi A, Moghofe E. Red Reactive 2 Dye Removal from Aqueous Solutions by Pumice as a Low-Cost and Available Adsorbent. Arch Hyg Sci. 2016; 5(3):145-52.
[27]. Balarak D, Mahdavi Y, Ghorzin F, Sadeghi S .Biosorption of acid blue 113 dyes using dried Lemna minor biomass. Sci J Environ Sci. 2015; 4(7):152-158.
[28]. Joghatayi A, Mahdavi Y, Balarak D. Biosorption of Reactive blue 59 dyes using dried Azolla filiculoides biomass. Scholars J Eng Technol 2015; 3(3B):311-318.
[29]. Peng X, Huang D, Odoom-Wubah T, Fu D, Huang J ,Qin Q. Adsorption of anionic and cationic dyes on ferromagnetic ordered mesoporous carbon from aqueous solution. J Colloid Interface Sci 2014; 430:272-282.
[30]. Kargozoglu B, Tasdemir M, Demirbas E, Kobya M. The adsorption of basic dye from aqueous solution onto sepiolite, fly ash and apricot shell activated carbon; Kinetic and equilibrium studies. J Hazard Mater. 2007; 17(147):297-306.
[31]. Parmer M, Thakur LS. Heavy metal Cu, Ni and Zn: Toxicity, health hazards and their removal techniques by low cost adsorbents: A short overview. Int. J. Plant Anim. Environ. Sci. 2013, 3, 143-157.
[32]. Yogesh Kumar K, Muralidhara HB, Arthoba Nayaka Y. Low- Cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution. Powder Technol 2013; 246:125-136.

[33]. Balarak D, Bazrafshan E, Kord Mostafapour F. Equilibrium, kinetic studies on the adsorption of acid green 3 (Ag3) dye onto Azolla filiculoides as adsorbent. American Chemical Science Journal. 2016; 11(1), 1-10.

[34]. Anirudhan TS, Ramachandran M. Surfactant-modified bentonite as adsorbent for the removal of humic acid from wastewaters. Appl Clay Sci. 2007; 35: 276-281.