



PHYSICAL CHEMISTRY 2018

14th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume II

September 24-28, 2018
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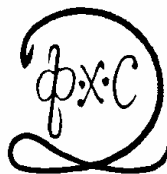
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PHYSICAL CHEMISTRY 2018

*14th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

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*The Society of Physical Chemists of
Serbia*

in co-operation with

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and

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KINETICS AND THERMODYNAMICS OF Mo(VI) AND Re(VII) SORPTION ON AMINO-FUNCTIONALIZED MAGNETIC POLYMER

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ABSTRACT

Kinetics and thermodynamics of Mo(VI) and Re(VII) sorption onto amino functionalized magnetic poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) [mPGME-deta] at 298 K and pH=4.0 were investigated. It was shown that Mo(VI) and Re(VII) sorption obeys the pseudo-second-order model with evident influence of pore diffusion. The maximum sorption capacity of 60 mg/g for Mo(VI) and 47 mg/g for Re(VII) were observed. Thermodynamic studies implied an endothermic and spontaneous process in nature.

INTRODUCTION

Molybdenum (Mo) is an essential element to all species. However, it can be highly toxic at larger doses and cause serious health problems, like anemia, liver and kidney abnormalities, sterility, etc. [1]. Typical industrial sources of waste molybdenum include pigments, lubricants, catalysts, fertilizer, and corrosion control chemicals. In aqueous environment, Mo exists mainly as molybdate and/or other molybdenum polyanions, depending on the solution pH and the initial metal concentration [2]. Rhenium (Re) does not occur freely in nature. It is mainly obtained as a by-product of the extraction and refinement of molybdenum and copper ores. Re is widely used for high temperature superalloy productions, in chemical and petrochemical industry, etc. So far, various mineral substances, natural materials, polymers and bioadsorbents have been studied as Mo(VI) and Re(VII) adsorbents [3-5].

EXPERIMENTAL

Magnetic macroporous mPGME nanocomposite of glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA) was prepared by suspension copolymerization in the presence of suspended magnetite nanoparticles and functionalized with diethylene triamine ($V_s=0.99 \text{ cm}^3/\text{g}$, $S_{Hg}=59 \text{ m}^2/\text{g}$, $D_{V/2}=104 \text{ nm}$), as described elsewhere [5]. The Mo(VI) and Re(VII) sorption kinetics was tested in batch non-competitive experiments ($T=298 \text{ K}$, $\text{pH}=4.0$). In each experiment, 0.3 g of mPGME-deta was added into 30 ml of aqueous solutions containing Mo(VI) ($C_i= 0.01$) or Re (VII) ($C_i= 0.005$). Sample aliquots were withdrawn at the predetermined time intervals and analyzed with ICP-OES.

RESULTS AND DISCUSSION

Sorption kinetic data were analyzed using the surface-reaction (pseudo-first-order, PFO and pseudo-second-order, PSO) and particle diffusion-based (intraparticle diffusion, IPD) [6] kinetic models to investigate the controlling mechanism of Mo(VI) and Re(VII) sorption by mPGME-deta.

The plots for the PSO and IPD models are shown in Figure 1.

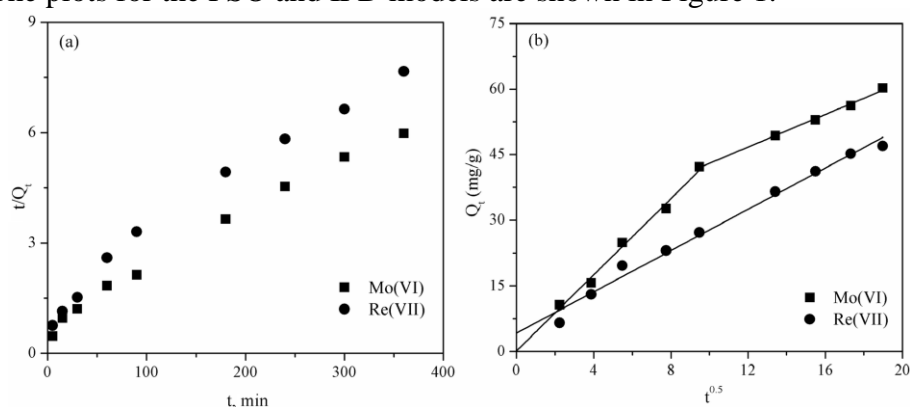


Figure 1. (a) PSO and (b) IPD kinetics for Mo(VI) and Re(VII) sorption on mPGME-deta ($\text{pH} = 4$, $T = 298 \text{ K}$).

Kinetic parameters calculated from these models are presented in Table 1, where: Q_t -amount of sorbed metal ions at time t , Q_e -amount of sorbed metal ions at equilibrium, k_1 -PFO rate constant, k_2 -PSO rate constant, k_{id} -IPD coefficient, C_{id} -intercept of IPD plot, S -rate parameter.

Table 1. The kinetic parameters for Mo(VI) and Re(VII) sorption on *m*PGME-deta (pH=4.0, *T*=298K)

	Mo(VI)	Re(VII)
Q_e^{exp} , mg/g	60	47
pseudo-first-order		
$k_1 \cdot 10^3$, 1/min	8.06	9.21
Q_e^{calc} , mg/g	46.4	42.2
R^2	0.987	0.960
pseudo-second-order		
$k_2 \cdot 10^3$, g/(mg min)	0.32	0.32
Q_e^{calc} , mg/g	65.8	52.6
R^2	0.992	0.982
intraparticle diffusion		
k_{1id} , mg/(g min ^{0.5})	4.35	2.35
C_{1id} , mg/g	0.14	4.22
R_1^2	0.991	0.987
k_{2id} , mg/(g min ^{0.5})	1.86	/
C_{2id} , mg/g	24.3	/
R_2^2	0.997	/

As it can be seen from Table 1, the Q_e values predicted by the PSO model agree very well with experimental Q_e values with rather high R^2 values. According to the IPD model, if a $Q_t-t^{1/2}$ plot is a straight line, IPD is the only rate-controlling step. If the data exhibit multi-linear plots, two or more steps influence the sorption process. The IPD plot for Mo(VI) sorption on *m*PGME-deta has two straight lines with different slopes with high R^2 (>0.99) indicating that two diffusion steps are involved in the sorption process. The first stage (the sharper portion)

represents the fast sorption over the outer surface and in the macropores, while the second one could be attributed to the IPD through mesopores. The IPD plot for Re(VII) sorption gives a straight line, indicating the IPD influence.

Table 2. Thermodynamic parameters for Mo(VI) and Re(VII) sorption onto *m*PGME-deta.

<i>T</i> , <i>K</i>	Mo(VI)				Re(VII)			
	$-\Delta G^\circ$, kJ mol ⁻¹	E_a , kJ mol ⁻¹	$T\Delta S^\circ$, kJ mol ⁻¹	ΔH° , kJ mol ⁻¹	$-\Delta G^\circ$, kJ mol ⁻¹	E_a , kJ mol ⁻¹	$T\Delta S^\circ$, kJ mol ⁻¹	ΔH° , kJ mol ⁻¹
298	7.50	35.1	104.5	97.0	4.38	43.1	17.3	12.9
313	12.8		109.8		5.25		18.1	
328	18.0		115.0		6.12		19.0	
343	23.3		120.3		6.99		19.9	

Thermodynamic parameters (ΔG° - free energy of adsorption, ΔH° -enthalpy change and ΔS° -entropy change) were determined from Van't Hoff equation. The activation energy, E_a , was calculated from the linearized

Arrhenius equation. The positive ΔH° values (Table 2) implies endothermic nature of Mo(VI) and Re(VII) sorption, characteristic for the chemical sorption. Also, the calculated E_a values for Mo(VI) and Re(VII) are outside the range of values of 8–22 kJ mol⁻¹ for diffusion-controlled processes [7]. The negative ΔG° values indicate that Mo(VI) and Re(VII) sorption is spontaneous, while the positive ΔS° values suggest an increased randomness at the solid–solution interface.

CONCLUSION

The rate-controlling mechanisms of Mo(VI) and Re(VII) sorption onto mPGME-deta was analyzed using PFO, PSO and IPD kinetic models. The sorption kinetics for both anions adhered to the PSO model, implying an important role of chemisorption in the sorption process, with the evident influence of the intraparticle diffusion. Thermodynamic parameters revealed spontaneous and endothermic nature of Mo(VI) and Re(VII) adsorption with increased randomness in the system.

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