

Isotherm investigation of the adsorption of cadmium onto modified poly(ethylene terephthalate) fiber

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ABSTRACT

Cadmium is known to be toxic for living organism even if it is present in low levels. This study deals with the use of the reactive poly (ethylene terephthalate) (PET) fibers for the removal of cadmium from aqueous solutions. In this study, PET was grafted with 2-hydroxy propyl methacrylate (2-HPMA) as a monomer in the presence of benzoyl peroxide (Bz_2O_2) as an initiator. Reactive fibers were used as a new adsorbent for the removal of Cd^{2+} ions from aqueous solutions. The effects of pH, contact time, adsorbent dose and adsorbate concentration were studied. The best conditions for removal of Cd^{2+} were determined ($pH = 6.70$, $t=60$ min, adsorbate concentration = 2.50 mg / l and Cd^{2+} concentration = 120mg/L). Adsorption isotherms parameters of Cd^{2+} on grafted PET were studied in batch experiments. The highest correlation coefficient (R^2) explaining adsorption data was observed for the Freundlich isotherm.

Keywords: Adsorption, Graft copolymerization, Isotherm adsorption models and cadmium.

INTRODUCTION

Cadmium is a toxic heavy metal found in the environment [1]. Cadmium increases naturally in the environment through gradual processes such as rock abrasion and soil erosion as well as from singular events such as volcanic eruptions and forest fires. It is also added to the environment by human activities such as the combustion of fossil fuels, the application of phosphate fertilizers, electroplating, metal production, and the manufacture of batteries, screens, and pigment [2-3].

Cadmium is, therefore, could naturally be present everywhere in soil, water, air, and foods. Greenockite, cadmium sulfide (77.6% Cd), is the most important cadmium mineral. Other minerals are cadmium carbonate (61.5% Cd), otavite, and pure cadmium oxide (87.5% Cd). Greenockite (CdS) is nearly always associated with sphalerite (ZnS) [4].

Cadmium has been classified as a human carcinogen and teratogen impacting the lungs, liver, kidneys, and reproductive organs [1- 5]. A well-known, major case of cadmium poisoning resulted in 'Itai-Itai' disease caused by cadmium contamination of the Jintsu River in Japan. The World Health Organization (WHO) has determined 0.003 mg L⁻¹ to be the maximum acceptable concentration of Cd^{2+} in drinking water [6].

Because of the low limit of cadmium pollution acceptable in drinking water, there is significant interest in the development of techniques to remove cadmium from polluted water. Different methods, such as ion exchange,

chemical precipitation, reverse osmosis, and ion adsorption cited for the removal of heavy metals from industrial wastewater have been used. The adsorption method, boasting high efficiency and ease of use, is one of the most widely used methods nominated [7]

Various adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash, and activated carbon have been used for cadmium removal [3,8-9]. Batch procedures were carried out to study the sorption of Cd²⁺ to the sorbents with particular focus on isotherms sorption.

Investigation of the possibility synthetic fibers for filtration of heavy metals has been started from the 1986 [10]. Zhang et al (1994) used of Carboxyl group containing hydrazine-modified polyacrylonitrile (PAN) fiber as adsorbant [11]. Investigation of this modified ion exchange fiber (IEF) revealed that the maximum capacities of the modified PAN fiber for the heavy metal ions (Cu²⁺, Cd²⁺, Zn²⁺, Co²⁺, Pb²⁺, Cr³⁺, Ni²⁺, Hg²⁺) were determined 1.33, 1.30, 1.03, 1.02, 0.98, 0.96, 0.95 and 0.63 mmol/g, respectively. The product could be reused after regeneration with diluted nitric acid. Poly (ethylene terephthalate)-grafted-acrylic acid/acryl amide fiber was used by Ahmad Panahi et al for removal of lead from human plasma and environmental samples [12]. They reported that the sorption capacity of functionalized resin is 44.1 mg g⁻¹ and recovery of 100% was obtained for the metal ion with 0.5M nitric acid as eluting agent. The modified PET for removal of Cd²⁺ ions and Cationic Brill Red X – 5 GN from aqueous solution were reported by Azizinezhad et al [8-13].

This research involves the use of poly (ethylene terephthalate) (PET) as an adsorbent. Polyester polymers have low hydrophilic, high crystalline properties, high stability at acidic and basic pH conditions, and can also resist biodegradation.

The objectives of this study were to investigate the sorption properties of (PET) grafted with 2-hydroxy propyl methacrylate for the removal Cd²⁺. It includes removal efficiency, sorption isotherms, and the effect of the initial solution pH, metal concentration, sorbent dose and shaking time.

MATERIALS AND METHODS

Preparation of Adsorbent

PET was used as the polymer base and was grafted with 2-hydroxy propyl methacrylate (2-HPMA) as a monomer using the method described by Azizinezhad, 2011, through the following steps.[14]

PET fibers (44 filaments, 167dTex) were produced by the Loom Department of Amir Kabir University of Technology (Tehran). They were fragmented to small hank size (0.1g) and then cleaned by Soxhlet for 6h with acetone. Finally they were dried at ambient temperature. To remove inhibitors existing in 2-HPMA, it was used after distillation under reduced pressure in inert atmosphere (23mmHg, T=99°C). Bz₂O₂ (Aldrich) was recrystallized twice from the methanol-chloroform mixture as solvent, dried in a vacuum desiccator, and stored in a refrigerator.

The grafting procedure was achieved in a Pyrex polymerization tube containing 0.5 mol/L monomer, 0.1g PET fiber ,2×10⁻³ mol/L initiator, and 45mL doubly distilled water at 75°C in a water bath (Lauda D 40 S, Germany) [15-16]. To provide various grafting yields, the operation was carried out in the range of 10-60 min. The removal of undesirable homopolymers was accomplished by N, N-dimethyl formamide (DMF) and (toluene-acetone) mixture for 6 and 8 h, respectively.

The percent of grafting was determined gravimetrically by the following formula (Eq.1) [17]:

$$\% \text{ Graft} = \frac{W_F - W_0}{W_0} \times 100 \quad (1)$$

Where W₀ is the weight of the raw PET (mg) and W_F is the weight of the PET after grafting (mg).

Various percentages of grafted copolymer were provided on 3 levels (0-20, 20-40, and higher than 40%).

Adsorption properties

All sorption experiments were conducted in batch experiments in 0.01M calcium chloride (CaCl₂). Experiments were conducted with the highest grafted copolymer at a cadmium concentration of 5 mg per liter, adsorbent concentration of 0.25%, shaker speed of 150 rpm, volume solution of 20 mL, and temperature of 25±2°C.

The amount of cadmium adsorbed was calculated using the following equation (2):

$$q = (C^\circ - C) \times V / m \quad (2)$$

where q is the amount of adsorbed cadmium on grafted fiber (mg/g), C° and C are the initial and equilibrium (final) cadmium ion concentrations in solution (mg/L), respectively, V is the volume of solution, and m is the mass of grafted fiber sample used (g).

Isotherms studies

Adsorption isotherms of Cd^{2+} on the adsorbent were studied at different concentrations of Cd^{2+} from 5 to 60 mg/L and at temperatures of 15°C, 25°C, and 40°C with a shaking speed of 150

RESULTS AND DISCUSSION

Factors affecting adsorption:

Solution pH

Adsorption increased sharply between pH of 5.0 and 6.70. The increase was likely due to the increase in negative pH dependent charges. The most appropriate pH for adsorption of Cd^{2+} on adsorbent was determined to be 6.70. At pH 3.72, the adsorption was 0.04 mg /g. It increased to 1.32 mg / g at pH 6.70. Maximum removal of cadmium was observed at pH 6.70. Increase of pH over 7 causes the precipitation of cadmium in control solution with no adsorbent. Results also showed that in an acidic environment, the hydrogen and cadmium ions on the sorption sites compete with each other. In alkaline pH's, insoluble cadmium hydroxide could precipitate which results in a decrease in adsorption (Fig.1) [16-19].

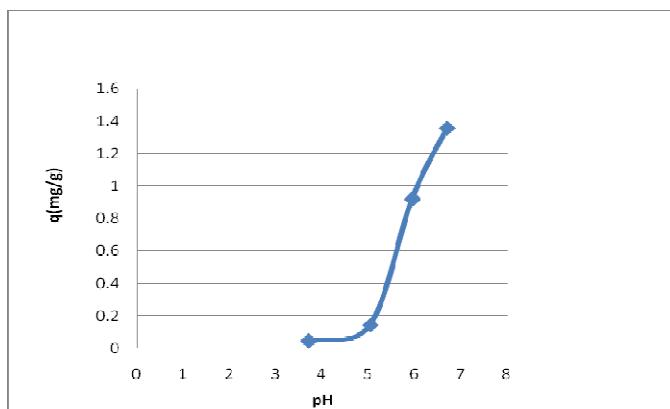


Fig .1 Effect of pH on adsorption

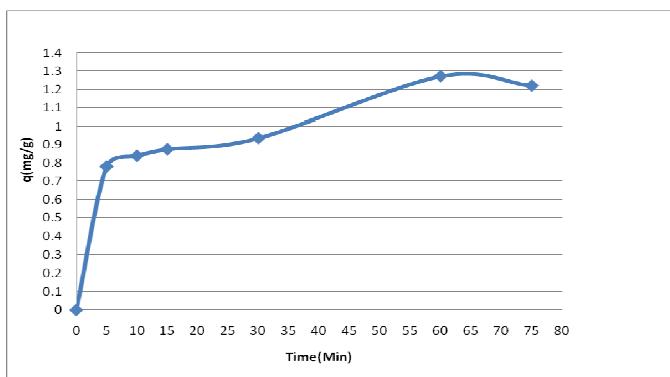


Fig .2 Effect of contact time on adsorption

Contact time

The effect of contact time on adsorption was investigated from 5 to 75 min at the fixation condition of other variables (pH = 6.70, solution volume = 20 mL, T = 298 °K, graft yield > 40 %, adsorbent = 0.05 g, adsorbate = 5 mg / L, and shaking rate = 150 rpm). As shown in Fig. 3, a rapid adsorption occurred at 30 min and was completed at 60 min. Adsorption increased sharply (from zero to 0.8 mg/g) in the first 5 min of contact time and then with much lower rate (from 0.8 to 1.32 mg/g) in 55 min after that (Fig.2). It seems that, there are two stages which show the

adsorption process. The first one is so fast with low activation energy and the second one is slowly. This is attributed to the covering the suitable places on modified PET chains. All of these results and E_a quantity emphasize that the process was physisorption. Since no significant adsorption occurred after 60 minutes, this time was chosen as the most appropriate time for removal of Cd^{2+} in subsequent experiments [15- 19].

Adsorbent effect

With increasing the quantity of the adsorbent (reactive fibers G % > 40 %) from 0.05 g to 0.20 g, the percentage amount of Cd^{2+} adsorption from solution increased from 65.80 to 67.40, respectively (Fig.3). This is likely due to the increase of sorption sites available of adsorption of Cd^{2+} [22].

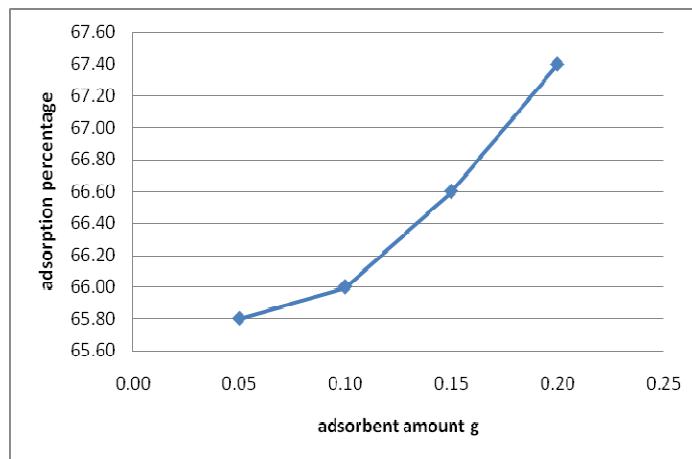


Fig .3 Effect of adsorbent amount on adsorption

Adsorbate concentration

Effect of Cd^{2+} concentration on adsorption is shown in (Fig.4). Adsorption of Cd^{2+} per unit of adsorbent increased almost linearly from zero at zero concentration of adsorbate to a maximum of adsorption (removal) of Cd^{2+} 23.44 mg/g for 120 mg/L of cadmium concentration. This is apparently due to the increase in diffusion flux of Cd^{2+} ions to reach surface of the fiber. Since adsorption decreased after 120 mg/L, 23.44 mg / g was recorded as the maximum sorption capacity of the fiber.

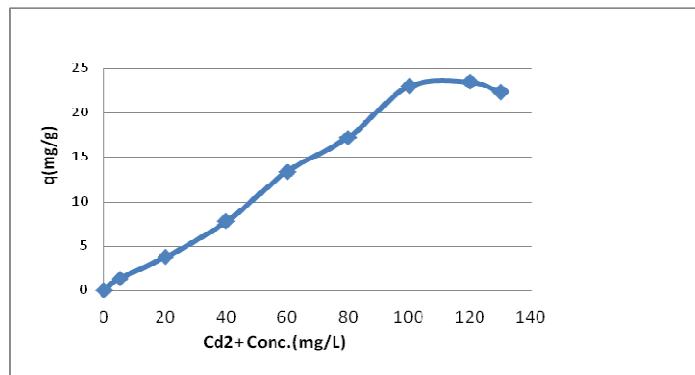


Fig .4 Effect of adsorbate on adsorption

Adsorption isotherm

Five isotherms including: Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Redushkevich were used to explain adsorption data. Formulas (Eq.3 to 6) for these isotherms are given bellow:

$$\text{Freunlich equation: } \frac{1}{q_e} = \frac{1}{K_a q_m} \frac{1}{C_e} + \frac{1}{q_m} \quad (3)$$

$$\text{Langmuir equation: } \frac{1}{q_e} = \frac{1}{K_a q_m} \frac{1}{C_e} + \frac{1}{q_m} \quad (4)$$

$$\text{Temkin-Pyzhev equation: } q_e = a + b \ln(C_e) \quad (5)$$

$$\text{Dubinin-Redushkevich equation } \ln q_e = \ln(q_0) - 2B_0 R T \ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

Isotherm parameters for adsorption of Cd²⁺ on the adsorbent for 3 different temperatures (288°K, 298°K, and 313°K) are given in Table 1 and Figs 5 to 8. The highest values of correlation coefficient (R²) in all temperatures was for the Freundlich and Langmuir models, therefore, these were selected as the most appropriate models to explain the experimental data. These results recognize that the surfaces of reactive fibers are heterogeneous, rough, and can be efficient on multilayer adsorption [23].

Table1. Isotherm parameters for removal of Cd²⁺

Isotherm model	Isotherm parameters	Temperature (K)		
		288	298	313
Freunlich	K _f ((mg/g)(l/mg)) ^{1/n}	0.90	0.89	0.98
	N	1.51	1.38	1.27
	R ²	0.994	0.996	0.999
Langmuir	K _a l/mg	0.08	0.06	0.05
	q _m mg/g	10.55	13.65	18.87
	R ²	0.991	0.995	0.997
Temkin-Pyzhev	A	-0.68	-1.02	-1.20
	B	2.62	3.10	3.88
	R ²	0.930	0.929	0.902
Dubinin-Redushkevich	B ₀ l/g	0.88	0.90	0.84
	q ₀ mg/g	8.41	9.67	11.66
	E	23.89	23.58	24.44
	R ²	0.921	0.928	0.928

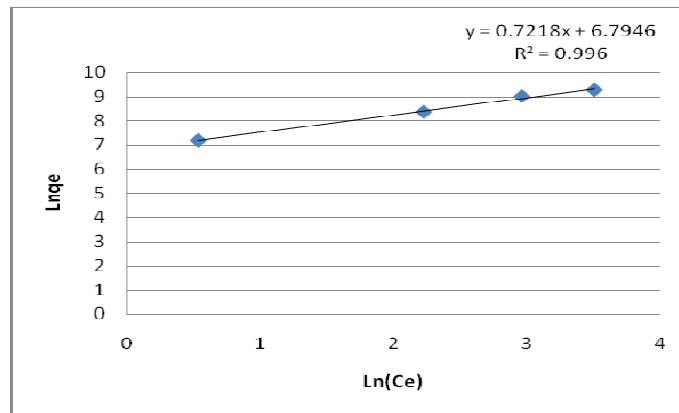


Fig5. Freundlich isotherm at 298 K

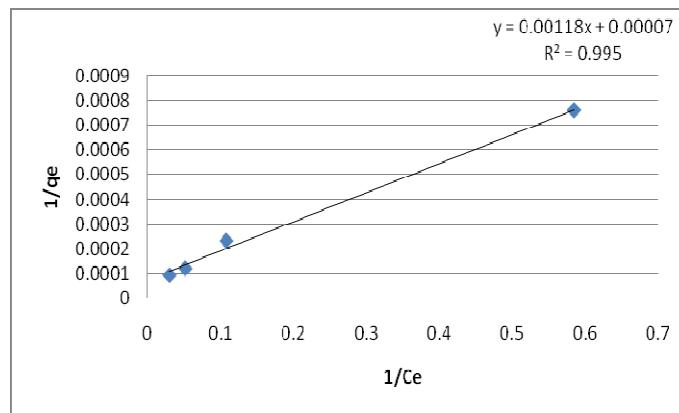


Fig6. Langmuir isotherm at 298K

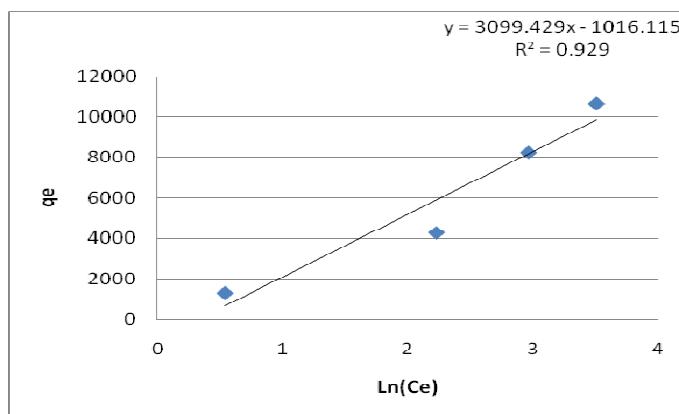


Fig7. Temkin-Pyzhev isotherm at 298K

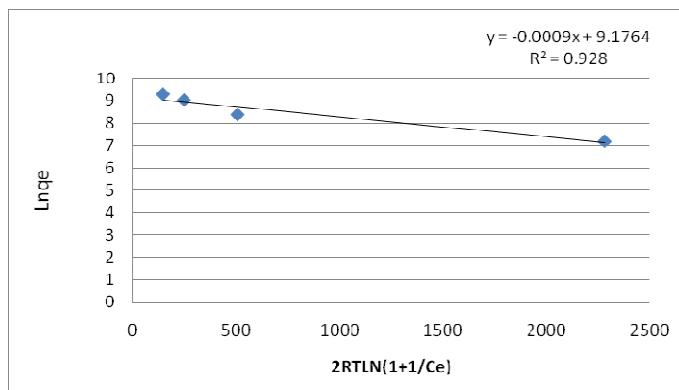


Fig8. Dubinin-Redushkevich isotherm at 298K

CONCLUSION

The results of the present study showed that PET-g-2-HPMA is an effective adsorbent for the removal of Cd²⁺ ions from aqueous solutions. The adsorption of Cd²⁺ ions is dependent on pH, contact time, adsorbent dose, and concentration of the metal ions. Isotherms studies showed that the adsorption equilibrium of Cd²⁺ ions onto the reactive fibers is well explained by the Freundlich model. Base on the Langmuir isotherm maximum adsorption capacity for Cd²⁺ removal was 18.87 mg/g.

REFERENCES

- [1] Waalkes M.P, *J. Inorg. Biochem.* 79 (2000) 241–244.
- [2] Perez-Marin AB, VM, Zapata, J.F. Ortuno, M. Aguilar, J. Saez, M. Llorens, *J. Hazard. Mater.* 139 (2007) 122–131.
- [3] Sharma YC, *Eng. J.* 145 (2008) 64–68.
- [4] Grayson M, K, Othumer, Encyclopedia of Chemical Technology, 43rd edition, John Wiley & Sons, 1978.
- [5] Mahalik MP, Hitner HW, WC, Prozialeck, *Toxicol. Lett.* 76 (1995) 195–202.
- [6] WHO, vol. 1, 3rd ed., World Health Organisation, Geneva, 2008.
- [7] Sakalar N, Bilir MH, Acemioglu B, MH, Alma. *Asian J. Chem* 2010; 22: 5649-5662.
- [8] Azizinezhad F, Borzou A, Abdouss M, M, Shabani, *Biological and Chemical Science*. 2013. 4, 1, 776-783.
- [9] Tan GQ, D, Xiao. *J. Hazard. Mater.* 164 (2009) 1359–1363.
- [10] Borrel P, Harrison PD, JC, Marriott, *Eur. Pat. Appl.*, EP 0 194, 766, A1, 1986.
- [11] Zhang BW, Fischer K, Bieniek D, A, Kettrup, *React. Funct. Polym.*, 24, 49-58, 1994.
- [12] Ahmad Panahi H, Abdouss M, Ghiabi F, Moniri E, A, Mousavi Shoushtari, *Journal of Applied Polymer Science* 2012. 124, 6, 5236–5246.
- [13] Azizinezhad F, M, Shabani, *Biological and Chemical Science*. 2012. 3, 4, 31-39
- [14] Azizinezhad F, *Asian. J. Chem.* 2011, 23, 899-902.
- [15] Nagashanmugam KB, K, Srinivasan. *Asian J. Chem.* 2010, 22, 5447-5462.
- [16] Rao KS, Mohapatra M, Anand S, P, Venkateswarlu. *International Journal of Engineering, Science and*

Technology Vol. 2, No. 7, **2010**, pp. 81-103

[17] Azizinezhad F, *Asian J Chem* **2011**;23:839-842.

[18] Chaari M, Feki M, M, Medhiube, J. Bouzid, E. Fakhfakh, F, Jamoussi. *J. Haz. Ma.* **2009**, 172,1623-1628.

[19] Abdelwaheb O, *Egyption J. Aquatic Res.* **2007**, 33, 125-143.

[20] Coskun R, Yigitoglu M, M, Sacak. *Polym. Sci.* **2000**; 75: 766-772.

[21] Coskun R, C, Soykan. *J. Polym. Res.* **2006**; 13: 1-8.

[22] Azizinejad F, Talu M, Abdouss M, M, Shabani. *Iran Polym. J.* **2005**, 14,33-38.

[23] Masel RI, Wiley , Principle of Adsorption and Reaction on Solid Surfaces, Wiley , New York ,**1996**.

[24] Lagergren S, Kungliga Svenska Vetenskaps-akademiens Handlingar, **1898**. 24(4):1-39.

[25] Weber WJ, Morris JC, J, Sanit. Eng. Div. **1963**; 89: 31-45. Us Public Health Service Publication., 999-Wp13.; Us Environmental Health Series., Wp-033. Government publication

[26] Krishna DG, G, Bhattacharyya. *Appl. Clay. Sd.* **2002**; 20: 295-300.

[27] Jaycock MJ, GD, Parfitt. Ellis Horwood Ltd, Onichester **1981**, 12-13.

[28] Benefield J, Judkins P, BL,Wend. Prentice Hall, Englewood Cliffs, N. J. **1982**.