

COMPARISON OF CR(VI) ADSORPTION ONTO POLYMER-BASED MAGNETIC HYBRID ADSORBENTS BY NONLINEAR ISOTHERM AND KINETIC MODELS

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Abstract— In the present study, polyglycidyl methacrylate graft copolymer (PG) and ethylene glycol dimethacrylate based polymers (EG) were synthesized and modified by iron oxides in order to have magnetic form (PG-M and EG-M). Batch hexavalent chromium (Cr(VI)) adsorption experiments were carried out as a function of pH. Adsorption data were applied to Langmuir, Freundlich, Dubinin-Raduskevich, Sips, Toth and Redlich-Peterson isotherm models by utilizing non-linear techniques. The Dubinin-Radushkevich isotherm model was found to be the most suitable one for PG-M sample, while Langmuir model fitted best to the experimental data of EG-M sample. The contact time needed for both adsorbents was relatively short, ranging from 1 to 30 min. Approximately 73% of Cr(VI) was rapidly removed by PG-M within ten minutes; and for EG-M sample, 88% of Cr(VI) was removed at the end of five minutes. The rate of the adsorption is governed by a pseudo-second order rate equation.

Keywords— Polymer, magnetic separation, Cr(VI) adsorption, nonlinear isotherm, kinetic model

I. INTRODUCTION

Chromium (Cr) is considered as a high priority environmental pollutant and it is on the top-priority list of toxic pollutants defined by the U.S. Environmental Protection Agency (EPA). According to the EPA reports, 29 million pounds of chromium is discharged from rainwater, and almost 100,000 pounds of chromium is released from surface water discharges per year (Luther *et al.*, 2013). Large amount of wastewater containing chromium has been released into the environment due to the erosion of certain rocks and volcanic eruptions and due to the industry processes such as electroplating, wood protection, leather tanning, magnetic tapes, pigments, metal finishing, electrical and electronic equipment, textile industries and chromate preparation (Singh *et al.*, 2011; Kimbrough *et al.*, 1999). Chromium essentially exists in the environment in two forms namely hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)]. Especially Cr(VI) is considered as one of the top 16 toxic pollutants because of its carcinogenic and teratogenic properties and threatens the natural life and public health (Bansal *et al.*, 2009).

Exposure to Cr(VI) causes health problems of epigastria, nausea, vomiting, severe diarrhea, dermatitis, kidney, liver and gastric damage (Yao-Xing *et al.*, 2011). The permitted maximum level of Cr(VI) into the inland surface water and potable water are 0.1 mg/L and 0.05 mg/L respectively. Therefore, Cr(VI) must be removed from contaminated-water before discharging into the environment in order to protect the living organisms (Nethaji *et al.*, 2013).

Several kinds of material were used as adsorbents for Cr(VI) removal, such as activated carbon, polymers, sands, zeolites, agriculture waste, etc. Recently functionalized polymers have been widely used as effective adsorbents in remediation of water according to their mechanical properties and capability of numerous functionalization possibilities. However, these kinds of adsorbents suffer from a common problem that it needs a next separation process from the solution, which increases the operation cost. Therefore, studies have focused on preparation new magnetic hybrid adsorbents using iron oxides.

Iron (oxy-hydr) oxides have been widely used adsorbents for chromium removal due to their excellent removal capacity. Compared with traditional adsorbents, they have extremely high surface area to volume ratio and short diffusion rate, which resulted in high removal efficiency and favorable kinetics for selective sorption. However, these tiny particles cannot be used in fixed-bed columns or any plug-flow-type configuration due to excessive pressure drops. Supporting of high-capacity magnetite nanoparticles into/onto porous matrix of larger size such as functionalized polymeric materials was proven to be effective method in wastewater treatment. The polymer-based magnetic hybrid adsorbents are also good candidates for selective adsorption properties with ease of phase separation, less susceptibility to fouling by natural organic matters, and durability (Bilgin Simsek *et al.*, 2012).

The objective of present study is to investigate the Cr(VI) adsorption efficiency of two polymer-based magnetic hybrid adsorbents. For this reason, polyglycidyl methacrylate graft copolymer (PG) and ethylene glycol dimethacrylate based polymers (EG) were magnetically activated by iron oxides. Batch adsorption experiments were carried out as a function of pH. Adsorption data were applied to the Langmuir,

Freundlich, Dubinin-Raduskevich, Sips, Toth and Redlich-Peterson isotherm models. The Cr(VI) adsorption kinetics were tested by using pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich kinetic models.

II. METHODS

A. Synthesis of Polymer-Based Magnetic Hybrid Adsorbents

Polyglycidyl methacrylate graft copolymer (PG) was synthesized by using atom transfer radical polymerization technique (Senkal *et al.*, 2007). Ethylene glycol dimethacrylate copolymer beads were produced by the suspension polymerization method (Senkal *et al.*, 2006).

The magnetic hybrid sorbent were prepared by coprecipitating Fe^{2+} and Fe^{3+} ions in NaOH solution by treating under hydrothermal conditions. The initial molar ratio of $\text{Fe}^{3+}:\text{Fe}^{2+} = 2:1$ was chosen for the production of Fe_3O_4 . Defined amount of polymer beads were added to aqueous solution containing FeCl_2 and FeCl_3 under vigorous stirring at 338 K. NaOH was added drop-wise into the solution till pH 10-11. Then, the precipitate was separated by an external magnetic field and rinsed with distilled water until neutral pH. The resultant magnetic adsorbents prepared by using PG and EG polymer beads were denoted as PG-M and EG-M, respectively.

B. Characterization

Potentiometric titration data for the adsorbents were obtained using a method described by Helfferich (1995). Basic titration data was transformed into proton-binding isotherms using a proton balance equation and a theoretical blank reference. The electrophoretic mobilities of the equilibrated samples were measured using a Malvern Instruments Zetasizer 3000HSA. XRD measurement was performed on a Philips Panalytical XPert Pro X-ray diffractometer using $\text{CuK}\alpha$ radiation. Magnetic characterization of PG-M and EG-M sorbents was conducted with magnetometer (Micromag 2900, Measurements, Princeton, USA).

C. Adsorption Experiments

Adsorption experiments were carried out using batch equilibration techniques. The effect of solution pH (2.0, 4.0, 6.0, 10.0) on adsorption was investigated with initial concentration of 30 mg/L at 298 K. Adsorption isotherms were obtained by varying amount of adsorbents. The suspensions were shaken at 130 rpm in a platform shaker at ambient temperature. pHs of the suspensions were kept constant during adsorption experiments and adjusted with NaOH or HCl twice a day. Once the equilibrium was established, suspension was filtered with a blue band filter paper. Experimental adsorption capacities were calculated by using the following equation:

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

where q_e is adsorption capacity (mg/g), C_0 and C_e are the Cr(VI) initial and equilibrium concentrations (mg/L),

respectively. V is the volume of the Cr(VI) solutions and m is the weight of adsorbent (g).

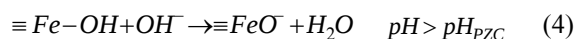
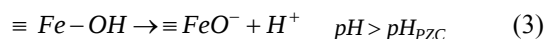
Kinetic experiments were conducted in a 500 mL glass vessel with of initial Cr(VI) concentration of 30 mg/L. Equilibrium Cr(VI) concentration in the aqueous solution was determined by UVvis spectrophotometer (Analytic Jena Specord 40 UV) at 540 nm.

The relationship between adsorbed Cr(VI) and the concentrations at equilibrium was described by two- and three-parameter isotherm models: Freundlich, Langmuir, Dubinin-Radushkevich, Redlich-Peterson, Sips, and Toth using the Statistica 8.0 programme. The kinetic data were applied to pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich models.

III. RESULTS AND DISCUSSION

A. Characterization

The proton binding curve which crosses the pH axis is called the point of zero charge (PZC) and defined as the pH value at which the net surface charge of the adsorbent is zero and changes depending on the type and number of functional groups present on the adsorbent (Bilgin Simsek *et al.*, 2012). The point of zero charge (pH_{PZC}) of PG-M and EG-M were about 6.3 and 6.8, respectively (Table 1). Below the pH_{PZC} , the adsorbent surface has positive charge and affinity to anions. On the other hand, above the pH_{PZC} adsorbent surface is negatively charged, and cation adsorption occurs. Dissociation reactions of magnetic polymers surface can be shown by Equations (2-4):



An important tool used to characterize the electrokinetic behavior of a solid-liquid interface is the electrophoretic mobility. The pH value at this point is called the isoelectric point (IEP) of the interface. The IEP for PG-M sample is 8.5, while that for EG-M is 7.8. The reason for higher pH_{IEP} values of samples is probably due to the fact that their surfaces have much positive groups of iron oxides.

According to the magnetic characterization (Fig.1); the saturation magnetization value of EG-M was found as 40.7 emu/g, while that of for PG-M was obtained as 21.6 emu/g. The magnetization values were found higher for both samples indicating ferromagnetic form has covered the polymeric surfaces.

The XRD pattern of both samples (data not shown) indicated characteristic peaks at about $2\theta=30.16^\circ$, 35.63° , 42.24° and 62.58° related to the Fe_3O_4 phases. The patterns also showed that the surface of magnetically activated sorbent was coated pure Fe_3O_4 .

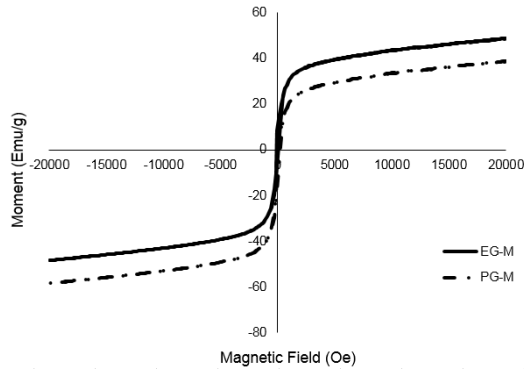


Fig. 1. Magnetization curves of samples

B. Adsorption Experiments

It is well known that pH is a critical and an important parameter in adsorption process as it influences chemical speciation of metal ions and active functional sites on surface of sorbent (Kragovic *et al.*, 2012; Chutia *et al.*, 2009). The maximum Cr(VI) adsorption capacities of PG-M and EG-M were determined at pH 4 as 106.2 and 78.2 mg/g, respectively (Fig. 2). The magnetic hybrid adsorbents have considerably high Cr(VI) sorption capacities when compared with other capacities of similar adsorbents reported in the literature (Hu *et al.*, 2005; Bayramoglu and Arica, 2008; Yuan *et al.*, 2009; Gang *et al.*, 2010).

Cr(VI) ions exist in several stable forms in aqueous solution. CrO_4^{2-} is predominant in basic solutions, while HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ are predominant at pH 2.0–6.0. It is possible that, under acidic conditions amine groups in PG-M and EG-M samples might be protonated and the HCrO_4^- anions attract $-\text{NH}_3^+$ groups. Therefore, electrostatic attraction could be responsible for that high adsorption capacity at this pH range. Moreover, due to the combined effects of Fe oxides and amine groups, -under acidic pH- higher Cr(VI) adsorption occurred via electrostatic interaction and complex formation with Lewis acid base reaction. Fe_3O_4 has FeOH_2^+ surface groups in aqueous solution and complex formation might be occurred between FeOH_2^+ and $\text{HCrO}_4^-/\text{CrO}_4^{2-}$. FeOH_2^+ surface groups act as electron acceptors (Lewis acid) while chromium species act as electron donors (Lewis base).

With increasing pH, maximum adsorption capacity of PG-M reduced to 27.82 mg/g at pH 10, while that of EG-M was found as 10.12 mg/g. The decrease in removal capacity above pH_{PZC} is attributed to the electrostatic repulsion between negatively charged surface groups and chromium ions and to the competition with OH^- ions in the reaction mixture. Moreover, the amine groups are dissociated at about pH of 10; hence, electrostatic repulsion is occurred resulting in declining adsorption capacity. It can be also mentioned that, increasing pH leads to shift the formation of HCrO_4^- to CrO_4^{2-} , which needed two active sites because of two minus charges of it. So, the interaction between the adsorbent surface and the CrO_4^{2-} anions are weaker.

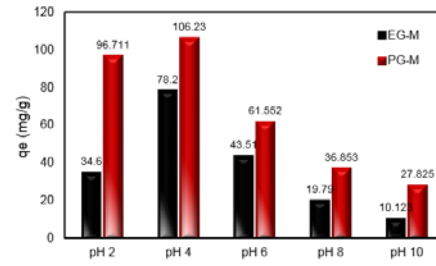


Fig. 2. Effect of pH on Cr(VI) adsorption

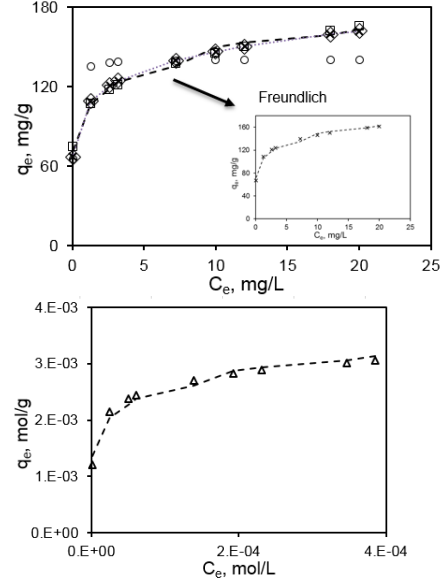


Fig. 3. Adsorption isotherms of EG-M (---: Experimental, ○: Langmuir, □: Sips, ◇: Toth, ×: Freundlich,: R-P, △: D-R)

Moreover, the effect of three different temperature 298, 308 and 318 K on Cr(VI) adsorption was investigated. The adsorption affinity of samples was increased by increasing temperature indicating exothermic nature of process. Enthalpy change of Cr(VI) adsorption was calculated as -24.65 kJ/mol and -11.84 kJ/mol for EG-M and PG-M adsorbents, respectively. These low values of enthalpy change demonstrated that the electrostatic interaction is the main mechanism for Cr(VI) adsorption onto both sorbents.

C. Isotherm Models

In order to evaluate the conformity of applied isotherms to experimental data, the coefficient of determination (R^2) and Chi-square values (χ^2) were calculated (Table 1) and experimental and theoretical capacities were given in Fig 3 and 4.

The obtained results for PG-M showed that the best-fitted adsorption isotherm models were in the order of: Dubinin-Raduskevich > Sips > Redlich-Peterson > Toth > Freundlich > Langmuir, on the basis of high regression coefficients (R^2) and lower χ^2 values. Among the two-parameter models Dubinin-Raduskevich -which assumes constant sorption potential- and among the three-parameter models Sips isotherms describe with satisfaction of the equilibrium data.

However, for EG-M sample Langmuir model fitted best to the experimental data indicating homogenous reactions occur during adsorption process.

D. Adsorption Kinetics

The controlling mechanism of the adsorption process was investigated by fitting the experimental data with pseudo-first-order (Fig. 5), pseudo-second-order (Fig. 6), intra-particle diffusion (Fig. 7) and Elovich (Fig. 8) kinetic models. According to experimental and theoretical kinetic data in Table 2, the experimental results obtained for the Cr(VI) adsorption onto PG-M and EG-M sorbents were found to obey the second-order kinetic and the intra particle diffusion. The theoretical capacity values estimated from the first-order kinetic model gave significantly different values compared to experimental values (q_{exp}), and the correlation coefficients were also found to be lower. This indicates that pseudo first-order equation might not be sufficient to describe the mechanism of Cr(VI) adsorption system.

The correlation coefficients (R^2) for the pseudo second-order kinetic model are in the range of 0.994–0.999 and the theoretical q_e (cal) values were closer to the experimental q_e (exp) values. The pseudo-second-order model is based on the assumption that the rate-determining step might be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

Table 1. Isotherm constants for Cr(VI) adsorption onto adsorbents (pH 4, C_0 : 30 mg/L)

Isotherm model	PG-M	EG-M
Langmuir	Q:	140.57
	b:	20.017
	R^2 :	0.6506
	χ^2 :	12.513
Freundlich	K_F :	105.151
	n:	6.970
	R^2 :	0.9909
	χ^2 :	0.3087
Dubinin-Raduskevich	Q:	0.004679
	β :	1.1 E-09
	R^2 :	0.9722
	χ^2 :	1.5 E-05
Toth	q_{mT} :	7.9 E+34
	K_T :	5.9644
	m_T :	2.0 E-03
	R^2 :	0.9907
Redlich-Peterson	K_{RP} :	4.2 E+09
	α_{RP} :	4.0 E+07
	β_{RP} :	8.5 E-01
	R^2 :	0.9909
Sips	q_{ms} :	0.0265
	K_S :	1.000
	m_S :	0.00003
	R^2 :	0.9908
Sips	q_{ms} :	0.0265
	K_S :	1.000
	m_S :	0.00003
	R^2 :	0.9908
Sips	q_{ms} :	0.0265
	K_S :	1.000
	m_S :	0.00003
	R^2 :	0.9908

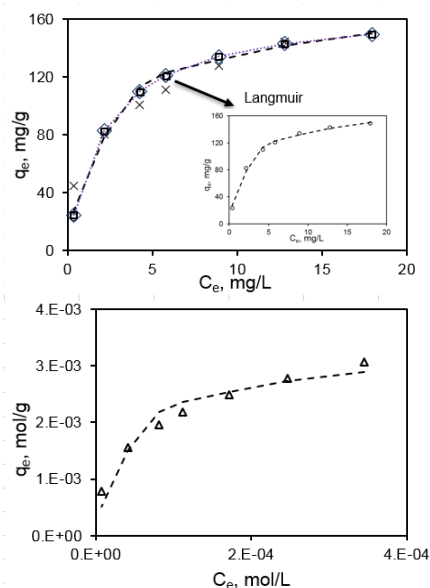


Fig. 4. Adsorption isotherms of EG-M (---: Experimental, $\circ$: Langmuir, $\square$: Sips, $\diamond$: Toth, $\times$: Freundlich, $\cdots$: R-P, Δ : D-R).

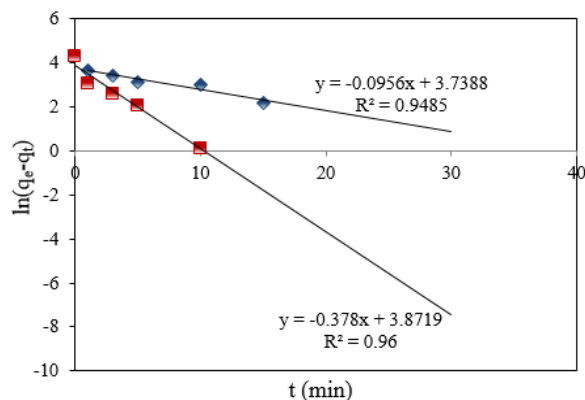


Fig. 5. Pseudo first order kinetic model for Cr(VI) adsorption onto PG-M ($\diamond$) and EG-M ($\square$)

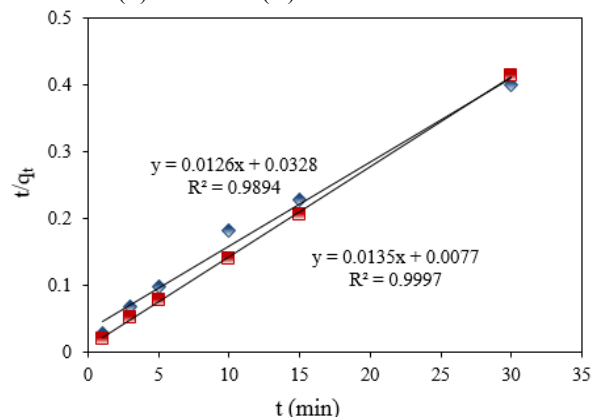


Fig. 6. Pseudo second order model for Cr(VI) adsorption onto PG-M ($\diamond$) and EG-M ($\square$)

Moreover, the plots of q_t versus $t^{0.5}$ indicates that the intra-particle diffusion models well the Cr(VI) adsorption processes (Fig. 7). The correlation coefficients of intra-particle model were in the range of 0.994–0.999 for both rapid and slow reactions. It is clear from the figure that two linear consecutive steps are observed: first linear portion (fast reaction) and second linear part (slow reac-

tion). In the first portion, approximately 73% of Cr(VI) was rapidly uptaken by PG-M within ten minutes; and for EG-M sample, 88% of Cr(VI) was removed within five minutes. This could be attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surface (Kumar *et al.*, 2009). The second phase indicates very slow diffusion of the adsorbate from the surface site into the inner pores.

Table 2. Kinetic model parameters of samples

Sample	PG-M	EG-M
q_{exp} (mg/g)	75.0	72.5
<i>Pseudo-First-order</i>		
q_e (mg/g)	42.04	35.21
k_1 (1/min)	0.220	0.769
R^2	0.948	0.960
<i>Pseudo-Second-order</i>		
q_e (mg/g)	79.53	74.18
k_2 (g/mg.min)	0.004	0.023
h (mg/g.min)	30.42	129.62
R^2	0.984	0.999
<i>Intra-particle diffusion</i>		
k_{id-1} (mg/g.min ^{0.5})	9.026	9.514
R^2	0.936	0.989
k_{id-2} (mg/g.min ^{0.5})	15.16	15.82
R^2	0.999	0.999
<i>Elovich</i>		
β (g/mg)	0.087	0.142
α (mg/g.min)	211.89	11.708
R^2	0.959	0.930

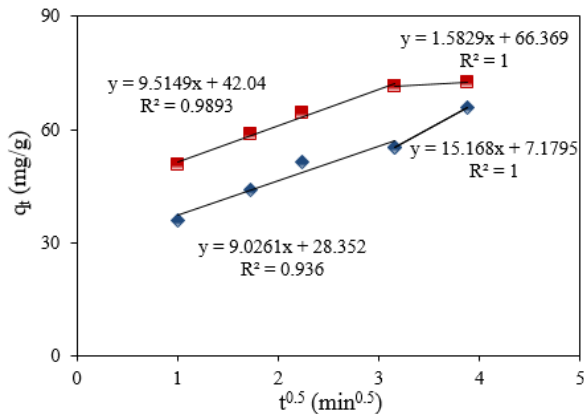


Fig. 7. Intra-particle diffusion model for Cr(VI) adsorption onto PG-M (♦) and EG-M (■)

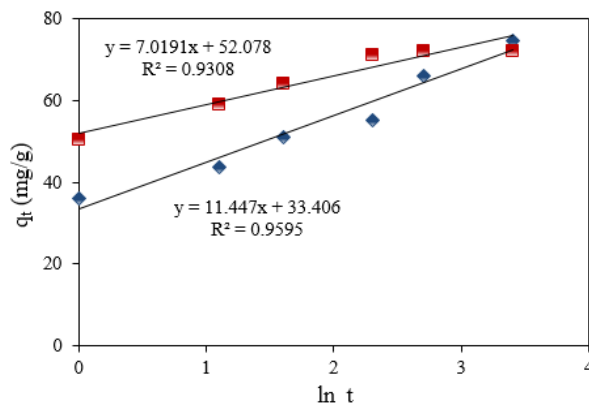


Fig. 8. Elovich model for Cr(VI) adsorption onto PG-M (♦) and EG-M (■)

The Elovich equation plots for the Cr(VI) adsorption are shown in Fig. 8. The plots are fairly linear. The R^2 values are quite high and show good fit according to the R^2 value of 0.93 and 0.95 for EG-M and PG-M, respectively. Thus, it could be said that Elovich equation is a good model for the sorption process.

IV. CONCLUSIONS

In the present study, polymer-based magnetic hybrid sorbents as PG-M and EG-M have been successfully synthesized using co-precipitation method. The magnetically activated adsorbents showed good adsorption capacity for Cr(VI) ions. The maximum adsorption capacity was observed under acidic pH. It was concluded that the electrostatic attraction could be responsible for that high adsorption capacity at this pH range. The equilibrium distributions of Cr(VI) ions between magnetic hybrid sorbents and liquid phases were modelled by isotherm equations. The Dubinin–Radushkevich isotherm model was found to be the most suitable one for PG-M sample, while Langmuir model fitted best to the experimental data of EG-M sample. The contact time needed for both adsorbents was relatively short, ranging from 1 to 30 min. The rate of the adsorption is governed by a pseudo-second order rate equation indicating that the rate-determining step might be chemical sorption.

Considering with the conventional separation techniques, magnetic separation is an advantageous method due to its rapidness, efficiency and simplicity.

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