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CONTENT

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NON-LINEAR KINETIC ISOTHERMS AND THERMODYNAMIC BEHAVIOR OF As(V) ONTO HYBRID NANOCOMPOSITE

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ABSTRACT

Kinetic, equilibrium and thermodynamic of arsenate sorption onto magnetic polymer sorbent based on glycidyl methacrylate were investigated. The maximum sorption capacity of 0.59 mg/g was obtained. The experimental data were analyzed by seven kinetic models and eight isotherm models. Nonlinear regression method was used to fit the data to the kinetic and isotherm models. Thus, two error functions; coefficient of determination and Chi-square statistic test were applied to evaluate the sorption data. It was shown that arsenate sorption obeys the pseudo-second-order model with evident influence of pore and film diffusion. The Freundlich and all three-parameter isotherm models proved to be the best representatives of arsenate sorption. Thermodynamic studies implied endothermic and spontaneous process in nature.

INTRODUCTION

The presence of arsenic (As) in surface and groundwater is a consequence of natural processes (mineral dissolution, biological activity, erosion) and anthropogenic impact (electronic, petrol, textile, dye and pharmaceutical industry, etc). In the environment, As occurs in oxidation states of $\pm$ 3, 5 and 0, predominantly as AsO_3^{3-} and AsO_4^{3-} [1, 2]. It is highly toxic, causing various detrimental effects on human health, such as problems in cognitive development and memory, skin lesions, diabetes and cardiovascular disease to cancer of the skin, lungs, urinary bladder, liver and kidney [3]. Due to the carcinogenic behavior of As, the World Health Organization (WHO) set the maximum contaminant level in drinking water to 10 ppb [4]. Therefore, the removal of As from water is a matter of vital importance. Magnetic polymer materials seem to be very promising adsorbents for the removal of toxic contaminants since they exhibit excellent adsorption properties and have the ability to regenerate and reuse. In this work, we have used a magnetic polymer sorbent based on glycidyl methacrylate (GMA) for removal of arsenate ions. In order to study the kinetics, mechanism and equilibrium of the removal process, the experimental data were analyzed by seven kinetic models and eight isotherm models. Also, the thermodynamic parameters were calculated to determine the feasibility, spontaneity, energy content, and degree of disorderliness of the process.

EXPERIMENTAL

The magnetic polymer sorbent based on GMA was synthesized by in-situ suspension copolymerization in the presence of nanoparticles of magnetite coated with (3-aminopropyl) trimethoxysilane and functionalized with diethylenetriamine according to the procedure described in our previous study [5]. Kinetic, equilibrium and thermodynamic studies of arsenate removal by magnetic polymer sorbent were carried out in non-competitive batch conditions at unadjusted pH

and dosage of sorbent of 10 g/L. The arsenate concentrations in solution were determined by inductively coupled plasma optical emission spectrometry (iCAP6500, Thermofisher Scientific, USA). Kinetic and isotherm parameters were estimated with the non-linear regression method.

RESULTS AND DISCUSSION

For analysis of the kinetic data, pseudo-first order model, pseudo-second-order model, as well as Elovich and fractional power model were used [6]. The resulting kinetic parameters and error function data are presented in Figure 1a and Table 1. Arsenate ion sorption kinetics discovers that removal was rapid during the first 25 min but subsequently decreased slightly and plateaued after approximately 60 min. The highest correlation coefficient ($R^2 = 0.987$) and the lowest Chi-square value ($\chi^2 = 0.005$), indicate the pseudo-second-order model is the best fit for arsenate ion sorption. Also, the sorption capacity at the equilibrium value obtained by the pseudo-second-order model ($Q_e^{cal} = 0.60$ mg/g) agrees very well with experimental sorption capacity ($Q_e^{exp} = 0.59$ mg/g) meaning that chemisorption plays an important role in the arsenate sorption onto magnetic polymer sorbent.
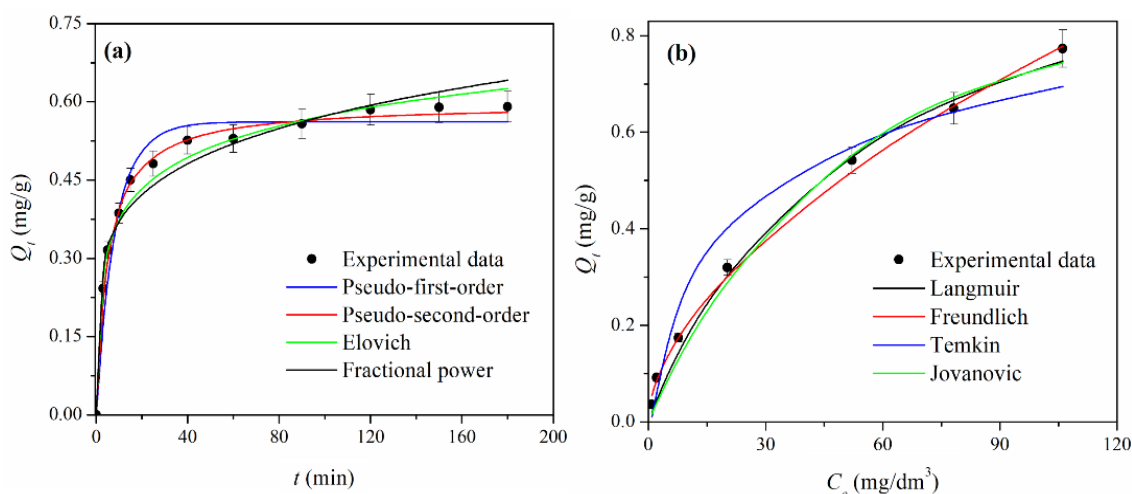
Figure 1. Predicted curve fits for the (a) kinetics and (b) two-parameters equilibrium isotherms of arsenate sorption onto magnetic polymer sorbent.

Table 1. Kinetic parameters and error function data for arsenate sorption onto magnetic polymer sorbent

Pseudo-first-order		Pseudo-second-order		Elovich		Fractional power	
k_1(1/min)	0.13	k_2 (g/mg min)	0.34	α	0.68	k_{FP} (mg/g)	0.24
Q_e^{cal} (mg/g)	0.56	Q_e^{cal} (mg/g)	0.60	β (g/mg min)	11.61	v(1/min)	0.19
R^2	0.924	R^2	0.987	R^2	0.960	R^2	0.919
χ^2	0.051	χ^2	0.005	χ^2	0.014	χ^2	0.030

Table 2. Sorption mechanism parameters for arsenate sorption onto magnetic polymer sorbent

Intra-particle diffusion model				Bangham diffusion model		Liquid film diffusion model	
Stage	I	II	III				
k_{id}(mg/g min$^{0.5}$)	0.09	0.03	0.01	$k_B \cdot 10^3$ (1/g)	0.21	k_{LFD}(1/min)	0.02
C_{id} (mg/g)	0.09	0.33	0.45	α	0.22	C_{LFD}	-0.84
R^2	0.985	0.999	0.986	R^2	0.913	R^2	0.963

In order to further clarify the rate–determining step and sorption mechanism of the removal process of arsenate ions by magnetic polymer sorbent, the intra-particle diffusion model, Bangham model, and liquid film diffusion model were used and the resulting parameters are shown in Table 2. The high values for the coefficient of determination ($R^2 > 0.900$) for intra-particle diffusion, Bangham, and liquid film diffusion model suggest the influence of pore diffusion as well as film diffusion on the arsenic removal process by magnetic polymer sorbent.

The equilibrium data obtained at different initial arsenate concentrations were fitted using Langmiur, Freundlich, Temkin, Jovanovic, Redlich–Peterson, Sips, Toth and Khan isotherm models [6]. Experimental data and the predicted two-parameters isotherms models by nonlinear analysis for the sorption of arsenate by magnetic polymer sorbent are shown in Figure 1b. The parameters for eight isotherms nonlinear fit are presented in Table 3. According to the high R^2 and the low χ^2 values, the Freundlich (two-parameters), Redlich–Peterson, Sips and Khan (three-parameters) isotherms provided a better fit than the other used models. These results suggested that sorption is favorable on the investigated magnetic polymer sorbent as well as that reversible sorption has a significant role in the arsenate sorption process.

Table 3. Isotherm parameters and error function data for arsenate sorption onto magnetic polymer sorbent

Two-parameters isotherm models							
Langmuir		Freundlich		Temkin		Jovanovic	
Q_{max} (mg/g)	1.09	K_F(L^n mg^{1-n}/mg)	0.06	b_T (kJ/mol)	15.29	$Q_{m,J}$ (mg/g)	0.81
K_L (L/mg)	0.02	n	1.81	K_T (L/mg)	0.69	K_J	0.02
R^2	0.991	R^2	0.998	R^2	0.940	R^2	0.987
χ^2	0.070	χ^2	0.007	χ^2	0.158	χ^2	0.114
Three-parameters isotherm models							
Redlich–Peterson		Sips		Toth		Khan	
A (L/g)	0.10	$Q_{m,S}$ (mg/g)	3.13	Q_T(mg/g)	0.42	Q_K(mg/g)	0.09
B (L/mg)	1.05	$K_S \cdot 10^4$ (L^β/mg^β)	1.62	K_T (L/g)	0.04	K	0.63
g	0.53	β	0.64	t	0.45	n	0.49
R^2	0.999	R^2	0.999	R^2	0.998	R^2	0.999
χ^2	0.003	χ^2	0.004	χ^2	0.007	χ^2	0.003

Thermodynamic parameters such as the standard Gibb's free energy change ($\Delta G°$), the standard enthalpy change ($\Delta H°$) and the standard entropy change ($\Delta S°$) were determined from Van't Hoff equation [6]. The calculated values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ for arsenate sorption by magnetic polymer sorbent at different temperatures are given in Table 4.

Table 4. Thermodynamic parameters for arsenate sorption by magnetic polymer sorbent

T, K	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/Kmol)	$T\Delta S°$ (kJ/mol)
298	-1.35			47.22
313	-3.25	45.87	0.16	49.12
328	-6.26			52.13
343	-8.48			54.35

At all investigated temperatures, the $\Delta G°$ values were negative, indicating the feasible and spontaneous nature of arsenate sorption. Sorption of arsenate was more favorable at higher

temperatures due to higher negative $\Delta G°$ values. The positive values of $\Delta H°$ for arsenate removal suggest that the sorption is endothermic in nature, while the positive values of $\Delta S°$ implied an increase in the degree of dispersion of the sorbed arsenate ions.

CONCLUSION

In this work, the sorption behavior of arsenate ions onto magnetic polymer sorbent was investigated. The kinetic data were analyzed using the pseudo-first-order, pseudo-second-order, Elovich, power function, intra-particle diffusion, Bangham and liquid film diffusion models while the equilibrium data were analyzed using Langmuir, Freundlich, Temkin, Jovanovic, Redlich–Peterson, Sips, Toth and Khan isotherm models. The sorption process followed the pseudo-second-order model with the evident influence of the pore and film diffusion. Equilibrium experimental results are the best fitted by the Freundlich, Redlich–Peterson, Sips, Toth as well as Khan isotherm model. Thermodynamic parameters demonstrated that the sorption process was spontaneous and endothermic.

REFERENCES

[1] H. Garelick, H. Jones, A. Dybowska, E. Valsami-Jones in: Reviews of Environmental Contamination, Vol. 197, D. M. Whitacre (Ed.), Springer, New York, 2009.
[2] B. Liu, K. Kim, V. Kumar, S. Kim, J. Hazard. Mater., 388 (2020) 121815.
[3] T. S. Y. Choong, T. G. Chuah, Y. Robiah, F. L. G. Koay, I. Azni, Desalination, 217 (2007) 139.
[4] G. M. Sawood, S. K. Gupka, Appl. Water Sci., 10 (2020) 131.
[5] B. M. Marković, V. V. Spasojević, A. Dapčević, Z. M. Vuković, V. B. Pavlović, D. V. Randjelović, A. B. Nastasović, Hem. Ind., 73 (2019) 25.
[6] A. Nastasović, B. Marković, Lj. Suručić, A. Onjia, Metals, 12 (2022) 814.