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Kinetic and Isotherm Studies of the Removal of Zn^{2+} Ions from Aqueous Solution by Modified Poly(ethylene terephthalate) Fibers

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Modified poly(ethylene terephthalate) fibers were synthesized by the mixture of methyl methacrylate-acrylic acid in the presence of benzoyl peroxide as a radicalic initiator. The prepared copolymer was used as a new adsorbent for the removal of Zn^{2+} ions from aqueous solution. The isotherm and the kinetics data were fitted with (Langmuir, Freundlich, Temkin-Pyozhev) and (Lagergren pseudo-first-order, Ho's pseudo-second-order, intra-particle-diffusion) models, respectively. R^2 values showed that the adsorption data were fitted by Freundlich isotherm and pseudo-second-order kinetics, as well. Thermodynamic parameters such as enthalpy (ΔHº), entropy (ΔSº) and Gibbs free energy (ΔGº) were determined, (0.0053 kJ/mol), (0.0085 kJ/mol K) and (-2.546, -2.675 and -2.803 kJ/mol), respectively. These results showed that the spontaneous and feasibility nature of the adsorption process. On the other hand, the overall activation energy (E_a) was calculated 1.895 kJ/mol.

Key Words: Kinetic, Isotherm, Poly(ethylene terephthalate), Fibers.

INTRODUCTION

Heavy metals are very toxic and injurious for human health. Zinc toxicity from plenty englut is less common, although, it may cause damage to various systems in the human body[1,2]. Therefore, the removal of excess toxic heavy metals from water and wastewater is urgent to protect human and environmental health. For this aim, various physicochemical and biological methods have been investigated for removal of toxic metallic elements from aqueous solution[3]. Adsorption is an urgent method for the removal of solutes from wastewaters. Hence, if the adsorption system is designed carefully, it will provide a high quality treated effluent. The grafted fibers with different monomers can be used for the adsorption of heavy metals. In our previous works, the grafted poly(ethylene terephthalate) fibers have been synthesized by the mixture methyl methacrylate-acrylic acid[4,5]. The present study reports the adsorption kinetics and thermodynamics of the methyl methacrylate/acrylic acid-g-poly(ethylene terephthalate) for the adsorption of Zn^{2+} from aqueous solution.

EXPERIMENTAL

Poly(ethylene terephthalate) (PET) fibers (stretch ratio 2, 30 filament, 110 dTex) were received from Amir Kabir University and Technology (Tehran). Methyl methacrylate (MMA) and acrylic acid (AA) were purchased by BDH Co. of England and after purification were used in all experiments. Bz_2O_2 after recrystallization was used in grafting procedure[4,5]. All ingredients, solvents and reagents were analytical grade and supplied by Merck and doubly distilled water used in experiments.

Grafting procedure: The fiber specimen was placed in a 100 mL Pyrex tube. The polymerization tube comprising monomers and 45 mL doubly distilled water was placed in water bath and kept there for 2 min and then 5 mL acetone appropriate amount of benzoyl peroxide was added. The grafted fibers were taken at different time (5-60 min), in order to provide different graft yield. After desirable time, washed with water at room temperature for 24 h, then soxhlet extracted with toluene for 8 h. Finally the samples were dried until they maintained a constant weight. The percentage of graft yields were computed from the difference between the weights of the ungrafted and grafted samples gravimetrically[4,5].

Adsorption studies: Adsorption experiments were accomplished using 0.1 g of the grafted fibers with 20 mL Zn^{2+} ions in a thermallized water bath at the fixed agitation speed (150 rpm) and pH = 6.5. After desirable time, the adsorption capacity of methyl methacrylate/acrylic acid-g-poly(ethylene terephthalate) in the solution, after filtration and measuring by using an atomic absorption spectroscopy with an air acetylene flame with hollow cathode lamp, according to the following equation has been fulfilled:

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

where C_0 and C are the initial and equilibrium concentrations of Zn^{2+} (mg/L), respectively. q is the amount of the adsorbed Zn^{2+} at the specified time (mg/g). m is the adsorbent amount (g) and V is the aliquots volume (L).

RESULTS AND DISCUSSION

Adsorption isotherm: The experimental data were determined according to the commonly used adsorption isotherms, like Langmuir, Freundlich and Temkin-Pyozhev. Langmuir isotherm is based on the hypothesis that point of valence exists on the surface of the adsorbent and that each of these sites is authoritative of one molecule. The Langmuir equation is given as follows[6]:

$$\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{C_e}{q_m}$$

C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g). q_m and b are Langmuir constants depend to adsorption efficiency and energy of adsorption. The linear plots of C_e/q_e *versus* C_e identify the applicability of the Langmuir isotherms. The values of qm and b can be determined from slope and intercepts of the curve Fig. 1.

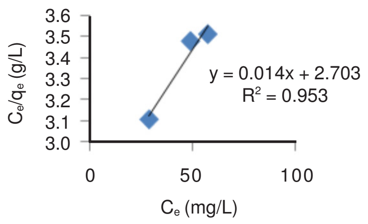

Fig. 1. Langmuir isotherm (T = 298 K)

The Freundlich isotherm is given by the following equation[7]:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e$$

K_f and n are constants the factors affecting the adsorption capacity and strength adsorption, respectively. The plots of ($\ln q_e$ - $\ln C_e$) and R^2 values in Figs. 2-4 showed that the adsorption of Zn^{2+} onto modified poly(ethylene terephthalate) fibers obey the Freundlich model. These results identify, the surfaces of modified fibers are rough and heterogeneous and can be proficient on multilayer adsorption[8].

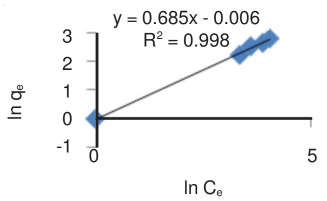

Fig. 2. Freundlich isotherm (T = 298 K)

Temkin-Pyozhev isotherm is a tentative relationship, that denotes an optimum model of experimental data[9,10]. The Temkin-Pyozhev isotherm is commonly written as:

$$q_e = B\ln A + B\ln C_e$$

or
$$q_e = a_t + 2.303 b_t \log C_e$$

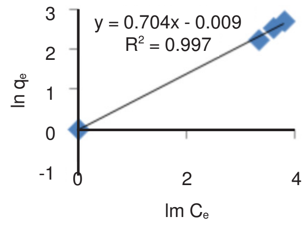

Fig. 3. Freundlich isotherm (T = 313 K)

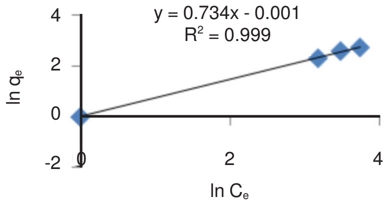

Fig. 4. Freundlich isotherm (T = 328 K)

The values of a_t (mg/g) and b_t (L/mg) can be determined by the curve of adsorption capacity (q_e) *versus* equilibrium concentration (C_e). As shown in Fig. 5, the results did not obey the Temkin-Pyozhev isotherm.

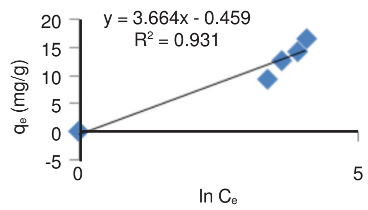

Fig. 5. Temkin-Pyozhev isotherm (T = 298 K)

Adsorption kinetics: Kinetics data have been investigated by the using[11-14]:

Lagergren pseudo-first-order:

$$\ln (q_e - q_t) = \ln q_e - K_1 t$$

Ho's pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{K_2} q_e^2 + \frac{t}{q_e}$$

Intra-particle-diffusion:

$$q = K_d t^{1/2} + I$$

where q_e and q_t denote the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min). K_1 (1/min) and K_2 (g/mg min) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively. I is a constant value of intra-particle-diffusion equation and identify the boundary layer thickness between adsorbate and adsorbent and K_d is the rate constant. In Ho's pseudo-second-order model, initial adsorption rate is equal to $h = K_2 q_e^2$. Kinetics studies were accomplished at the fixed condition of the other variables (T = 298 K, [Zn^{2+}] = 100 (mg/L), grafted fibers = 0.1 g, pH = 6.5, solution volume = 20 mL, shaking rate = 0.0). As shown in Fig. 6-8, the best correlation coefficient observed for pseudo-second-order model and the amount of q_e is in harmony with experimental data. Thereupon, the adsorption process obeys this kinetic model. This fact may be ascribed to a chemical interaction between adsorbate with the functional groups of modified poly(ethylene terephthalate).

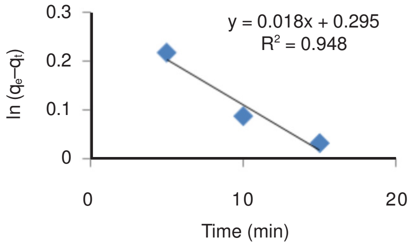

Fig. 6. Pseudo-first order kinetics

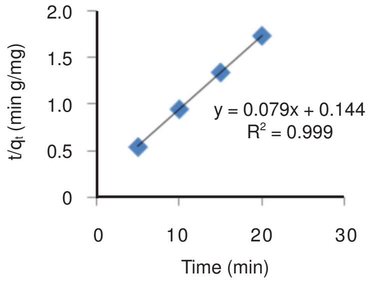

Fig. 7. Pseudo-second order kinetics

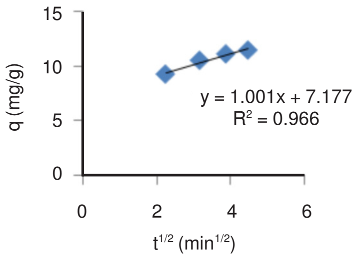

Fig. 8. Intra-particle diffusion kinetics

Thermodynamic studies: The effect of temperature for determination of the thermodynamic parameters was investigated in the range of 298-328 K. These parameters have been calculated according to:

$$\Delta G^{o} = -RT \ln K_d$$

$$\ln K_d = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT}$$

$$K_d = \frac{q_e}{C_e}$$

In above equations, K_d is the equilibrium constant, T is the temperature (K), R is the gas constant. ΔH° and ΔS° are the change of enthalpy and entropy and by the help of Van't Hoff plots have been determined. Results presented in Table-1 and Fig. 9.

TABLE-1
THERMODYNAMIC PARAMETERS FOR REMOVAL OF Zn^{2+} AT DIFFERENT TEMPERATURES

T (K)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)
298			-2.546
313	0.0053	0.0085	-2.675
328			-2.803

The low value of the ΔH° demonstrates the physisorption is much more possible and the process is endothermic[15]. The

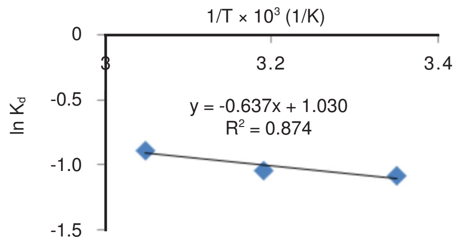

Fig. 9. van,t Hoff plot for thermodynamic

positive value of ΔS° specify increased disorder at the adsorbent-solution interface during the adsorption of Zn^{2+}. Meanwhile, during the adsorption of Zn^{2+} onto poly(ethylene terephthalate) fibers the freedom degrees increase. The negative quantities of ΔG°, show that the adsorption process are thermodynamically favorable and spontaneous. Amounts of ΔG° for physisorption are between -20_0 kJ/mol[16].

Effect of temperature on adsorption: Determination of the activation energy was computed by the Arrhenius equation. From the dependence of ln q *versus* 1/T, the activation energy was determined (1.895 kJ/mol) Fig. 10. The low quantity of E_a emphasize the adsorption process is so easy[8,17]. The desorption activation energy was calculated according to the following equation:

$$E_d = \Delta H + E_a$$

E_d computed 1.900 kJ/mol. This value is negligible and desorption process is so easy.

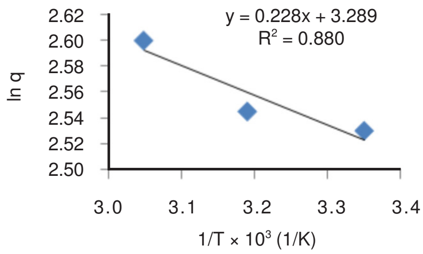

Fig. 10 . Plot of ln q - 1/T

Conclusion

In this study, the positive values of ΔH° and ΔS° showed that the adsorption of Zn^{2+} onto poly(ethylene terephthalate) fiber was endothermic. On the other hand, the results emphasized the adsorption of Zn^{2+} were increased by increasing the temperature. The quantities of ΔG°, ΔH° and E_a proposed the adsorption of Zn^{2+} onto reactive poly(ethylene terephthalate) fibers was physisorption and spontaneous. The best isotherm and kinetic models were Freundlich and pseudo-second-order models, respectively.

REFERENCES

1. C. Lu, H. Chiu and C. Liu, *Ind. Eng. Chem. Res.*, **45**, 2850 (2006).
2. C. Lu and H. Chiu, *Chem. Eng. Sci.*, **61**, 1138 (2006).
3. M.G. da Fonseca, M.M. de Oliveira and L.N.H. Arakaki, *J. Hazard. Mater.*, **B137**, 288 (2006).
4. F. Azizinejad, M. Talu, M. Abdouss and M. Shabani, *Iran Polym. J.*, **14**, 33 (2005).
5. F. Azizinezhad, R. Harutunyan and M. Abdouss, *Asian J. Chem.*, **22**, 7803 (2010).

6. M.K. Sreedhar and T.S. Anirudhan, *Indian J. Environ. Protect*., **8**, 19 (1999).
7. A. Mittal, L. Kurup and J. Mittal, *J. Hazard. Mater*., **146**, 243 (2007).
8. S.L.C. Ferreira, H.M.S. Andade and H.C. de Santos, *J. Colloid Interf. Sci*., **270**, 276 (2004).
9. G. Saswati and U.C. Ghosh, *Water SA*, **31**, 597 (2005).
10. J.A. Otun, I.A. Oke, N.O. Olarinoye, D.B. Adie and C.A. Okuofu, *J. Appl. Sci.*, **6**, 2368 (2006).
11. S. Lagergren, *Handlingar*, **24**, 1 (1898).
12. Y.S. Ho and G. McKay, *Process Biochem.*, **34**, 451 (1999).
13. W.J. Weber Jr. and J.C. Morris, *J. Saint. Eng. Div*., **89**, 31 (1963).
14. N. Kannan and M.M. Sundaram, *Dyes Pigments*, **51**, 25 (2001).
15. D.J. Krishna and G. Bhattacharyya, *Appl. Clay Sci.*, **20**, 295 (2002).
16. M.J. Jaycock and G.D. Parfitt, Chemistry of Interfaces, Ellis Horwood Ltd., Onichester, 12 (1981).
17. M. Arslan, *Fibers Polym*., **11**, 177 (2010).