



## Adsorption intrinsic kinetics and isotherms of lead ions on steel slag

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### ABSTRACT

Batch experiments were carried out to investigate the kinetics of adsorption of lead ions by steel slag on the basis of the external diffusion, intra-particle diffusion and adsorption reaction model (pseudo-first-order, pseudo-second-order). The results showed that the controlling step for the adsorption kinetics changed with the varying experimental parameters. When the particle size of steel slag was larger than 120 mesh, intra-particle diffusion of  $\text{Pb}^{2+}$  was the controlling step, and when the initial concentration of  $\text{Pb}^{2+}$  was less than  $150 \text{ mg L}^{-1}$  or the shaking rate was lower than 150 rpm, external diffusion of  $\text{Pb}^{2+}$  was promoted. Contrary to the former experimental conditions the adsorption reaction was the controlling step, and the adsorption followed second-order kinetics, with an adsorption rate constant of  $13.26 \text{ g mg}^{-1} \text{ min}^{-1}$ . The adsorption isotherm of  $\text{Pb}^{2+}$  with steel slag followed the Langmuir model, with a correlation coefficient of 0.99.

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### 1. Introduction

It is well known that some metals, such as Cr, Cu, Pb, Sb, Hg and Cd are harmful to life. They are significantly toxic to human beings and ecological environments [1]. Lead, which is a heavy metal, is widely used in many important industrial applications, such as storage battery, manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing, but is also one of the most toxic heavy metals [2]. Its presence in drinking water above the permissible limit ( $5 \text{ mg L}^{-1}$ ) may cause adverse health effects such as anemia, encephalopathy, hepatitis and nephritic syndrome [3]. Therefore, the elimination of these metals from water and wastewaters is important to protect public health. Traditional technologies for the removal of heavy metals from wastewaters include chemical precipitation, ion-exchange, membrane separation, reverse osmosis, evaporation and electrolysis [4–6]. However, most of them do not exhibit high treatment efficiency, especially at metal concentrations in the range of  $0.01\text{--}0.1 \text{ g L}^{-1}$  [1]. Precipitation methods are particularly reliable but require large settling tanks for the precipitation of voluminous alkaline sludges, and a subsequent treatment is needed. Ion-exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. Adsorption on solid solution interface is an important means for controlling the extent

of pollution due to heavy metal ions [1]. Activated carbons are widely used because of their high adsorption abilities for a large number of heavy metal ions. However, the price of activated carbons is relatively high, which limits their usage. This has led many researchers to search for low cost materials such as coal, fly ash, agricultural wastes and biosorbents [7]. In general, an adsorbent can be assumed as “low cost” if it requires little processing, is abundant in nature, or is a by-product or waste material from industry [1].

Steel slags as metallurgical by-products which show a complex mixture of alkali-earth silicates and aluminosilicates formed at high temperatures are being used as filler or in the production of slag cement. It has been reported that granulated steel slag can be converted into an effective adsorbent and used for the removal of dye and metal ions. For its sorptive characteristics, slag has been used in water and wastewater treatments as a low cost adsorbent replacing granular activated carbon (GAC) [8–11]. Adsorptions of dye, nickel, phosphorus, and lead are the examples. The rate at which adsorption takes place is of utmost importance when designing batch adsorption systems; consequently it is important to establish the time dependence of such systems under various conditions. In 1984, McKay [12] developed a model to predict the rate of adsorption of Astrazone Blue dye onto Sorbsil silica which is controlled by the internal mass transport processes based on a pore diffusion mechanism. The author presented a two resistance mass transfer models which are based on film resistance and homogeneous solid phase diffusion for the adsorption. In addition, McKay et al. [13] presented a three-step model for the adsorption of Astrazone Blue dye on peat. In the case of the adsorption of dyes on chitin, McKay et al. [14] found that there is a branched pore mechanism

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**Table 1**  
Composition of the steel slag.

Ingredient	MnO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	Cr <sub>2</sub> O <sub>7</sub>	Others
Contents (%)	3.29	38.83	0.18	12.33	32.73	10.00	0.20	2.44

and that the rate of adsorption of dyes in the initial stages of the adsorption process depends on the film mass transfer coefficient.

The main objective of this study was to investigate the controlling step of adsorption lead ions by steel slag under different experimental conditions, and obtained kinetics of lead ion adsorption on steel slag. The factors studied include the influence of the size of the steel slag particles, initial concentration and adsorption reaction on the diffusion processes and the adsorption isotherms of the system. A rate parameter,  $k$ , has been defined and used to describe the adsorption of lead ion on steel slag and a method for determining the diffusion rate coefficients, using data plotting techniques, has been developed. A comparison of a pseudo-second-order adsorption parameter,  $k_1$ , and a pseudo-first-order rate parameter,  $k_2$ , is also discussed.

## 2. Materials and methods

### 2.1. Materials

The steel slag was obtained from a steelmaking plant in Sichuan province, China. Its composition was determined using an X-ray-fluorescent quantometer type “ARL-72000 S” and is shown in Table 1.

The steel slag was washed with distilled water to remove surface impurities and dried at 100 °C for 24 h, crushed, ground and sieved into various particle size ranges. The BET and mean pore size of the different particle size steel slag were shown in Table 2.

The lead bearing solutions for the experiments were prepared by a suitable dilution of the standard lead nitrate solution (concentration 1000 mg L<sup>-1</sup>) with distilled water. The pH value was maintained at a defined value of 5 regulated by 1 mol L<sup>-1</sup> HNO<sub>3</sub> or NaOH.

### 2.2. Effect of shaking rate on diffusion

At room temperature 20 °C, a 3 g sample of steel slag was added to each 100 mL volume of lead solution (concentration of Pb<sup>2+</sup> was 100 mg L<sup>-1</sup>). The particle size of steel slag was 0.18–0.125 mm. The rates of shaking were 30 rpm, 100 rpm, 150 rpm, 180 rpm, 210 rpm and 240 rpm. The removal efficiency of lead is shown in Fig. 1.

### 2.3. Effect of initial concentration of lead on diffusion

At room temperature of 20 °C, a sample of steel slag was added to each 100 mL volume of lead solution, particle size of steel slag was 0.18–0.125 mm, the rate of shaking was 210 rpm, initial concentrations of lead ion were 10 mg L<sup>-1</sup>, 50 mg L<sup>-1</sup>, 150 mg L<sup>-1</sup>, 200 mg L<sup>-1</sup>, 300 mg L<sup>-1</sup>, 400 mg L<sup>-1</sup>, and 500 mg L<sup>-1</sup>. The mass ratio of liquid/solid was kept constant. The removal of lead is shown in Fig. 2.

**Table 2**  
The BET and mean pore size of the different particle size steel slag.

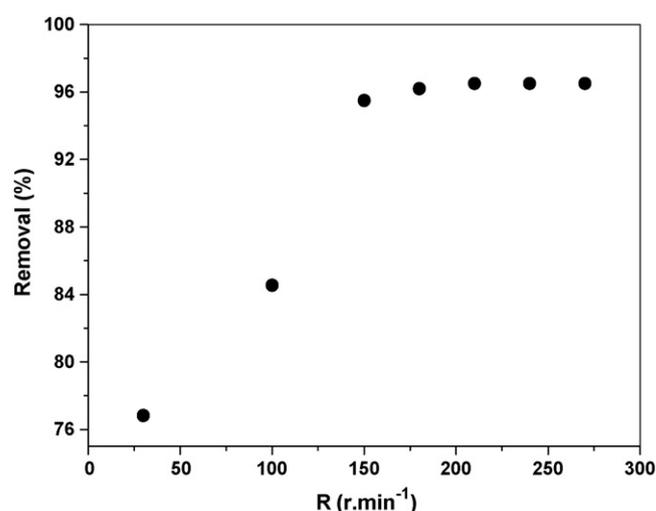
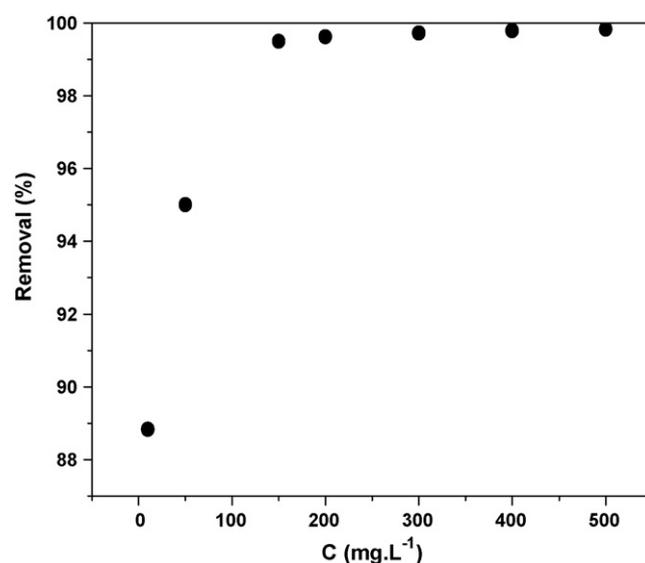
Particle size/mm	BET (m <sup>2</sup> g)	Mean pore size (Å)
0.85–0.425	0.822	266.7
0.425–0.18	1.078	236.8
0.18–0.125	1.354	207.5
0.125–0.08	1.850	170.3

### 2.4. Effect of particle size on diffusion

At room temperature 20 °C, a 3 g sample of steel slag was added to each 100 mL volume of lead solution (100 mg L<sup>-1</sup>). The shaking rate was 210 rpm. The steel slag particle size ranges were 25–18 mm, 18–9 mm, 0.85–0.425 mm, 0.425–0.18 mm, 0.18–0.125 mm, 0.125–0.09 mm, and <0.075 mm. The removal efficiency of lead is shown in Fig. 3.

### 2.5. Sorption dynamics

A 3 g sample of steel slag was added to each 100 mL volume of lead solution. The concentration and shaking rate were selected as 150 mg L<sup>-1</sup> and 210 rpm, respectively. The steel slag particle size was chosen with 0.18–0.125 mm.

**Fig. 1.** Effect of oscillating rate on removal of Pb<sup>2+</sup>.**Fig. 2.** Effect of initial concentration of Pb<sup>2+</sup> on the removal of Pb<sup>2+</sup>.

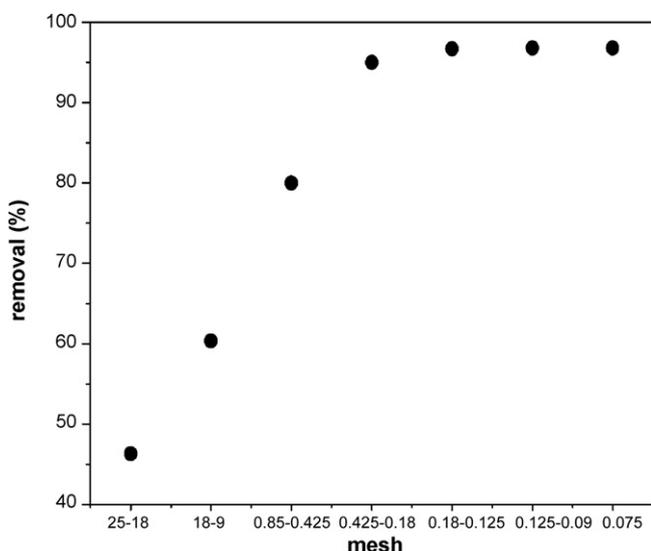


Fig. 3. Effect of the size of steel slag on the removal of  $Pb^{2+}$ .

The suspension was then filtered and the lead concentration in the filtrate and the initial solutions were determined by an atomic absorption spectrophotometer (Model Z-5000, Japan).

The adsorption capacity of lead ion was calculated using the general equation [15,16]:

$$Q = \frac{V(C_0 - C_t)}{m} \quad (1)$$

where  $Q$  is the amount of  $Pb(II)$  ion adsorbed on the steel slag ( $mg\ g^{-1}$ ),  $C_0$  and  $C_t$  are the  $Pb(II)$  concentrations in solution before and after adsorption ( $mg\ L^{-1}$ ), respectively,  $V$  the volume of the medium (L) and  $m$  is the amount of the steel slag used in the reaction mixture (g).

The adsorption efficiency was calculated using the following equation [15,16]:

$$\eta = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

### 3. Results and discussion

McKay et al. [17,18] presented a three-step model for the adsorption of Astrazone Blue dye on peat. The sorption rate is known to be controlled by several factors including the following: (i) diffusion of the solute from the solution to the particle surface (external diffusion), (ii) diffusion from the surface to the internal sites (pore diffusion) and (iii) uptake which can involve several mechanisms such as physical–chemical adsorption, ion-exchange, precipitation or complexation.

#### 3.1. External diffusion

External diffusion is bulk diffusion. The rate of external diffusion is corresponding to the shaking rate and the initial concentration of lead ions. So, the experiments were performed at various shaking rate and at different initial concentration of lead ions, respectively. The obtained results are shown in Figs. 1 and 2.

From Fig. 1, the removal efficiency of lead ion increased with the increase in shaking rate from 30 rpm to 150 rpm. When the shaking rate was further increased the removal of lead was kept constant at 96%. This phenomenon can be explained as follows: as the shaking rate increased, the diffusion coefficient of lead ion in the liquid bulk was increased, and the mass transfer flux was increased. When the shaking rate was less than 150 rpm, the adsorption rate was there-

fore controlled by external diffusion, and when the shaking rate was more than 150 rpm, the resistance of liquid bulk diffusion was eliminated.

From Fig. 2, the removal of lead ion increased with the increasing in initial concentration of lead ion from  $10\ mg\ L^{-1}$  to  $150\ mg\ L^{-1}$ . When the concentration of lead continued to be increased the removal was kept constant at 99% at the same mass ratio of liquid/solid. Initial concentration of lead is an important factor to external diffusion. The higher the initial concentration was, the higher the concentration gradient was, and the faster the lead ions transferred from liquid bulk to the surface of steel slag. At lower initial concentration of lead ions (lower than  $150\ mg\ L^{-1}$ ), the adsorption rate was increased with the increasing in the initial concentration of lead ion, the adsorption rate was controlled by initial concentration. At higher initial concentrations of lead ions, the adsorption rate kept constant, the resistance of external diffusion was eliminated.

#### 3.2. Intra-particle diffusion

Intra-particle diffusion is fairly related to the particle size. The experiments were performed by different particle size slag, and the result is shown in Fig. 3.

Fig. 3 shows that the removal efficiency increases from 46.5% to 96% with decrease of the steel slag particle size ranging from 25–18 mm to 0.125–0.09 mm, and the removal of lead ions stays constant with a further decrease of the particle size ranging from 0.125–0.09 mm to <0.075 mm. This indicates that the smaller the steel slag particle size is the more surface area is made available at particle size ranging from 25–18 mm to 0.125–0.09 mm with a given mass of steel slag, and the adsorption rate is increased. These surface area data are shown in Table 2. But particle size is less than 0.425–0.18 mm, with surface area increasing, the removal efficiency of lead ions are not increased. From the data shown in Table 2, the pore size of steel slag decrease with surface area increasing. According to the experimental results, the pore size plays more important influence on removing lead ions and surface area is not an important effect factor. So, for steel slag particle sizes ranging from 25–18 mm to 0.125–0.09 mm, the adsorption rate control step was intra-particle diffusion. And particle size was less than 0.09 mm, the resistance of intra-particle diffusion was eliminated.

#### 3.3. Adsorption kinetics

Traditionally, the kinetics have been described by the first-order equation typical of that derived by Lagergren [19]. However, Gosset et al. [20], Sharma and Forster [21] as well as Ho et al. [22] have used a second-order equation to describe metal-peat sorption and Tien and Huang [23] have presented a second-order expression for metal sorption onto sludge solids.

##### 3.3.1. Pseudo-first-order model

The sorption kinetics may be described by a pseudo-first-order. The integrating equation is the following:

$$\lg\left(\frac{Q_e}{Q_e - Q_t}\right) = \frac{k_1}{2.303}t \quad (3)$$

where,  $Q_e$  is the amount of lead ions adsorbed at equilibrium,  $mg\ g^{-1}$ ;  $Q_t$  is the amount of lead ions adsorbed at time  $t$ ,  $mg\ g^{-1}$ ;  $k_1$  is the equilibrium rate constant of pseudo-first-order adsorption,  $min^{-1}$ . Eq. (3) can be rearranged to obtain a linear form:

$$\lg(Q_e - Q_t) = \lg Q_e - \frac{k_1}{2.303}t \quad (4)$$

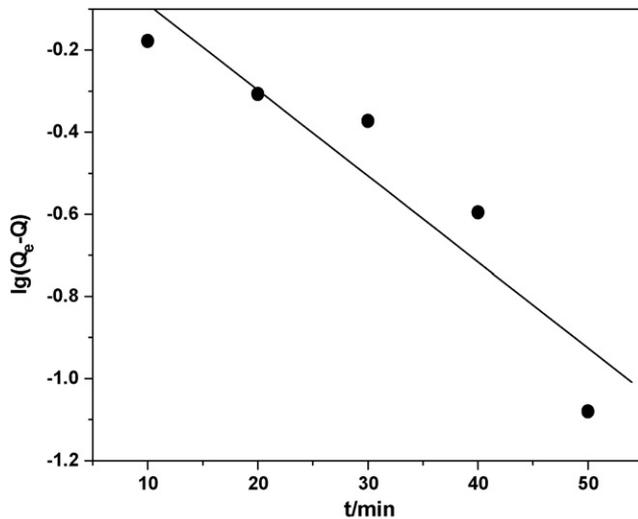


Fig. 4. Pseudo-first-order equation of steel slag absorbing  $Pb^{2+}$ .

In order to obtain the rate constants, the straight line plots of  $\lg(Q_e - Q_t)$  against  $t$  for different experimental conditions have been analyzed. The rate constant,  $k_1$ , and correlation coefficients,  $r_1^2$ , values of the lead ions under different conditions were calculated from these plots.

### 3.3.2. Pseudo-second-order model

The adsorption kinetics may be described by a pseudo-second-order mechanism. The integrating equation is the following:

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + k_2 t \quad (5)$$

Where,  $Q_e$  is the amount of lead ion adsorbed at equilibrium,  $mg\ g^{-1}$ ;  $k_2$  is the equilibrium rate constant of pseudo-second-order adsorption,  $g\ (mg\ min)^{-1}$ . Eq. (5) can be rearranged to obtain a linear form:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (6)$$

The straight line plots of  $t/Q_t$  against  $t$  have also been tested to obtain rate parameters. The  $k_2$ , and correlation coefficients,  $r_2^2$ , under different conditions were calculated from these plots.

A series of experiments were undertaken to study the adsorption reaction kinetics. The concentration and shaking rate were selected as  $150\ mg\ L^{-1}$  and  $210\ rpm$  respectively, which could eliminate the resistance of external diffusion. The steel slag particle size was chosen with  $0.125\text{--}0.09\ mm$ , which could eliminate the intra-particle diffusion. Every 10 min, the lead solution was sampled, and the adsorption capacity was calculated according to formula (1).

Fig. 4 shows a plot of  $\lg(Q_e - Q_t)$  against  $t$  for the second-order equation for the adsorption of lead ion, and Fig. 5 shows a plot of  $Q$  against  $t$  for the first-order equation. The pseudo-first-order rate parameter  $k_1$  and  $r_1^2$  are presented in Table 3, too. The correlation coefficients,  $r_2^2$ , and the pseudo-second-order rate parameter,  $k_2$ , are shown in Table 3 and compared with  $k_1$  and  $r_1^2$  values for the first-order reaction mechanism. The data show a good compli-

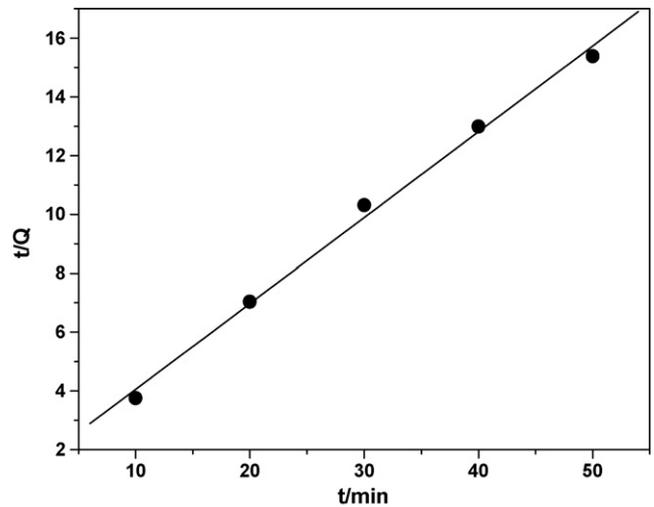


Fig. 5. Pseudo-second-order equation of steel slag adsorbing  $Pb^{2+}$ .

Table 4

Parameter of Langmuir and Freundlich isotherms models.

	Isotherm models	$K, b, n$	$r^2$
Langmuir equation	$\frac{1}{Q_e} = 1.5 + 6.78 \times \frac{1}{C_e}$	$b = 0.221$	$r^2 = 0.99$
Freundlich equation	$\lg Q_e = -1.82 + \frac{1}{4} \lg C_e$	$K = 0.015, n = 4$	$r^2 = 0.85$

ance with the pseudo-second-order equation and the regression coefficient for the linear plots is higher than 0.872.

### 3.4. Adsorption isotherms

The adsorption studies were conducted at fixed adsorbent dosage by varying initial concentrations of heavy metals. The equilibrium data obtained were analyzed in the light of Langmuir and Freundlich isotherms.

The Freundlich equation was given by Freundlich [24]:

$$\lg Q_e = \frac{1}{n} \lg C_e + \lg K \quad (7)$$

Langmuir equation was given by Langmuir [25]:

$$\frac{1}{Q_e} = \frac{1}{Q_{\max} b} \times \frac{1}{C_e} + \frac{1}{Q_{\max}} \quad (8)$$

where  $K\ (L\ g^{-1})$  and  $n$  are Freundlich isotherm constants;  $Q_e$  and  $Q_{\max}$  are the observed and maximum uptake capacity ( $mg\ g^{-1}$ );  $C_e$  is the equilibrium concentration ( $mg\ L^{-1}$ );  $b$  is the Langmuir equilibrium constant ( $L\ mg^{-1}$ ).

Fig. 6 shows the Langmuir adsorption isotherm plot of  $\log 1/Q_e$  versus  $\log 1/C_e$ . The values of  $b$  obtained from intercept and slope of the plot are given in Table 4. The Freundlich adsorption isotherm plot for  $\lg Q_e$  versus  $\lg C_e$  is shown in Fig. 7. The values of Freundlich constants  $K$  and  $1/n$  are presented in Table 4.

Comparing with the correlation coefficient and data, the data showed a good compliance with the Langmuir equation and the regression coefficients for the linear plots were higher than 0.85. This indicated that the adsorption process of lead ion adsorption by surface of steel slag was a monolayer adsorption.

Table 3

Parameters of kinetic models.

	Kinetic model	$k$	$r^2$
Pseudo-first-order	$\lg(1.32 - Q) = 1.32 - 0.021t$	$0.05\ min^{-1}$	0.872
Pseudo-second-order	$\frac{1}{Q} = \frac{0.29}{t} + 1.13$	$13.26\ g\ mg^{-1}\ min^{-1}$	0.995

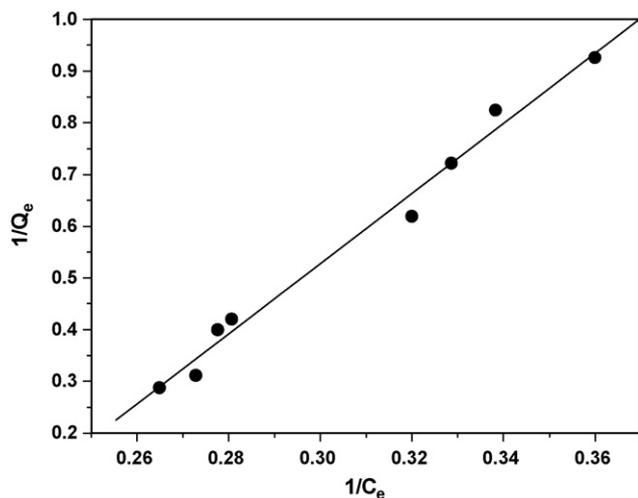


Fig. 6. Langmuir absorption isotherm.

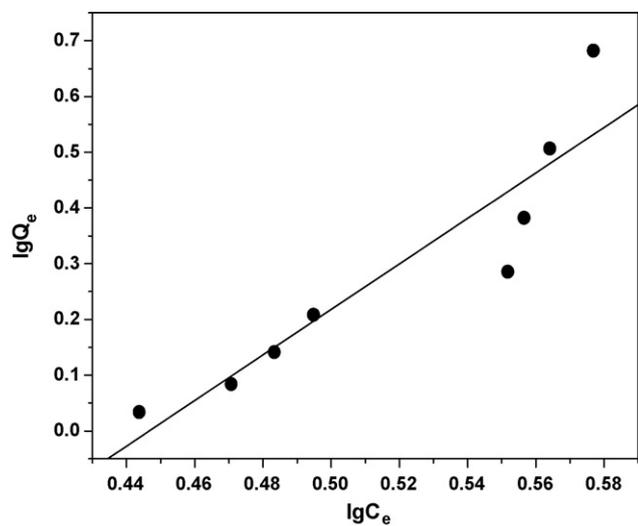


Fig. 7. Freundlich absorption isotherm.

#### 4. Conclusions

The kinetics of adsorption of lead ion on steel slag was studied on the basis of the external diffusion, intra-particle diffusion and adsorption reaction model (pseudo-first-order, pseudo-second). The results showed that the controlling step changed with experimental parameters varied. The removal efficiency of  $Pb^{2+}$  increased from 46.5% to 96% with decrease of the steel slag particle size ranging from 25–18 mm to 0.125–0.09 mm, and the removal of lead ion kept constant with decrease of the particle size ranging from 0.125–0.09 mm to <0.075 mm. With a particle size of steel slag larger than 0.09 mm intra-particle diffusion of lead ions was the controlling step of adsorption kinetics, and when the initial concentration of  $Pb^{2+}$  was less than  $150 \text{ mg L}^{-1}$  or the shaking rate was lower than 150 rpm, external diffusion of lead ions was promoted, the removal of  $Pb^{2+}$  increased to 99% and finally kept constant.

Contrary to the former experimental conditions, the adsorption reaction was the controlling step of adsorption kinetics, and the adsorption followed second-order kinetics, with a adsorption rate constant of  $13.26 \text{ g mg}^{-1} \text{ min}^{-1}$ . The adsorption isotherm of  $Pb^{2+}$  with steel slag followed the Langmuir model, with a correlation coefficient is 0.99.

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