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## Pb<sup>2+</sup> Adsorption by Calcium Silicate Hydrate Synthesized from Steel Slag



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### ABSTRACT

This study aims to investigate the adsorption properties of Pb<sup>2+</sup> by calcium silicate hydrate synthesized from steel slag. The influence of various factors on the adsorption properties was investigated. The static desorption test was conducted to investigate the leaching of Pb<sup>2+</sup>. The kinetic model and isotherm model of adsorption are then discussed. Results show that Pb<sup>2+</sup> adsorption capacity of C-S-H depends on Ca/Si ratios. Kinetic adsorption data is in consistence with Lagergren pseudo-second-order model, and steady-state data fits to Langmuir isothermal model. Leaching result demonstrates that Pb<sup>2+</sup> ions are stably adsorbed by C-S-H structures.

**Key words:** Pb<sup>2+</sup> adsorption, calcium silicate hydrates, steel slag, adsorption model.

## 1. INTRODUCTION

Recently, solidification/stabilization technology (S/S) of cement-based material is widely studied on treating the heavy metal pollution and water treatment [1-5]. It is attributed to calcium silicate hydrate (C-S-H,  $C=CaO$ ,  $S=SiO_2$ ,  $H=H_2O$ ), the main hydration product of cement paste. The main structures of C-S-H (Ca/Si molar ratio from 0.6 to 2) are disordered forms of 1.4 nm tobermorite and jennite, with a large specific surface area, high porosity and active sites such as hydroxyl groups [6,7]. Calcium silicate hydrates exhibit a large number of structural sites available for cation and anion binding [8]. Therefore, C-S-H structure plays an essential role in adsorption of heavy metals. The mechanism includes ion-exchange, adsorption and chemical trapping. Heavy metals such as Nd(III), Zn(II), Cd(II), Cr(IV), U(IV) and Sr(II) adsorbed by C-S-H have been studied by many researchers [9-14]. The results show that the heavy metals are incorporated into the Ca-O sheets, adsorbed in the interlayer of C-S-H, or ion-exchange with  $Ca^{2+}$  as the curing age increases.

Apart from cement hydration, C-S-H can also be obtained from waste slags, such as steel slag, which has a large amount of emission but low utilisation especially in China [15]. Wang et al. synthesized 11.3 Å tobermorite structures from steel slag by hydrothermal treatment [16]. Kuwahara and co-workers [17] reported that C-S-H prepared from the waste slag had good adsorption properties for removal of  $Cu^{2+}$ , phosphate ions and model protein diluted in water. Therefore, synthesized C-S-H is considered as a candidate for water purification on the heavy metals.

Lead (Pb), harmful to the health of human beings, is one of the main contaminations around the world; hence, how to treat it has become widely discussed. Xonotlite secondary particles were used to treat lead-bearing wastewater by Han, et al. [18], which indicated high  $Pb^{2+}$  removal. Investigations of Lee [19], Pierrard, Rimbault, and Aplincourt [20] suggested that  $Pb^{2+}$  fixed by C-S-H was affected by pH value of its pore solution. The main formation of Pb was  $Pb_4SO_4(CO_3)_2(OH)_2$  and  $3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$  at short time curing. The lead was adsorbed on the silica-rich surface to form C-Pb-S-H after long time cured together with acid attack.  $Pb^{2+}$  adsorbed by 1.1 nm tobermorite was also studied by Coleman, Trice, and Nicholson [21], indicating that the sorption conforms to the pseudo-second-order model and the uptake was up to 467 mg  $g^{-1}$  after 168-hour curing. However, the adsorption properties and mechanisms of lead on C-S-H are still poorly understood. In particular, there is seldom investigation on lead uptake in mild acidic medium.

This study explores the possibility of  $Pb^{2+}$  adsorption on calcium silicate hydrates synthesized from steel slag in mild acidic solutions. The influence of various factors, e.g. the properties and amount of C-S-H powder, adsorption time,  $Pb^{2+}$  concentrations, and pH values of the solution, on the adsorption properties are investigated. Furthermore, the kinetic and isotherm behaviours of adsorption by C-S-H are discussed.

## 2. EXPERIMENTAL

### 2.1 Materials

The main chemical compositions of steel slag (Shougang Group, Beijing) used in this study are listed in Table 1. It was obvious that the steel slag consisted of CaO,  $SiO_2$ , MgO,  $Al_2O_3$ , and  $Fe_2O_3$ , with Ca/Si molar ratio of 2.17. The specific surface area measured by Blaine Air

Permeability was  $474 \text{ m}^2 \text{ kg}^{-1}$ . The main mineral phases in this steel slag were  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  according to XRD analysis. There is no doubt that the slag was available for synthesizing calcium silicate hydrate.

*Table 1 – Main chemical composition of steel slag*

Components	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	P <sub>2</sub> O <sub>5</sub>
Content (%)	42.80	21.14	5.74	5.86	9.58	0.58

## 2.2 C-S-H synthesis

Calcium silicate hydrate powder was synthesized in an autoclave (Weihai Chemical Machinery Co. Ltd). Steel slag was mixed with lime (87.9% CaO) and quartz (99.09% SiO<sub>2</sub>) at the Ca/Si molar ratio between 0.8 and 1.5. The mixture was cured at temperatures ranging from 150°C to 185°C, for 7 hours, with the water to solid ratio (w/s, in mass) of 6, filtered and oven-dried at 80 °C. The details of hydrothermal synthesis are in Table 2.

*Table 2 – the hydrothermal synthesis of calcium silicate hydrates*

index	Raw materials (%)			Ca/Si	w/s	Curing temperature (°C)	Curing time (h)
	Steel slag	quartz	lime				
A	70	20.00	10.00	1.2	6	150	7
B	70	20.00	10.00	1.2	6	185	7
C	70	14.19	15.81	1.5	6	150	7
D	80.28	19.72	0	1.5	6	185	7
E	70	27.96	2.04	0.8	6	185	7

## 2.3 Adsorption of Pb<sup>2+</sup> by C-S-H

Pb<sup>2+</sup> solutions were prepared by dissolving lead acetate (research grade, Jinshan Chemical Reagent Co., Ltd., Chengdu) in distilled water. 100mL solution was added in the beaker with a proper amount of C-S-H powder, adjusting the pH value of the solution to 2 to 7, stirring (100 rpm). These tests were all carried out at the room temperature. The concentration of Pb<sup>2+</sup> after adsorption was measured, and influences of the powder amount, adsorption time, pH of solution, initial Pb<sup>2+</sup> concentrations on C-S-H capacity were discussed. The removal ratio(R) and adsorption capacity (q) of Pb<sup>2+</sup> by C-S-H were calculated as followed formulas:

$$R(\%) = 100\% \times (C_0 - C) / C_0 \quad (1)$$

$$q = (C_0 - C) \times V / m_p \quad (2)$$

Where  $C_0$  is the initial concentration of Pb<sup>2+</sup> (in mg L<sup>-1</sup>);  $C$  indicates Pb<sup>2+</sup> concentration after adsorption (in mg L<sup>-1</sup>);  $V$  represents volume of solution (in L);  $m_p$  is the mass of hydrated calcium silicate powder (in g); and  $q$  is the amount of Pb<sup>2+</sup> adsorbed by per unit C-S-H (in mg g<sup>-1</sup>)

## 2.4 Desorption test

To investigate the leaching of lead after having been adsorbed by C-S-H, static desorption measurement was carried out at room temperature. 1.5 gram powder with  $Pb^{2+}$  after equilibrium adsorbed was added into 100 ml distilled water or acetic acid solution (pH value of 5), respectively. After stirring (100 rpm) for 75 minutes, the solution was filtered and  $Pb^{2+}$  concentration of the solution was measured. The desorption ratio ( $\epsilon$ ) is calculated as following formula:

$$\epsilon(\%) = \frac{C_1 V_1}{(C_0 - C)V} \times 100\% \quad (3)$$

$C_0$ ,  $C$  and  $V$  are described in the above section, where  $C_1$  and  $V_1$  represent the  $Pb^{2+}$  concentration and volume of the solution after desorption, respectively.

## 2.5 Product characterisation

XRD was applied to identify the crystalline phases of the synthesized C-S-H powders. The samples were detected by a Rigaku D/max-1200 X-ray powder diffraction apparatus (Cu  $K\alpha$  radiation), at a step size of  $0.02^\circ$  with scanning rate of  $2^\circ \text{ min}^{-1}$ , and a scan range from  $5^\circ$  to  $70^\circ$   $2\theta$ . SEM (scanning electron microscope Morphology, TESCAN VEGA II) with a voltage of 20KV and magnitude of 4~100,000 X was also employed for detecting the morphology of the hydrothermal products. FTIR spectroscopy (Nicolet5DXC) equipped with a KBr beam splitter was used for functional group analysis, with scanning wavenumber from 4000 to  $400 \text{ cm}^{-1}$ .

$Pb^{2+}$  concentrations were measured via spectrometric atomic absorption apparatus (Hitachi Z-8000), at a wavelength of 283 nm, according to the standard of GB/T 9723-2007 (General rule for flame atomic absorption spectrometric analysis). The measurement was calibrated by measuring the absorbance at Pb concentrations of 0, 1, 2, 4, 6, 8, and  $12 \text{ mg L}^{-1}$ . Background was removed during analysis.

## 2.6 Adsorption models

### *Kinetic models*

The Lagergren pseudo-first-order rate model and pseudo-second-order rate expression are used to study the adsorption kinetic model of  $Pb^{2+}$  by calcium silicate hydrates. These models describe adsorption of a solute by a solid surface, and adsorption processes in which the reaction rate is proportional to square [21-23].

The pseudo-first-order rate model can be expressed as following:

$$q^e = \frac{V(C_0 - C_e)}{m_p} \quad (4)$$

$$\log(q^e - q_t) = \log q^e - \frac{k_1}{2.303} t \quad (5)$$

Where  $q^e$  (in  $\text{mg}\cdot\text{g}^{-1}$ ) is the extent of sorption at equilibrium according to equation (2),  $C_e$  (in  $\text{mg}\cdot\text{L}^{-1}$ ) is the steady-state concentration of the metal ion in solution,  $q_t$  (in  $\text{mg}\cdot\text{g}^{-1}$ ) is the extent of adsorption at time  $t$ , and  $k_1$  (in  $\text{min}^{-1}$ ) is the apparent pseudo-first-order rate constant of adsorption.

The expression of pseudo-second-order rate is:

$$\frac{t}{q_t} = \frac{1}{k_2(q^e)^2} + \frac{1}{q^e}t \quad (6)$$

Where  $k_2$  is the apparent pseudo-second-order rate constant of adsorption (in  $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ). If there is a linear plot of  $t/q_t$  against  $t$ , pseudo-second-order rate equation is satisfied.

### *Isothermal models*

Adsorption isothermal equation reflects the relation between adsorptive capacity and the concentration of solution under a fixed temperature. There are mainly two models. One is Langmuir isotherm model reflecting the monolayer adsorption onto solid surfaces, and the other is Freundlich isothermal model which is also widely applied in liquid-solid adsorption system.

The linear form of the Langmuir isothermal model, used to illustrate uptake of metal ions from solution by a solid substance, can be described as follows [22, 23]:

$$\frac{C_e}{q^e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (7)$$

In equation (7)  $q_m$  is the maximum adsorptive capacity (in  $\text{mg}\cdot\text{g}^{-1}$ ) and  $b$  is the Langmuir constant (in  $\text{L}\cdot\text{mg}^{-1}$ ). Other parameters are described as above.  $q_m$ , and  $b$  is estimated from the intercept and the slop of the plot of  $C_e/n_s$  against  $C_e$ .

Freundlich isothermal model is described as:

$$\log q^e = \log K + \frac{1}{n}(\log C_e) \quad (8)$$

Where  $K$  is Freundlich constant and  $1/n$  is constant as well. This model is based on the assumption that the enthalpy of sorption becomes less negative [22].

## **3. ADSORPTION MODELS**

### **3.1 Microstructures of synthesized C-S-H**

#### *XRD analysis*

The XRD patterns of the synthetic samples are shown in Figure 1. Poorly crystalline C-S-H formed in all the samples due to the only appearance of diffraction peaks with the d-spacing of 0.302 nm ( $2\theta$  29°), 0.182 nm ( $2\theta$  18°) and 0.280 nm ( $2\theta$  32°) [7]. However, the final hydration phases were influenced by the hydrothermal curing process, such as the addition of lime, and the different Ca/Si molar ratios. Powder A and B consisted of C-S-H, and semi-tobermorite (d-spacing of 3.08 Å, 2.98 Å and 1.84Å) [16]. It is also found that  $\text{SiO}_2$  was still present in Powder

A because of the appearance of intensive diffraction peak at 3.34 Å. As the Ca/Si ratio increased to 1.5 in Powder C, the dominant phase was poorly crystallized C-S-H. Besides, a zeolite-like gel was also generated due to the appearance of the peak at 3.17 Å. This phase is beneficial to the heavy metal incorporation. The main phase of Powder E was disordered C-S-H. In addition quartz was not completely consumed.

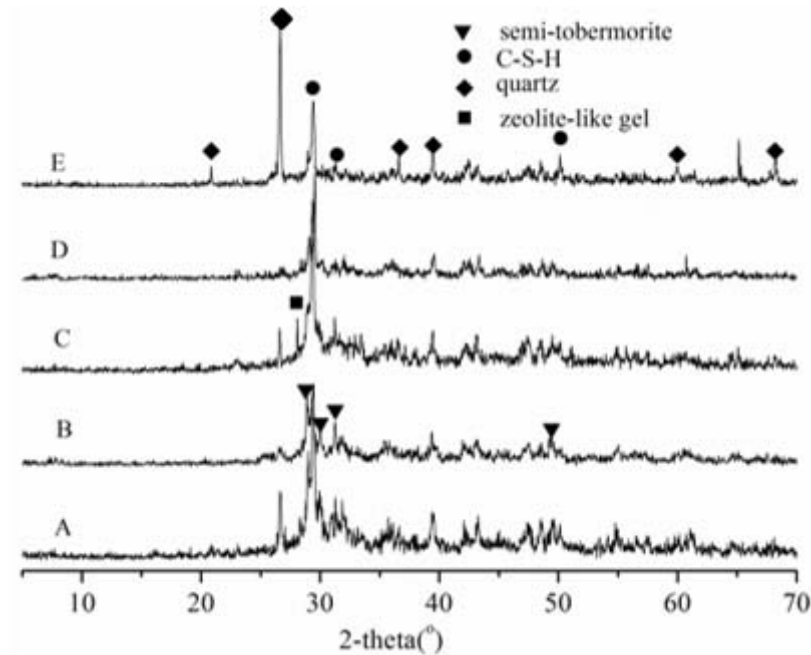
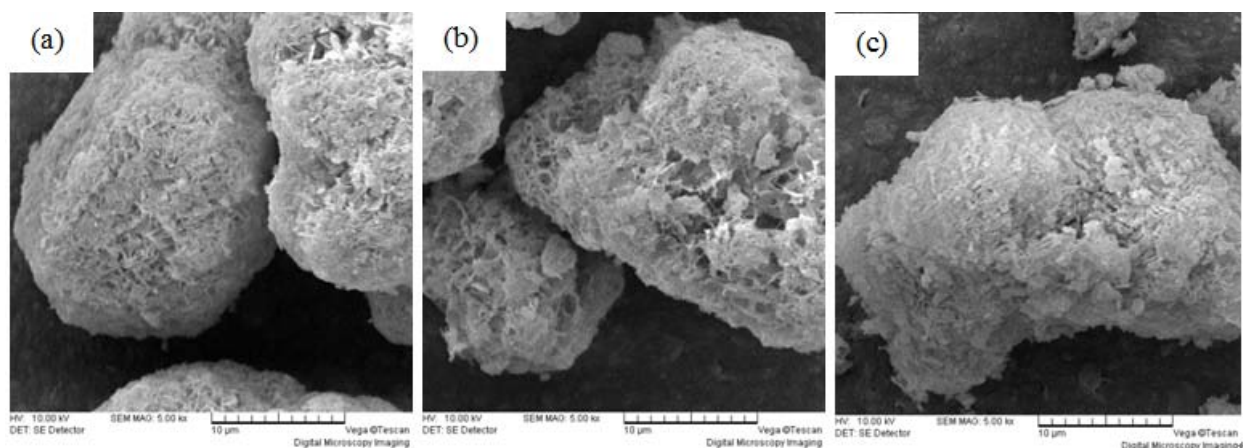


Figure 1 – XRD patterns of C-S-H samples made from steel slag by weight at the water/solid ratio of 6 and curing for 7 hours. The details for hydrothermal synthesis are shown in Table 2.

#### SEM analysis

The morphology of the synthetic C-S-H samples was investigated with SEM microscope (Figure 2). The powder particles showed non-crystallized structures, and were an aggregation of micro-scale morphology, which was 1 μm. It can be seen that the curing method, especially the Ca/Si molar ratio, affects the final morphology of the product. In sample A, which was prepared at 150 °C for 7 hours at the Ca/Si ratio of 1.2, foil or sheet-like structure appeared. When the Ca/Si ratio increased to 1.5, in sample C, C-S-H made up of fibril shaped grains with a loose reticular structure. It presented a porous surface, which is a so called as zeolite-like structure. In powder D, however, it exhibited a more compacted morphology with a lack of pronounced pores on the surface, which was attributed to the lack of lime addition.



**Figure 2 – SEM Photographs of the synthetic C-S-H:**

- (a) powder A synthesized from the mixture of 70wt% steel slag, 20wt% quartz and 10wt% lime with 1.2 Ca/Si molar ratio at 150 °C for 7 hours;  
 (b) Powder C synthesized from the mixture of 70wt% steel slag, 14.19wt% and 15.81wt% lime, with the Ca/Si molar ratio of 1.5 at 150 °C for 7h; and  
 (c) Powder D is corresponded to the product from 80.28wt% steel slag and 19.72wt% quartz without lime addition, the Ca/Si molar ratio of 1.5 at 185 °C for 7 hours

### 3.2 $Pb^{2+}$ adsorption properties on C-S-H

#### *The adsorption of $Pb^{2+}$ by different C-S-H powders*

C-S-H powders produced from different hydrothermal curing conditions were used to adsorb the  $Pb^{2+}$  with the concentration of  $200 \text{ mg L}^{-1}$ , and the results are shown in Figure 3. The adsorption properties were influenced by the synthesis process, generally on the Ca/Si molar ratio and the content of the lime. The sample C which was synthesized at 150 °C for 7 hours with the molar ratio of 1.5 presented the highest removal efficiency (about 99.67 %), and the adsorption capacity of  $Pb^{2+}$  was up to  $19.53 \text{ mg g}^{-1}$ . However, there were no satisfying results of  $Pb^{2+}$  adsorption by other types of powder, as the removal and adsorption capacity were lower than 90% and  $18 \text{ mg g}^{-1}$  respectively. The higher incorporation of  $Pb^{2+}$  in Powder C than other samples is attributed to its porous surface of the particles. In this case, Powder C was used for thermodynamic analysis on the subsequent adsorption study.



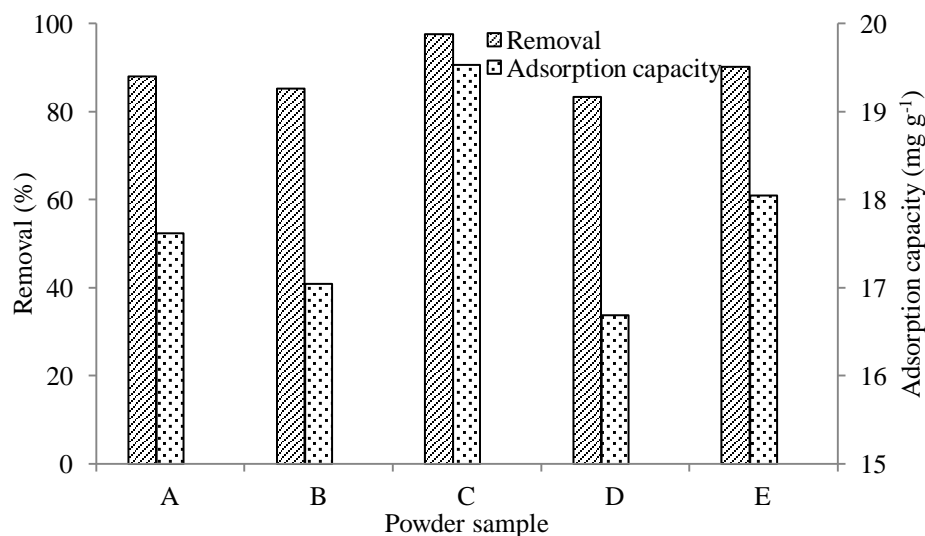


Figure 3 – Adsorption of  $Pb^{2+}$  by different kinds of C-S-H powders, synthesis of powder is in Table 2

#### Effect of C-S-H amount on $Pb^{2+}$ adsorption

Different amount of calcium silicate hydrate powder were mixed with 100 mL  $Pb^{2+}$  solution (200 mg L<sup>-1</sup>), adjusting the initial pH value of the mixture to 5. Adsorption time of 1 hour was applied. The result of adsorption is shown in Figure 4.

It can be seen that the removal efficiency increased rapidly from 31% to 96%, corresponding to the mass of C-S-H powder from 5 g L<sup>-1</sup> to 15 g L<sup>-1</sup>, followed by the stable adsorption efficiency. When 20 g L<sup>-1</sup> of C-S-H powder was used, the removal of  $Pb^{2+}$  was up to 99%, with the residual concentration of  $Pb^{2+}$  solution 0.96 mg L<sup>-1</sup>. Additionally, the adsorption capacity of  $Pb^{2+}$  by C-S-H was first increased and then declined as the amount of the powder increased. The maximum of adsorption capacity was 14.46 mg g<sup>-1</sup> with the amount of 10 g L<sup>-1</sup> powder, demonstrating that excessive amount of powder cannot be completely utilized. Therefore, in the following adsorption experiments, 15 g L<sup>-1</sup> C-S-H powder is used.

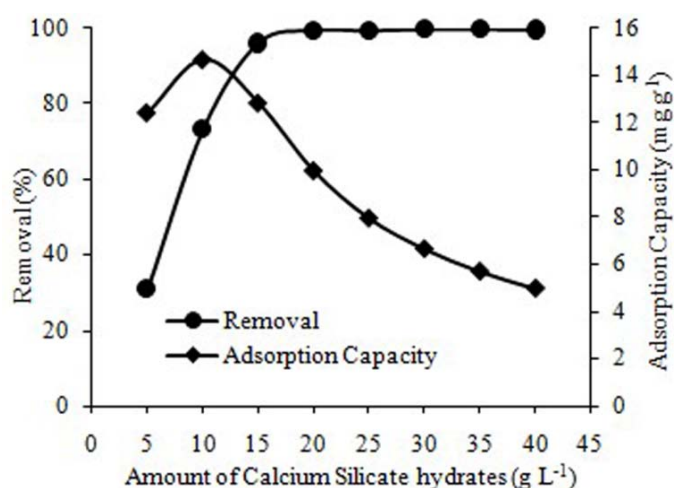


Figure 4 –  $Pb^{2+}$  removal at different amount of C-S-H powder

#### Effect of pH on $Pb^{2+}$ adsorption

1.5 g calcium silicate hydration powder was mixed with 100 mL  $Pb^{2+}$  solution ( $Pb^{2+}$  concentration 200 mg L<sup>-1</sup>). The initial pH values of the solution ranged from 2 to 7, with stirring

time of 1 hour (Figure 5). The removal efficiency and adsorption capacity of  $Pb^{2+}$  by C-S-H is influenced obviously by pH. At pH value of 2, the removal efficiency and adsorption capacity were only 11% and  $1.52 \text{ mg g}^{-1}$ , respectively. With pH increasing to 5, both the removal and adsorption capacity soared up to 96% and  $12.73 \text{ mg g}^{-1}$ , respectively. The data gradually increased when the pH value varied between 5 and 7. It is apparent that  $Pb^{2+}$  can be effectively adsorbed on C-S-H via weak acidic solution, since there are negative charges on the surface of C-S-H particles when pH of the solution is close to 7 [24]. On the other hand, the structure of C-S-H was damaged by strong acid solution, resulting in the poor adsorption.

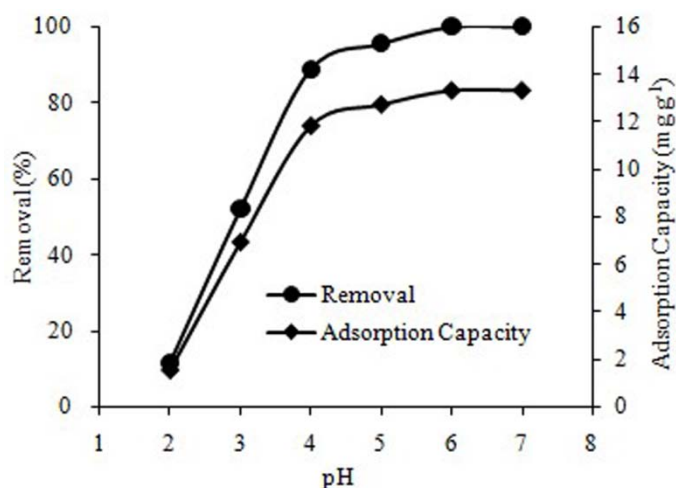


Figure 5 –  $Pb^{2+}$  adsorption in the solution of different pH values

#### Influence of stirring time on $Pb^{2+}$ adsorption

Stirring time is another key factor on  $Pb^{2+}$  adsorption and reflects its equilibrium status. In this section, the adsorption properties of the duration from 30 minutes to 180 minutes were investigated (Figure 6). The curves indicated that the powder had an excellent adsorption property on  $Pb^{2+}$  even for only 30-minute reaction. The removal efficiency and the adsorption capacity were approximate 96% and  $12.78 \text{ mg g}^{-1}$ , respectively. Afterward, the removal efficiency increased to 99.4% and adsorption capacity of  $13.25 \text{ mg g}^{-1}$  at 75 minutes' adsorption. With stirring time extended, the values gradually improved, and residual  $Pb^{2+}$  concentration of the solution declined to  $0.44 \text{ mg L}^{-1}$  at 180 min, far below the emission standard of  $1.0 \text{ mg L}^{-1}$  (GB 8978-1988). According to Figure 6, the balance of adsorption was achieved after 75-minute adsorption.

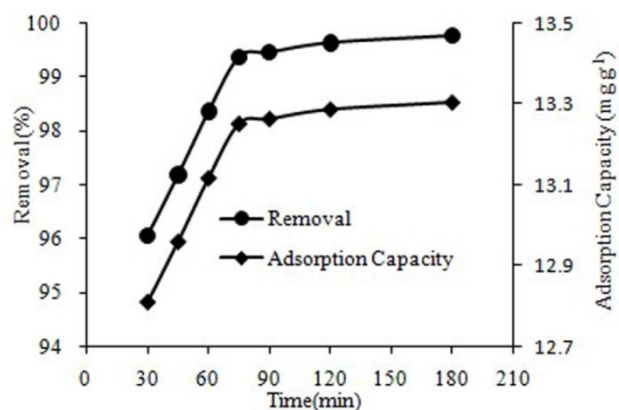


Figure 6 –  $Pb^{2+}$  adsorption properties at different stirring time

### *Influence of initial concentration of $Pb^{2+}$ on adsorption*

Herein, the results about adsorption of  $Pb^{2+}$  concentrations between  $50 \text{ mg L}^{-1}$  and  $400 \text{ mg L}^{-1}$  were discussed (Figure 7). With the increase of  $Pb^{2+}$  concentration from  $50 \text{ mg L}^{-1}$  to  $400 \text{ mg L}^{-1}$ , the adsorption capacity and  $Pb^{2+}$  concentration rapidly went up to  $24.46 \text{ mg g}^{-1}$  from  $3.35 \text{ mg g}^{-1}$ , which was attributed to the increase of contact sites between the calcium silicate hydrate powder and  $Pb^{2+}$ . On the contrary, the curve of removal appeared different tendency. It was stable at around 99% as the concentration ranged from  $50 \text{ mg L}^{-1}$  to  $200 \text{ mg L}^{-1}$ , and the maximum value was 99.4% at the  $Pb^{2+}$  concentration of  $200 \text{ mg L}^{-1}$ . The removal efficiency declined to 91.7% corresponding to the  $Pb^{2+}$  concentration of  $400 \text{ mg L}^{-1}$ .

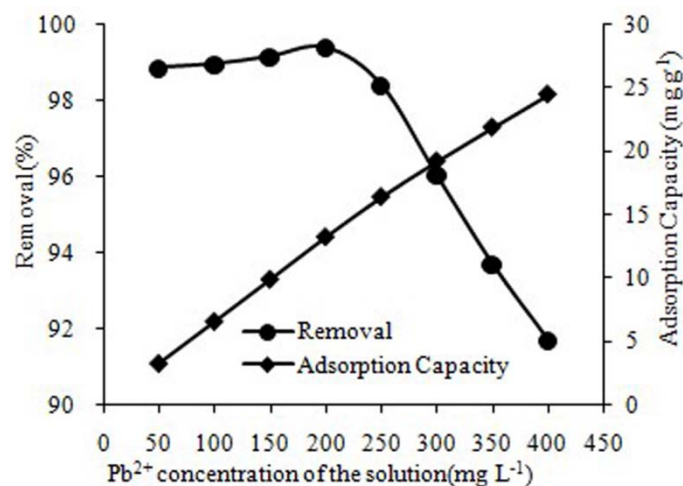


Figure 7 – adsorption properties with various  $Pb^{2+}$  concentration

### 3.3 Desorption of $Pb^{2+}$ on C-S-H

Desorption tests were carried out both under distilled water and acidic solution, corresponding to the pH of 7.0 and 5.0. Results showed that the  $Pb^{2+}$  concentration was  $0.16 \text{ mg L}^{-1}$  after leaching experiment, indicating that the desorption ratio in water was as low as 0.08% according to equation (3). When acidic solution with pH of 5.0 was adopted, the leaching concentration of  $Pb^{2+}$  increased to  $0.64 \text{ mg L}^{-1}$ . It means that the desorption rate was 0.3%. The results demonstrate that  $Pb^{2+}$  can strongly adsorbed by C-S-H powder and leaching ratio in neutral solution is quite low, which might attribute to the combination between  $Pb^{2+}$  and functional groups.

## 4. ADSORPTION MODELS

### 4.1 Kinetic models

As mentioned previously, adsorption kinetic is analyzed by applying Lagergren pseudo-first-order model (equation (5)), and pseudo-second-order model (equation (6)). According to the data in Figure 6, the parameters of the two kinetic models are obtained (Figure 8, Table 3). The results show that higher correlation of the pseudo-second-order kinetic model ( $R^2$  value of 1) than pseudo-first-order kinetic model ( $R^2$  value of 0.96), demonstrating that the former affords a more appropriate description of the sorption process. Thus, the equilibrium adsorption  $q^e$  and constant rate  $k_2$  are  $13.09 \text{ mg g}^{-1}$  and  $7.82 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ , respectively. The kinetic results of

adsorption of metal cations by C-S-H powder is likely to reveal that the reaction is controlled by a number of transport and interaction process.

Table 3 – Statistical and kinetic datas of  $Pb^{2+}$  sorption on C-S-H

Lagergren (pseudo-first-order)			Lagergren(pseudo-second-order)		
$q^e /(\text{mg g}^{-1})$	$k_1 \times 10^{-2} /(\text{min}^{-1})$	$R^2$	$q^e /(\text{mg g}^{-1})$	$k_2 \times 10^{-2} /(\text{g mg}^{-1} \text{min}^{-1})$	$R^2$
13.30	6.86	0.96	13.09	7.82	1

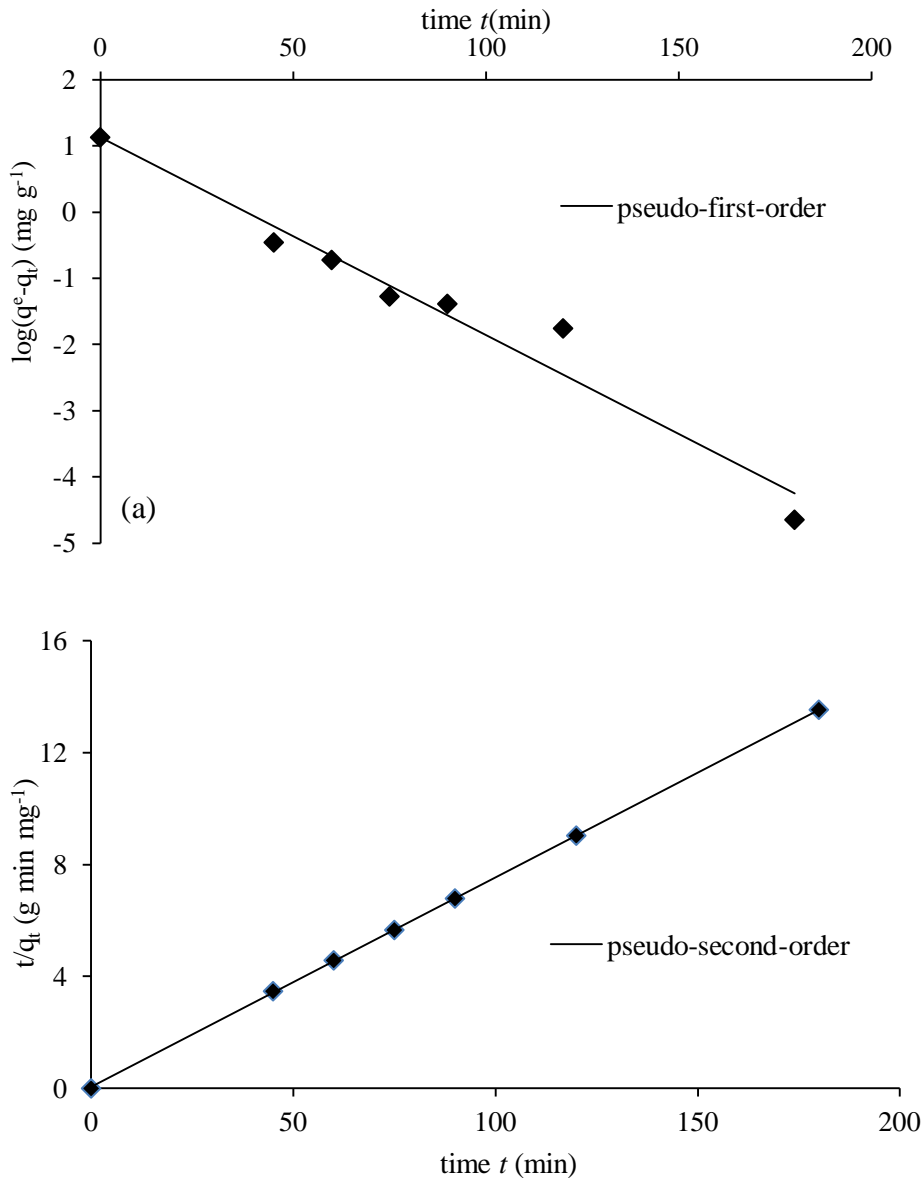


Figure 8 – kinetic model fitted to experimental data for the uptake of  $Pb^{2+}$  (a) pseudo-first-order model, and (b) pseudo-second-order model

Thus, adsorption rate is an important indicator to reflect the interaction between adsorbent and adsorbate. Generally, the adsorption processes include three stages [25], which are external-particle diffusion stage, intra-particle diffusion stage and adsorption-reaction stage. Weber-Morris equation (equation (9)) was used to describe the diffusion and transfer procedure of  $Pb^{2+}$  on C-S-H particle surface[26, 27]:

$$n_t^s = k_{id} t^{\frac{1}{2}} + b \quad (9)$$

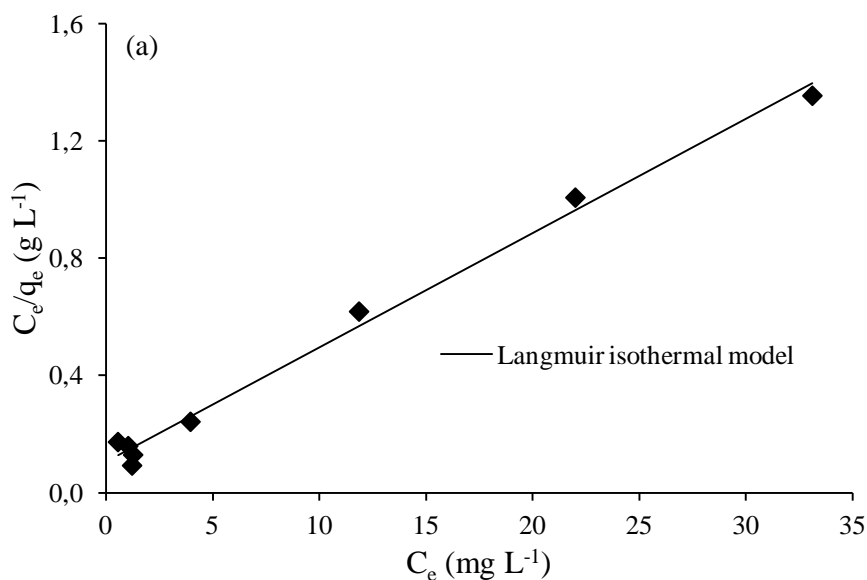
Where  $b$  represents intercept, and  $k_{id}$  is intra-particle diffusion constant (in  $\text{mg g}^{-1} \text{min}^{-1/2}$ ). In accordance with Figure 6, the adsorption rate tends to be constant after 75 minutes. By fitting the experiment data depending on the equation above, the correlation coefficient  $R^2$  is 0.92, an indication of linear relationship. As a result, it can be considered that before 75 minutes the adsorptive process is controlled by external-particle diffusion stage, followed by intra-particle procedure [28]. The value of  $k_{id}$  is  $0.016 \text{ mg g}^{-1} \text{min}^{-1/2}$ , and  $b$  of 13.10.

## 4.2 Isothermal models

In order to describe the adsorption properties on the the surface of the powder, adsorption isothermal is studied. The adsorption isothermal curve obtained from Figure 7 is shown in Figure 9, which means the adsorption capacity of C-S-H on different  $\text{Pb}^{2+}$  equilibrium concentration. It can be inferred from equation (7) and (8) that the data are well correlated with the Langmuir isothermal model with  $R^2$  of 0.99. While the Freundlich model is less appropriate for its  $R^2$  of only 0.77 (Table 4). Thus, the adsorption conforms to monolayer adsorption and there are many active sites on the surface of C-S-H particles.

Table 4 – Langmuir and Freundlich isothermal parameters for the absorption of  $\text{Pb}^{2+}$  on C-S-H

	Langmuir			Freundlich	
$q_m / (\text{mg} \cdot \text{g}^{-1})$	$b / (\text{L} \cdot \text{mg}^{-1})$	$R^2$	$K / (\text{mg} \cdot \text{g}^{-1})$	$n$	$R^2$
25.71	0.37	0.99	7.38	2.59	0.77



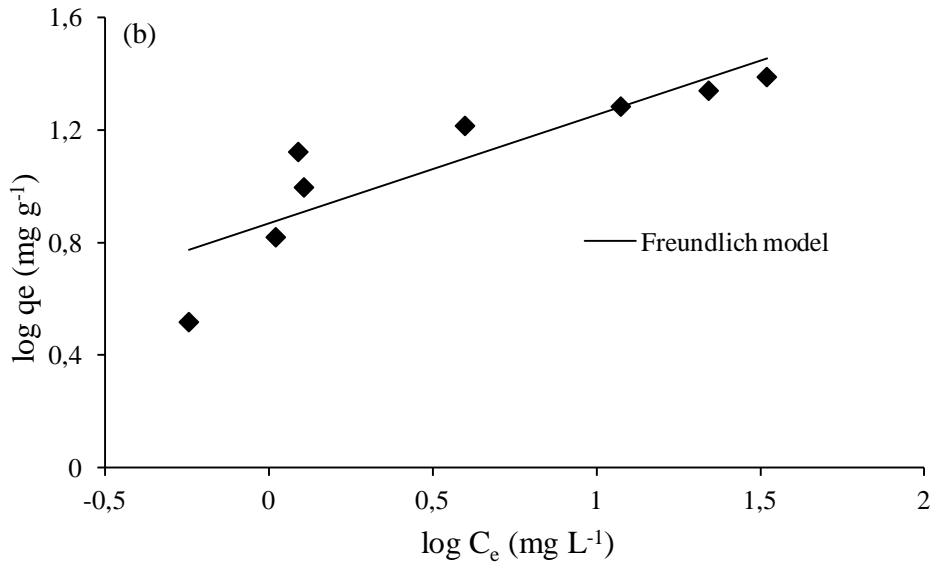
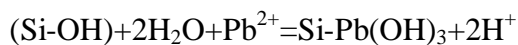


Figure 9 – Isothermal model fitted to experimental data for the uptake of  $Pb^{2+}$  (a) Langmuir isothermal model, and (b) Freundlich isothermal model

### 4.3 Microstructure analysis

FTIR was applied to study the structure variation of C-S-H powder before and after adsorption (Figure 10). In both samples,  $CO_3^{2-}$  asymmetric stretching bands due to contamination with  $CO_2$  during samples preparation and drying were detected at  $1432\text{ cm}^{-1}$  and  $873\text{ cm}^{-1}$ . The bending vibration band of molecular  $H_2O$  appeared at  $1632\text{ cm}^{-1}$ , while the stretching vibration of O-H groups or hydroxyls appeared in the  $3433\text{--}3440\text{ cm}^{-1}$  region. The most intensive vibration of silicate appeared as a band at the range of  $900\text{--}1100\text{ cm}^{-1}$  which was attributed to stretching vibration of  $[SiO_4]^{4-}$  tetrahedral. The vibration band in C-S-H was at  $982\text{ cm}^{-1}$ , however, it shifted to  $1075\text{ cm}^{-1}$  after adsorbing  $Pb^{2+}$ , demonstrating that the polymerisation of silicate chain varied. In addition, the bands corresponding to  $\delta$ -Si-OH stretching vibration appeared at  $1280\text{ cm}^{-1}$  and  $756\text{ cm}^{-1}$  in C-S-H, but disappeared after adsorbing  $Pb^{2+}$ , suggesting that coordination reaction between Hydroxyl functional group and  $Pb^{2+}$  took place as following way:



This reaction agrees with the adsorption of  $Cu^{2+}$  by asbestos tailings in [29]. It indicates that the presence of active sites in C-S-H structures can cooperate with  $Pb^{2+}$  in a relative stable state, which is demonstrated by the desorption results.

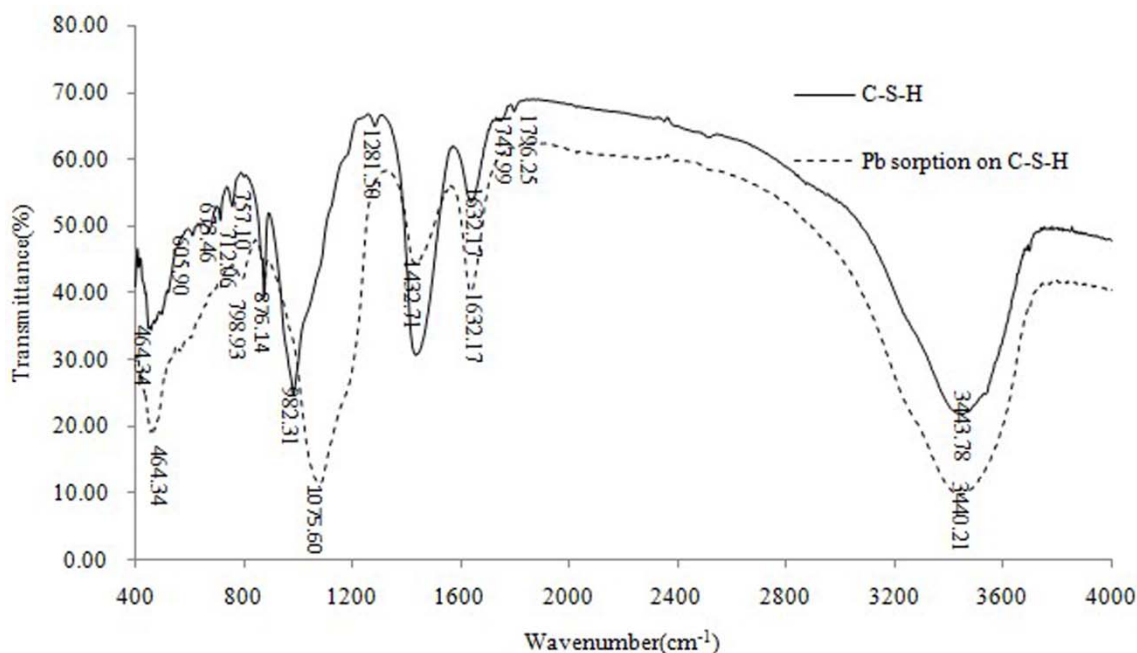


Figure 10 – FTIR spectra of C-S-H powder and the powder after  $Pb^{2+}$  sorption

## 5. CONCLUSION

This study shows that the calcium silicate hydrate synthesized from steel slag is a potential  $Pb^{2+}$  adsorbent. The adsorption depends on the Ca/Si molar ratio and lime addition which further affect on the surface properties of powder particles. The most efficient adsorption of the C-S-H has a Ca/Si ratio of 1.5.  $Pb^{2+}$  can be effectively removed by this C-S-H powder at the pH value of the solution between 5 and 7. The equilibrium adsorption occurs at 75 minutes when  $15 \text{ g L}^{-1}$  C-S-H is mixed with  $200 \text{ mg L}^{-1}$   $Pb^{2+}$  solution. The removal of  $Pb^{2+}$  and adsorption capacity is 99.4% and  $13.25 \text{ mg g}^{-1}$ , respectively. The concentration of  $Pb^{2+}$  in the solution after adsorption for more than 120 minutes is lower than  $0.5 \text{ mg L}^{-1}$ . The low leaching ratio from desorption result indicates that  $Pb^{2+}$  can be stably combined by C-S-H.

Kinetic sorption data were in agreement with the Lagergren pseudo-second-order with the equilibrium adsorption of  $13.09 \text{ mg g}^{-1}$ . In terms of the sorption isotherm, it can be described by the Langmuir adsorption isotherm, the equilibrium adsorption capacity of which is  $20.41 \text{ mg g}^{-1}$ . The adsorption is controlled by external-particle diffusion stage before equilibrium state, followed by intra-particle diffusion procedure.

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