

ORIGINAL RESEARCH PAPER

Effective removal of hexavalent mercury from aqueous solution by modified polymeric nanoadsorbent

Lida Rahmanzadeh¹; Mohsen Ghorbani^{*2}; Mohsen Jahanshahi²

¹ Babol University of Technology, P.O.Box 484, Babol, Iran

² Faculty of Chemical Engineering, Babol University of Technology, P.O.Box 484, Babol, Iran

Received 2015-12-06

Accepted 2016-01-17

Published 2016-07-01

Abstract

Mercury is one of the most toxic metals present in the environment. Adsorption has been proposed among the technologies for mercury adsorbent. The kinetics of adsorption depends on the adsorbent concentration, and the physical and chemical characteristics of adsorbent. In this study we were used a novel adsorbent, magnetite-polyrhodanine core-shell nanoparticles, for removing Hg(II) from aqueous solution. The effect of pH, initial Hg(II) concentration, initial adsorbent concentration and contact time on the efficiency of Hg(II) removal were investigated systematically by batch experiments. The maximum adsorption capacity was obtained 29.14 mg g⁻¹ at PH=6.5 and 25°C with 10 g L⁻¹ nano adsorbent. The kinetic data of adsorption of Hg(II) ion on the synthesized adsorbent were best described by a pseudo-second-order equation, indicating their chemical adsorption. The Freundlich, Langmuir and Temkin isotherms were used to modeling of mercury adsorption on Hg(II) in aqueous medium which modeled best by the Freundlich isotherm is whole concentration range.

Keywords: Adsorption; Core-shell polymer; Mercury; Morphology; Nanocomposite

How to cite this article:

Rahmanzadeh L, Ghorbani M, Jahanshahi M, Effective removal of hexavalent mercury from aqueous solution by modified polymeric nanoadsorbent. J. Water Environ. Nanotechnol., 2016; 1(1):1-8. DOI: 10.7508/jwent.2016.01.001

INTRODUCTION

Water pollution by heavy metal ions has become a serious problem nowadays [1-2]. The heavy metal ions are not only toxic to living organisms in water, but also harmful effects to land animals including humans through food chain transfer [3-4]. The existence of heavy metals in wastewaters contributes to water toxicity and represents an increasing danger for the environment, human beings and other living organisms [5].

Mercury is well known for its extremely high toxicity and the serious threat to human life and natural environment. Inorganic mercury in water is mainly seen in the +2 oxidation state. Mercury is released into the atmosphere through a variety of natural sources [6]. The world of organization

* Corresponding Author Email: M.Ghorbani@nit.ac.ir

(WHO) recommends a maximum uptake of 0.3 mg/week and 1 µg/L as maximum acceptable concentration in drinking water [7].

Various processes and methods such as adsorption, electrochemical treatment, membrane separation, solvent extraction, ion exchange, amalgamation and chemical precipitation have been employed to remove metal pollutants from aqueous solutions [8-18]. However, most of these methods suffer from low removal efficiency, especially when large volumes of dilute heavy metal solution are present [19]. Among the available technological alternatives for the removal of trace metals from water, adsorption has been considered an economically feasible one [20-24]. Different adsorbents such as

activated carbon [25], zeolites [26, 27], resins [28], biosorbents [29], hydrogel and magnetic hydrogel [30-31] have been used for removal of heavy metal ions by adsorption. Despite the availability of a number of adsorbents for the removal of low concentrations of heavy metal ions from aqueous solutions, there is still a need for the development of new adsorbent with superior adsorption capacity, facile adsorption-desorption kinetics, high stability, and easiness of operation. Recently, nanometer-sized materials have been used for wastewater treatment [32-34]. In particular, the use of magnetite nanoparticles as adsorbents in water treatment provides a convenient approach for separating and removing the contaminants by applying external magnetic fields. Bare magnetite nanoparticles are susceptible to air oxidation and are easily aggregated in aqueous systems [35]. Thus, for the application of these nanoparticles in various potential fields the stabilization of the iron oxide particles by surface modification is desirable. The magnetic structure of the surface layer, which is usually greatly different from that in the core of the nanoparticles, can have a notable effect on the magnetic properties of nanoparticles [36].

Polyrhodanine has attracted considerable attention in various application fields such as anticorrosion [37], antibacterial [38], and antihistaminic agents [39]. In addition, they can be used for detecting or adsorbing of metal ions because the Rhodanine mono-meric unit has a metal-binding functional groups. Polyrhodanine can be expected as a promising candidate for efficient adsorbent of heavy metal ions because it contains oxygen, nitrogen, and sulfur atoms in its monomeric structure [40-42].

There are many reports on the use of magnetic nanoparticles (MNP) as sorbent for removal of heavy metal ions. Unmodified magnetic Fe_2O_3 and Cu(II) ion imprinted Fe_3O_4 nanoparticles were employed as adsorbents for the removal of Cr(VI) [43] and Cu(II) [44], respectively, from wastewater. Zhu and coworkers have investigated a removal of mercury ions from aqueous solutions by Modifying activated carbon (MAC) with hybrid ligands. Kinetics and isotherm studies demonstrated that the Hg sorption by MAC was faster (<30 min) and higher (>200%) than that by AC, suggesting a high affinity of MAC for Hg ions. The sorption by MAC occurred in a wider pH range (4-10 vs. 5-7), and low ionic strength appeared to enhance Hg sorption. In another work, Ian and coworkers was used Carapace from the edible crab for the biosorption of Hg from aqueous solutions. Batch

adsorption studies were used to determine the effects of contact time, pH, concentration, particle size and Cu(II) as a co-ion. Results indicated that, the removal of Hg was fast and efficient, attaining >80.0% from 500 mg/L by 60 min [45-46].

The aim of this work was to study the influence of experimental parameters such as pH, contact time, adsorbent dosage on Hg (II) removal. The best kinetic and isotherm models were found from experimental data.

MATERIALS AND METHODS

Synthesis of adsorbent

The synthesis of Polyrhodanine coated Magnetite nanoparticles ($\text{Fe}_3\text{O}_4@\text{PRh}$) was in accordance with previously published work of our research team [47].

Batch removal experiments

Adsorption of Hg(II) was carried out by batch technique at room temperature. The isotherm studies were performed by mixing 10 mg adsorbent (dry) with 10 ml of solution containing $\text{Hg}(\text{NO}_3)_2$ at known concentration into a tube and insert in the shaker. In all experiments, the flasks were shaken at 350 rpm on the orbital shaker at room temperature. After agitation, the adsorbent was separated by filtration, then metal analysis of the solutions was performed by ICP (ICPS-7000 Sequential Plasma Spectrometer).

The equilibrium concentration of the adsorbed Hg(II), q_e (in mg g^{-1}) was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

Where C_0 and C_e (in mg L^{-1}) are the initial and equilibrium concentrations of Hg(II) in solution, respectively, V (in L) is the total volume of solution, and M (in g) is the adsorbate mass.

The effect of PH on adsorption was conducted by mixing adsorbent (10 g L^{-1}) with Hg aqueous solution (10 ml, $C_{0,\text{Hg(II)}} = 50 \text{ mg L}^{-1}$). The PH was adjusted in the range of 2-12, by adding appropriate amount of 0.1M HCl (hydrochloric acid) or 0.1M NaOH (Sodium hydroxide). The flask was shaken at 350 rpm on shaker for 5 hours. The optimum pH selected was 6.5.

Kinetic studies were performed under similar conditions used for isotherm studies and at pH 6.5 which was the optimum pH for Hg(II) removal. In these studies aliquots of the supernatant were withdrawn for Hg(II) analysis at different periods time.

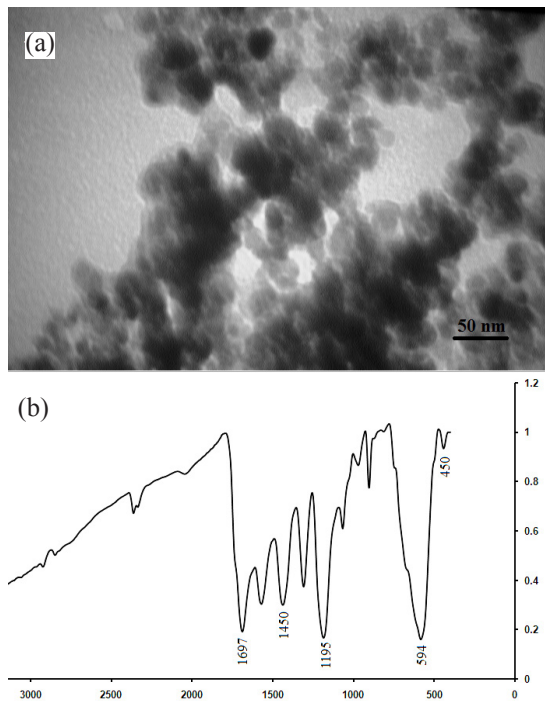


Fig. 1: a) TEM and b) FTIR images of polyrhodanine-Fe₃O₄ nanocomposite

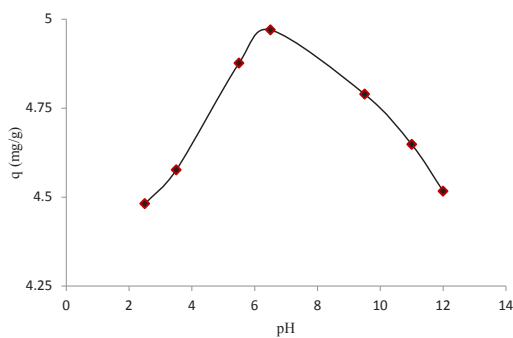


Fig. 2: Effect of pH on the adsorption of Hg (II) onto Fe₃O₄ -Polyrhodanine

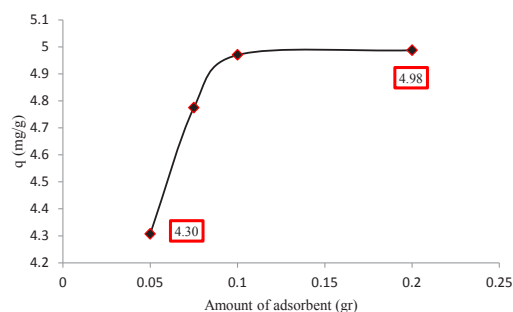


Fig. 3: Effect of adsorbent dosage on the adsorption of Hg (II) onto Fe₃O₄ -Polyrhodanine

RESULTS AND DISCUSSION

Characterization of Nanocomposite

Fig. 1 show TEM and FTIR analysis of Fe₃O₄-Polyrhodanine core-shell nanocomposite. Fig. 1(a) indicates the morphology of the core-shell nanoparticles was rather homogeneous and a thin film of polyrhodanine was coated on the surface of Fe₃O₄ nanoparticles. The dark spaces are magnetite nanoparticles (core) and the clear spaces are polyrhodanine (shell). The mean diameter of core and shell is 15 and 8 nm, respectively. Fig. 1(b) shows FTIR spectra of the Fe₃O₄-polyrhodanine core-shell structure. All Peaks in the core-shell structure exist in the core (Fe₃O₄) and shell (Polyrhodanine) structure, which indicate that there is some interaction between PRh and magnetite nanoparticles. The peaks at 594, 1697, 1450 and 1195 cm⁻¹ were observed. These peaks were attributed to the stretching vibration of Fe-O, C-C groups, C-N, and C-O stretching vibration, respectively[48, 49].

Effects of PH

It is well documented that solution PH is an important parameter affecting the sorption of heavy metal ions. Therefore, the dependence of Hg(II) uptake on PH was studied at a constant Hg(II) concentration (10 mg.L⁻¹) using 10 mg of nanoadsorbent. As shown in Fig. 2, Hg(II) adsorption increase with increasing PH in the range of 2-6.5 and decrease with increasing PH in the range of 6.5-12. Thus, PH 6.5 was adopted for further studies.

The adsorption of the metal ions on adsorbent depends on the nature of the adsorbent surface and species distribution of the metal ions. Lower adsorption percentage of Hg(II) on nanoparticles at acidic conditions (PH≤7) is probably due to the presence of high concentration of H⁺ ions on the adsorbent surface competing with Hg(II) for adsorption sites. The adsorption at PH above 7 shows a decreasing trend because Polyrhodanine destroyed in alkaline environment.

Effects of nanoadsorbent dosage

For investigation effect of nanoadsorbent dosage on adsorption efficiency was conducted by mixing amounts of nanoadsorbent (0.05, 0.075, 0.1, 0.2 gr) in Hg aqueous solution (10 ml, C_{0,Hg(II)} = 50 mg L⁻¹). All experiments were performed at 25 °C and in the solution PH 6.5. In Fig. 3 Hg(II) adsorption increase with increasing

Table 1. Kinetic parameters for Hg(II) sorption onto nanocomposite

Kinetic model		Parameter	
Pseudo-first-order	K	(min) ⁻¹	0.0335
	q _c	mg g ⁻¹	0.317969
	R ₂		0.9159
Pseudo-second-order	K	(g mg ⁻¹ min ⁻¹)	0.373685
	q _s	mg g ⁻¹	4.98008
	R ²		1
First-order	K	(min) ⁻¹	0.0203
	R ²		0.8089
Second-order	K	(g mg ⁻¹ min ⁻¹)	0.0105
	R ²		0.8214

Table 2. Isotherm models for Hg(II) sorption onto nanocomposite

Isotherm model		Parameter	
Freundlich	K	L mg ⁻¹	9.9741
	η		0.5347
	R ²		0.9917
Langmuir	K _s	L mg ⁻¹	0.40265
	q _m	mg g ⁻¹	36.6300
	R ²		0.9847
Temkin	K _T	L mg ⁻¹	5.03947
	B _T	mg g ⁻¹	7.3128
	R ²		0.9702

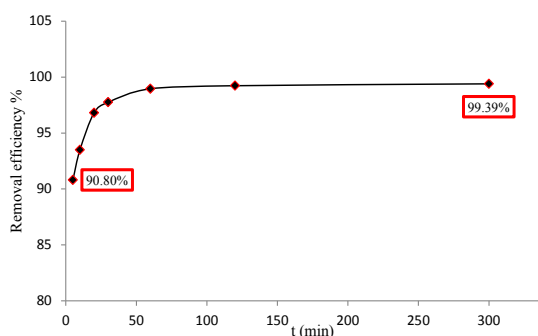


Fig. 4: Effects of contact time on the adsorption of Hg (II) onto Fe3O4 -Polyrhodanine

nanoadsorbent in the range of 0.05-0.1 gr and is approximately independent of nanoadsorbent in the range of 0.1-0.2 gr. Thus, 0.1 gr of nanoadsorbent was adopted for further studies.

Effects of contact time and the metal sorption kinetics

Fig. 4 shows the time dependant behavior of the removal of Hg(II) ions from aqueous solution by the nanoadsorbents. From the plot, it is clear that the removal amount of Hg(II) increased as the contact time elapsed. The equilibrium time was reached within 30 min. The initial adsorption rate was very fast which may be due to the existence of greater number of nanoadsorbent sites available for metal ion adsorption. As the remaining vacant surface sites decreases, the adsorption rate slowed down due to the formation of repulsive forces between the metals on the solid surface and in the liquid phase.

The pseudo-first-order, pseudo-second-order,

first-order and second-order kinetic equations were chosen to fit the obtained adsorption kinetics data and to estimate the rate constant of the adsorption phenomenon.

First-order model

The linear form of first-order rate equation is the following:

$$\ln \frac{C_0}{C_t} = K_1 t \quad (2)$$

Where C₀ is initial concentration (mg L⁻¹), C_t is the concentration at any time t, t in time (min) and K₁ is the rate constant of first-order adsorption (min⁻¹). Fig. 5 shows a plot of Ln(C₀/C_e) versus t.

Second-order model

The linear form of second-order rate equation is expressed as:

$$\frac{1}{C_t} = K_2 t + \frac{1}{C_0} \quad (3)$$

Where C₀ is initial concentration (mg L⁻¹), C_t is the concentration at any time t, t in time (min) and K₁ is the rate constant of second-order adsorption (g mg⁻¹ min⁻¹). Plot of 1/C_t versus t shows in Fig. 6.

Pseudo-first-order model

The sorption kinetics may be described by a pseudo-first-order equation [50]. The linear form of pseudo-first-order rate equation is expressed as:

$$\ln(q_e - q) = \ln q_e - K_1 t \quad (4)$$

Where q_e and q are the amount of species adsorbed per unit mass of adsorbent (mg g⁻¹) at equilibrium and at any time t, respectively, and K₁ is the rate constant of pseudo-first-order adsorption (min⁻¹). Fig. 7 shows a plot of linearized form of pseudo-first-order at all concentrations studied. The slope and intercepts of plot of Ln(q_e - q) versus t were used to determine the pseudo-first-order rate constant K₁ and equilibrium adsorption density q_e. a comparison of the results with the correlation coefficients is shown in table 1.

Pseudo-second-order model

The adsorption kinetics may also be described by a pseudo-second-order equation [51]. The linear form is the following:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

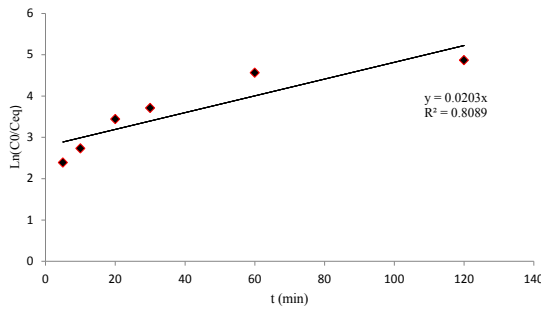


Fig. 5. First-order kinetic model for adsorption of Hg(II) onto Fe3O4-Polyrhodanine at 25 °C

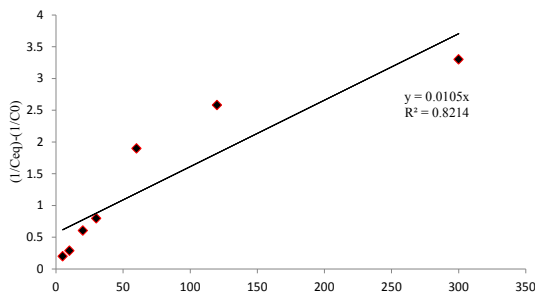


Fig. 6. Second-order kinetic model for adsorption of Hg(II) onto Fe3O4-Polyrhodanine at 25 °C

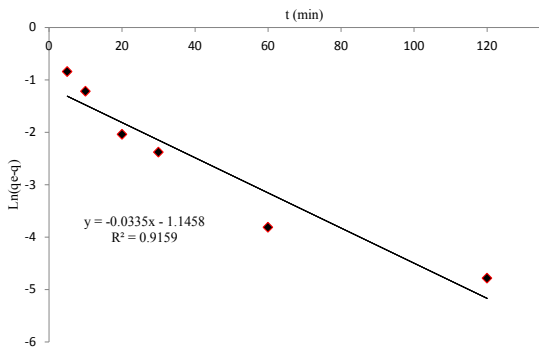


Fig. 7. Pseudo-first-order kinetic model for adsorption of Hg(II) onto Fe3O4-Polyrhodanine at 25 °C

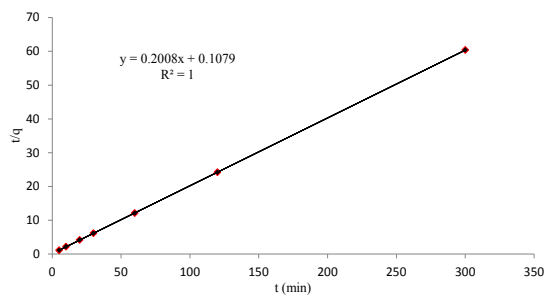


Fig. 8. Pseudo-second-order kinetic model for adsorption of Hg(II) onto Fe3O4-Polyrhodanine at 25 °C

Where t is time (min), q_e and q_t are the amount of species adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium and at any time t , respectively, and K_2 is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The straight line in plot of t/q_t versus t (Fig. 8) shows the good agreement of experimental data with the pseudo-second-order kinetic model for different initial concentrations. As shown in table 1, the adsorption of Hg(II) onto Fe_3O_4 -PRh nanoparticles is more appropriately described by a pseudo-second-order kinetic model since its correlation coefficient (1.00) is greater than other.

Effect of Initial Hg(II) Concentration and Metal Sorption Isotherm

Lead adsorption is significantly influenced by the initial concentration of Hg^{2+} ions in aqueous solution. In the present study, the initial Hg^{2+} concentration is varied from 50 to 300 mg/L while maintaining the adsorbent dosage at 10 g/L (PH=6 and time=5 h). Fig. 9 shows the effect of initial concentration on percentage removal of Hg^{2+} ions. The experimental data were fitted to Langmuir [52], Freundlich [53] and Temkin [54] isotherm model.

Langmuir isotherm

The Langmuir model represents chemisorption on a set of well defined localized adsorption site, having the same adsorption energies independent of surface coverage and no interaction between adsorbed molecules. Langmuir isotherm assumes monolayer coverage of adsorbate onto adsorbent. The linear form of the Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{K_s q_m} + \frac{1}{q_m} C_e \quad (6)$$

Where C_e is the equilibrium concentration of metal (mg/L), Q_0 and b are Langmuir constants related to adsorption capacity and adsorption energy respectively. The plot of C_e/q_e against C_e gives a straight line (Fig. 10) showing the applicability of Langmuir isotherm. The values of Q_0 and b are obtained from slope and intercept of the plot and are presented in table 2. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called, the equilibrium parameter R_L defined by:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (7)$$

Where C_0 is the initial Hg(II) ion concentration (mg/L). As the R_L values obtained lies between 0 and 1, the adsorption process is favorable.

Freundlich isotherm:

Freundlich isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm dose not predict any saturation of the adsorbent surface; thus, infinite surface coverage is predicted, indicating physisorption on the surface. The linear representation of the freundlich adsorption equation is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

Where K_F is the energy term and n is an exponent term related to the strength of the adsorption. The Freundlich plot is shown in Fig. 11 and the K_F and $1/n$ parameters with the corresponding determination coefficient, R^2 , are presented in Table 2.

Temkin isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent-adsorbate interactions. The linear model is given by the following equation:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (9)$$

$$B_T = \frac{RT}{b_T} \quad (10)$$

Where K_T is Temkin isotherm equilibrium binding constant (L/g), B_T is Temkin isotherm constant, R is universal gas constant (8.314 J mol⁻¹ K⁻¹), T is temperature at 298 K and b_T is constant related to heat of sorption (J/mol). The Temkin plot is shown in Fig. 12 and K_T , B_T and R^2 are presented in table 2.

Table 2 shows that the adsorption behavior of Hg(II) ions onto the magnetic nanoparticles is best described by Freundlich isotherm model because this model yields a higher determination coefficient.

CONCLUSIONS

The obtained results indicate that magnetite-polyrhodanine is a suitable and effective adsorbent for the removal of Hg(II) from aqueous solutions. Its adsorption capacity at PH 6.5 is 29.14 mg g⁻¹. It was found that the adsorption behavior of Hg(II)

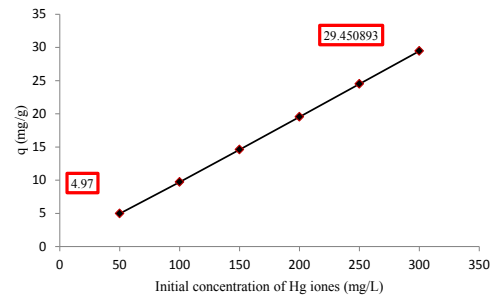


Fig. 9. Effect of initial Hg (II) concentration for adsorption of Hg (II) onto Fe3O4 –Polyrhodanine at 25 °C

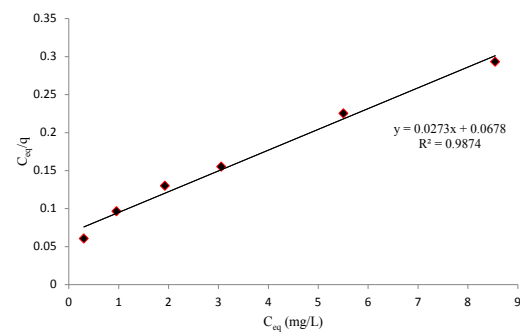


Fig. 10. Langmuir isotherm plot for adsorption of Hg (II) onto Fe3O4-Polyrhodanine at 25 °C

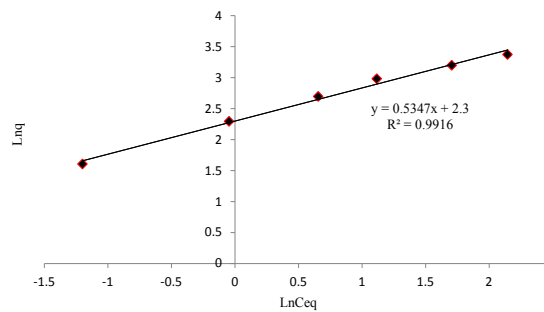


Fig. 11. Freundlich isotherm plot for adsorption of Hg (II) onto Fe3O4-Polyrhodanine at 25 °C

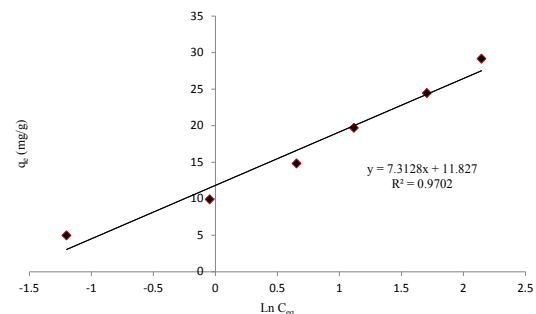


Fig. 12. Temkin isotherm plot for adsorption of Hg (II) onto Fe3O4-Polyrhodanine at 25 °C

ions onto the adsorbent is best described by the Freundlich isotherm model and Hg(II) showed fast sorption kinetics following pseudo- second- order model.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Yardim, M.F., T. Budinova, E. Ekinci, N. Petrov, M. Razvigorova and V. Minkova, 2003. Removal of mercury (II) from aqueous solution by activated carbon obtained from furfural. *Chemosphere*, 52: 835–841.
2. Sari, A. and M. Tuzen, 2008. Biosorption of cadmium(II) from aqueous solution by red algae (*Ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies. *Journal of Hazardous Materials*, 157: 448- 454.
3. Silver, S., 1998. The Bacterial View of the Periodic Table: Specific Functions for All Elements. *Microbes and Environments*, 13 : 177-192.
4. Liu, X., Q. Hu, Z. Fang, X. Zhang and B. Zhang, 2009. Magnetic chitosan nanocomposites: a useful recyclable tool for heavy metal ion removal. *Langmuir*, 25: 3-8.
5. Nriagu, J. O. and J. M. Pacyna, 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, 333: 134-139.
6. Schroeder, W. H. and J. Munthes, 1998. Atmospheric mercury-and overview. *Atmospheric Environment*, 32: 809-822.
7. Forster, C. and J. Wase, *Biosorbents for Metal Ions*. Taylor & Francis, New York: 1997.
8. Lin C.J. and S.O. Pehkonen, 1999. The chemistry of atmospheric mercury : a review. *Atmospheric Environment*, 33 : 2067-2079.
9. Ekino, S., M. Susa, T. Ninomiya, K. Imamura, T. Kitamura and J. Neurol Minamata, 2007. disease revisited an update on the acute and chronic manifestations of methyl mercury poisoning. *Journal of the Neurological Sciences*, 262: 131-144.
10. World Health Organization. *Guidelines for Drinking Water Quality*. 3rd ed. Geneva: 2004.
11. Zahir, F., S. J. Rizwi, S. K. Haq and R. H. Khan, 2005. Low dose mercury toxicity and human health. *Environmental Toxicology and Pharmacology*, 20: 351–360.
12. Park, H. G., T.W. Kim, M. Y. Chae and I. K. Yoo, 2007. Activated Carbon Containing Alginate Adsorbent for the Simultaneous Removal of Heavy Metals and Toxic Organics. *Process Biochemistry*, 42: 1371-1377.
13. Verma, V. K., S. Tewari and J. P. N. Rai, 2008. Ion exchange during heavy metal biosorption from aqueous solution by dried biomass of macrophytes. *Bioresour Technology*, 99: 1932-1938.
14. Navarro, R. R., S. Wada and K. Tatsumi, 2005. Heavy metal precipitation by polycation–polyanion complex of PEI and its phosphonomethylated derivative. *Journal of Hazardous Materials*, 123: 203–209.
15. Kumbasar, R. A., 2010. Extraction of cadmium from solutions containing various heavy metal ions by Amberlite LA- 2. *Journal of Industrial and Engineering Chemistry*, 16: 207–213.
16. Bessbousse, H., T. Rhlalou, J. F. Verchère and L. Lebrun, 2008. Removal of Heavy Metal Ions from Aqueous Solutions by Filtration with a Novel Complexing Membrane Containing Poly(Ethyleneimine) in a Poly(Vinyl Alcohol) Matrix. *Journal of Membrane Science*, 307: 249-259.
17. Choi, M. and J. Jang, 2008. Heavy metal ion adsorption onto polypyrrole-impregnated porous carbon. *Journal of Colloid and Interface Science*, 325; 287-289.
18. Lee, J. Y., T. S. Kwon, K. Baek and J. W. Yang, 2009. Adsorption characteristics of metal ions by CO₂-fixing *Chlorella* sp. HA-1. *Journal of Industrial and Engineering Chemistry*, 15: 354-358.
19. Cochrane, E. L., S. Lu, S. W. Gibb and I. Villaescusa, 2006. A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media. *Journal of Hazardous Materials*, 137(1): 198–206.
20. Babic, B., S. Milonjic, M. Polovina, S. Cupic and B. Kaludjerovic, 2002. Adsorption of zinc, cadmium and mercury ions from aqueous solutions on an activated carbon cloth. *Carbon*, 40(7): 1109-1115.
21. Velicu, M., H. Fua, R. P. S. Suri and K. Woods, 2007. Use of adsorption process to remove organic mercury thimerosal from industrial process wastewater. *Journal of Hazardous Materials*, 148(3): 599-605.
22. Inbaraj, S. and N. Sulochana, 2006. Mercury adsorption on a carbon sorbent derived from fruit shell of *Terminalia catappa* B. *Journal of Hazardous Materials*, 133(1-3): 283-290.
23. Antochshuk, V., O. Olkhovik, M. Jaroniec, I. Park and R. Ryoo, 2003. Benzoylthiourea-modified mesoporous silica for mercury (II) removal. *Langmuir*, 19(7): 3031-3034.
24. Costa, L., M. Araujo, K. Sapag, M. Sardella, H. Silva, C. Deiana and R. M. Lago, 2005. High surface area functionalized carbon briquettes: A novel adsorbent for metals from water. *Journal of the Brazilian Chemical Society*, 16(5): 899-902.
25. Kantarli, I. C. and J. Yanik, 2010. Activated carbon from leather shaving wastes and its application in removal of toxic materials. *Journal of Hazardous Materials*, 179(1-3): 348–356.
26. Çoruh, S., G. Şenel and O. N. Ergun, 2010. A comparison of the properties of natural clinoptilolites and their ion-exchange capacities for silver removal. *Journal of Hazardous Materials*, 180(1-3): 486–492.
27. Doula, M. K., 2009. Simultaneous removal of Cu, Mn and Zn from drinking water with the use of clinoptilolite and its Fe-modified form. *Water Research*, 43(15): 3659–3672.
28. Mahmoud, M. E., I. M. M. Kenawy, M. A. H. Hafez and R. R. Lashein, 2010. Removal preconcentration and determination of trace heavy metal ions in water samples by AAS via chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidene- propylamine ion exchanger. *Desalination*, 250(1): 62–70.
29. Luna, A. S., A. L. H. Costa, da A. C. A. Costa and C. A. Henriques, 2010. Competitive biosorption of cadmium(II) and zinc(II) ions from binary systems by *Sargassum lipendula*. *Bioresour Technology*, 101(14): 5104–5111.
30. Ozay, O., S. Ekici, Y. Baran, N. Aktas and N. Sahiner, 2009. Removal of toxic metal ions with magnetic hydrogels. *Water Research*, 43(17): 4403–4411.
31. Sharma, R. K. and A. Lalit, 2011. Synthesis and characterization of graft copolymers of N-Vinyl-2-Pyrrolidone onto guar gum for sorption of Fe²⁺ and Cr⁶⁺ ions. *Carbohydrate Polymers*, 83(4): 1929-1936.
32. Zhou, Y. T., H. L. Nie, C. Branford-White, Z. Y. He and L. M. Zhu, 2009. Removal of Cu from aqueous solution by

- chitosan- coated magnetic nanoparticles modied with α -ketoglutaric acid. *Journal of Colloid and Interface Science*, 330(1): 29–37.
33. Kalfa, O. M., Z. Yalçinkaya and A. R. Türker, 2009. Synthesis of nano B₂O₃/TiO₂ composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium. *Journal of Hazardous Materials*, 166(1): 455–461.
34. Zhang, Q., B. Pan, W. Zhang, K. Jia and Q. Zhang, 2008. Selective sorption of lead, cadmium and zinc ions by a poly-meric cation exchanger containing nano-Zr(HPO₃S)₂. *Environmental Science & Technology*, 42(11): 4140–4145.
35. Maity, D. and D. C. Agrawal, 2007. Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media. *Journal of Magnetism and Magnetic Materials*, 308: 46–55.
36. Zhang, L., R. He and H. C. Gu, 2006. Oleic acid coating on the monodisperse magnetite nanoparticles. *Applied Surface Science*, 253: 2611–2617.
37. Solmaz, R., G. Kardaş, B. Yazıcı, M. Erbil, 2007. The Rhodanine Inhibition Effect on the Corrosion of a Mild Steel in Acid Along the Exposure Time. *Protection of Metals*, 43: 476–482.
38. Kong, H., J. Song and J. Jang. 2009. One-step Preparation of Antimicrobial Polyrhodanine Nanotubes with Silver Nanoparticles. *Macromolecular Rapid Communications*, 30: 1350–1355.
39. Sortino, M., P. Delgado, S. Juárez, J. Quiroga, R. Abonía, B. Insuasty, M., Noguerras, L. Rodero, FM Garibotto, RD Enrize and SA.Zacchinoa 2007. Synthesis and antifungal activity of (Z)-5-arylidenerhodanines. *Bioorganic & Medicinal Chemistry*, 15: 484–494.
40. Song, J., H. Oh, H. Kong and J. Jang, 2011. Polyrhodanine modified anodic aluminium oxide membrane for heavy metal ions removal. *Journal of Hazardous Materials*, 187: 311–317.
41. Mohammadi, S. Z., N. Seifollahi and D. Afzali, 2010. Separation and preconcentration trace amounts of gold by using modified organo nanoclay closite 15A. *Quim Nova*, 33: 1496–1499.
42. Rastegarzadeh, S., N. Pourreza, A. R. Kiasat and H. Yahyavi, 2010. Selective solid phase extraction of palladium by adsorption of its 5(p-dimethylaminobenzylidene)rhodanine complex on silica-PEG as a new adsorbent. *Microchim Acta*, 170 : 135–140.
43. Hu, J., G. Chen and I. Lo, 2005. Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles. *Water Research*, 39(18): 4528–4536.
44. Ren, Y., X. Wei and M. Zhang, 2008. Adsorption character for removal Cu(II) by magnetic Cu(II) ion imprinted composite adsorbent. *Journal of Hazardous Materials*, 158(1): 14–22.
45. Jianzhong, Z., B. Deng, J. Yang, D. Gang, 2009. Modifying activated carbon with hybrid ligands for enhancing aqueous mercury removal. *Carbon*, 47: 2014–2025.
46. Ian, B. R., S. Gibb and S. Lu, 2009. Biosorption of Hg from aqueous solutions by crab carapace. *Journal of Hazardous Materials* 164: 1601–1604.
47. Rahmanzadeh, L., M. Ghorbani and M. Jahanshahi, 2014. Synthesis and Characterization of Fe₃O₄ @ Polyrhodanine Nanocomposite with Core–Shell Morphology. *Advances in Polymer technologies*, 1: 1–6
48. Kardas, G. and R. Solmaz, 2007. Electrochemical synthesis and characterization of a new conducting polymer: Polyrhodanine. *Applied Surface Science* 253: 3402–3407.
49. Liu, J. F., Z. Shanzhao, and G. Binjiang, 2008, Coating Fe₃O₄ Magnetic Nanoparticles with Humic Acid for High Efficient Removal of Heavy Metals in Water. *Environmental Science Technology* 42: 6949–6954.
50. Lagergren, S., 1898. About the theory of so-called adsorption of soluble substances. *Handlingar*, 24: 1–39.
51. Ho, Y. S., J. C. Y. Ng and G. McKay, 2000. Kinetics of pollutant sorption by biosorbents: Review. *Separation and Purification Methods*, 29: 189–232.
52. Vermeulan, T. H., K. R. Vermeulan and L. C. Hall, 1966. *Industrial & Engineering Chemistry Fundamentals*, 5: 212–223.
53. Hutson, N. D. and R. T. Yang, 2000. Adsorption. *J Colloid Interf Sci*, p.189.
54. Tempkin, M. I. and V. Pyzhev, 1940. Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Physico-Chimica Sinica, USSR*, 12: 327–356.