Lead sorption performance on active silica derived from fly ash

Xizhu Zhang and Zhibao Zhu

ABSTRACT

The object of this study was to estimate the sorption property of active silica derived from fly ash after separation of silica and aluminum. The specific surface area of active silica enlarged to 115 m^2/g was compared with the original fly ash (4 m^2/g). Field emission scanning electron microscopy displayed the active silica, which looked like a honeycomb or curly layer with many lamellae that formed many mesopores. The uptake kinetics indicated that the residual concentration of Pb^{2+} in the aqueous solution decreased rapidly from the initial 1.25 mg/L to less than 10 μg/L within 45 min. The removal efficiency of Pb^{2+} on active silica was pH dependent. The increase in pH value promoted Pb^{2+} removal because the negative surface provided more electrostatic attraction sites. A stepwise non-linear isotherm was obtained because the lamellae of active silica provided a heterogeneous surface with various kinds of active sites. The maximum sorption amount of Pb on active silica was more than 90 mg/g, which was better than some pristine-activated carbon.

Key words | active silica, fly ash, lead, sorption

Xizhu Zhang (corresponding author)
Ministry of Environmental Protection,
Appraisal Center for Environment and Engineering,
Beijing 100012,
China
E-mail: zhangxz@acee.org.cn

Zhibao Zhu
Changzhou University,
Changzhou 213164,
China

INTRODUCTION

The pollution by heavy metals has caused worldwide concerns due to their toxicity, stability and bioaccumulation in recent years (Fu & Wang 2011; Sharma & Lee 2013; Zhou et al. 2013). Wastewater containing lead ions is discharged from many industries such as battery manufacturing, electroplating and mining and so on (Googerdchian et al. 2012; Ugochukwu et al. 2012). Lead ion (Pb^{2+}) is toxic and not biodegradable, which causes serious ecological damage and various diseases in humans (Benhima et al. 2008; Jiang et al. 2012). Therefore, it is necessary and urgent to develop technologies to eliminate/reduce the concentrations of Pb^{2+} from wastewater before release. Various methods have been used to remove Pb^{2+} including coagulation, chemical precipitation, filtration, membrane, ion exchange and sorption (Boudrahem et al. 2009; Safa et al. 2012; Cankilic et al. 2013). Among all these methods, sorption is the most operable, effective and widely used.

So far, searches for good sorbents have been focused on the carbon materials, clay or metal oxide (Kadirvelu et al. 2008; Googerdchian et al. 2012; Jiang et al. 2012; Kragovic et al. 2013; Sharma & Lee 2013). However, commercial activated carbon had high cost and the pristine-activated carbon showed low sorption capacity of Pb^{2+} (Boudrahem et al.

2009). Although other modified sorbents including aminated resin and acrylamide modified nanocomposite possessed better sorption ability for Pb^{2+}, the preparation process of resulting materials was complicated (Niu et al. 2010; Sharma & Lee 2013).

Fly ash is one of the largest industrial wastes in the world, and is a by-product from power plants (Wang 2006). However, less than 25% of fly ash is utilized in some areas including road base, cement and mining (Ahmaruzzaman 2009; An & Huang 2012). Most of the wastes were disposed of as landfill or slag heap. The application with high values was restricted due to the low specific surface area of fly ash (ca. 4 m^2/g) (Wang 2006). The silica and alumina separation technology developed by the Engineering Laboratory of High Value Application of Coal-based Solid Wastes, Inner Mongolia Autonomous Region, generated new insights (Wei et al. 2012). Powder active silica with low cost and high specific surface area was obtained after separation of silica and alumina. In this study, the physicochemical properties of active silica including composition, structure and morphology were characterized. The sorption performances for Pb^{2+} including uptake kinetics, effect of pH value and sorbent dose

and sorption isotherm were investigated. The objective of this study was to develop a high-value application of active silica as effective sorbent instead of the multifunctional but expensive activated carbon. The cost of active silica is ~ 1,500 RMB/ton, which is much lower than activated carbon (2,800 RMB/ton ~ 3×10^6 RMB/ton). Note that the prices of active silica and activated carbon quoted here were from a commercial company in China.

MATERIALS AND METHODS

Materials

The lead nitrate (Pb $(NO_3)_2$, >99%) and nitric acid (HNO_3, 65–68%) were purchased from China National Medicines Corporation Ltd. The standard solution of Pb was obtained from the National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (China). The active silica derived from fly ash was supplied by Engineering Laboratory of High Value Application of Coal-based Solid Wastes, Inner Mongolia Autonomous Region. The Milli-Q water used in the experiment was from Millipore (Boston, PA, USA). All the other reagents used in the experiment were of analytical grade.

Characterization of active silica

The morphology of active silica was observed using field emission scanning electron microscopy (FE-SEM, HITACHI SU8020, Japan). Before FE-SEM observation, the sample was directly stuck on the sample holder through the conductive double-sided adhesive and the excess powder was blown off with an air gun. The physical structure including specific surface area, pore size and pore volume was obtained according to the Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda (BJH) method from the N_2 adsorption-desorption isotherm at 77 K with a surface area analyzer (ASAP 2020 HD88, Micromeritics, GA, USA). The zeta potential was measured as described in previous report (Zhou *et al*. 2010) with ZETASIZER 2000 instrument (Malvern, PA, USA).

Sorption experiments

The experiments included uptake kinetics, sorption isotherm and the effect of pH and sorbent dose on the removal efficiency of lead. The stock solution of lead nitrate was 1,000 mg/L with 1% HNO_3 to prevent hydrolysis. Batch sorption experiment was conducted in 50 mL flask

containing 50 mL of Pb $(NO_3)_2$ solution with initial concentration 20 mg/L. A mass of 50 mg active silica was added into the flasks which were shaken at room temperature (25 °C) and 150 rpm for 24 h. In the kinetics experiment, the system contained 1,000 mL solution of 2 mg/L Pb $(NO_3)_2$ and 1 g sorbent and the initial pH value was adjusted to 5.0 ± 0.2 (no pH adjustment during the sorption process). In the pH effect experiment, the initial pH values ranged from 2.3 to 5.5 and the solution pH was adjusted to keep constant during the process. In the isotherm experiment, the initial concentration of Pb $(NO_3)_2$ ranged from 2 to 1,000 mg/L with the constant pH of 5.0 ± 0.2. A range of 10 to 200 mg active silica was adopted to identify the effect of sorbent dose on removal efficiency of Pb and the solution pH value was kept constant at 5.0 ± 0.2. Note that the increased volume of alkali and acid was negligible. All of the sorption experiments were conducted in duplicate and the average values were used.

Determination of Pb

After sorption, 10 mL of the suspension was filtered with 0.22 μm membrane. Note that the effect of membrane on Pb concentration was negligible through our preliminary experiment. The Pb concentrations were determined by inductively coupled plasma optical emission spectrometry (PerkinElmer ICP-OES Optima 8,300). Serial dilutions of Pb standard solution were used to construct a standard curve ($R^2 =$ 0.999978). The uptake amount (q_e) and removal efficiency (R, %) of Pb were calculated with Equations (1) and (2). Note that the sorption amount and removal efficiency were calculated depending on the element Pb not Pb $(NO_3)_2$.

$$q_e = \frac{(C_0 - C_e)V_0}{M_s} \tag{1}$$

$$R(\%) = (C_0 - C_e)/C_e \times 100\% \tag{2}$$

where C_0 (mg/L) is the initial concentration of Pb; C_e (mg/L) is the equilibrium concentration of Pb; V_0 is the initial volume and M_s is the mass (g) of active silica.

RESULTS AND DISCUSSION

Characteristics of active silica

The main compositions of active silica are shown in Table 1, which included 39% SiO_2. The result indicated that alumina

SiO$_2$ (%)	CaO (%)	Fe$_2$O$_3$ (%)	MgO (%)	Ignition loss (875 °C) (%)	BET (m^2/g)	Pore volume (m^3/g)	Pore size (nm)
39.0	41.0	≤0.32	≤1.88	18.0	115	0.5	19.5

had been separated thoroughly from the fly ash after silica and aluminum separation. The BJH adsorption cumulative volume of pores between 1.7 and 300 nm diameters was 0.5 m^3/g and the average pore diameter of active silica was 19.5 nm. The active silica belongs to mesoporous material. The BET surface area reached 115 m^2/g, which was much higher than the original fly ash (4 m^2/g). The higher BET area would provide more effective sites and interaction space.

The morphology of active silica was observed through FE-SEM graphs with different scales, which looked like honeycomb or curly layers with many lamellae (Figure 1), which also were observed by Wei *et al.* (2012). The space between lamellae formed many mesopores (Wei *et al.* 2012), which were important reaction places for the removal of lead ions.

Kinetics

Kinetics governs the reaction rate, which is an important parameter defining the sorbent efficiency. In this study, the residual concentration of Pb^{2+} in the aqueous solution was used as evidence to estimate the efficiency of active silica. Figure 2 displays the kinetics of Pb^{2+} on the active silica. It was observed that the removal of Pb^{2+} was a quick process. When the initial Pb^{2+} concentration was 1.25 mg/L, the residual concentration of Pb^{2+} in the aqueous solution decreased rapidly by one-half within 5 min and reached less than 10 μg/L within 45 min after reaction with active silica. A maximum allowed value of lead concentration was 50 μg/L in

drinking water (Singh *et al.* 2007; Sharma & Lee 2013). The result indicated that the treatment of Pb^{2+} by active silica could achieve the requirement of water quality standard. Equilibrium was reached within about 1 h and no change in the residual concentration up to 2 h. To reach equilibrium, the reaction time in the next sorption experiment was 24 h.

Effect of pH

The influence of solution pH value on the removal efficiency of Pb^{2+} on active silica is shown in Figure 3(a). Solution pH not only affects the surface property of sorbent, but also dominates the existing formation of solute. The lead exists as Pb^{2+}, Pb(OH)$^+$, Pb(OH)$_2$, Pb(OH)$_3^-$, Pb(OH)$_4^{2-}$, which depends on the different pH value in the aqueous solution as shown in Figure 3(c). The initial pH value of the sorption system ranged from 2.3 to 5.5 and the pH value was kept constant during the experiment process. Thus, the lead exists as Pb^{2+} in this study according to Figure 3(c). Sorption beyond pH 5.5 was rejected to avoid the adverse influence of other formation of lead. Figure 3(a) shows us the removal efficiency of Pb^{2+} increased dramatically from 54 to 97% with the increase in pH from 2.3 to 5.5. It can be observed from Figure 3(b) that when the pH value was above 2.3, the surface of active silica was negative, which was beneficial for the Pb^{2+} removal by electrostatic attraction. On the other hand, the substitution of protons of the silanol by lead ions was accomplished because of the existing of abundant silanols on the surface of active silica (Abo-El-Enein *et al.* 2009). Based on the results above mentioned, an optimum pH value of 5.0 ± 0.2 was adopted in the next sorption experiments.

Effect of sorbent dose

The relationship between Pb^{2+} removal, residual concentration and dose of active silica is shown in Figure 4. The
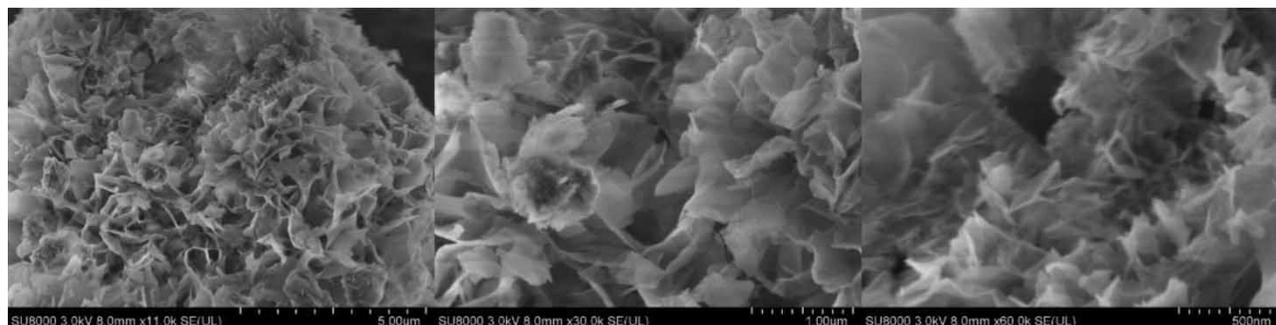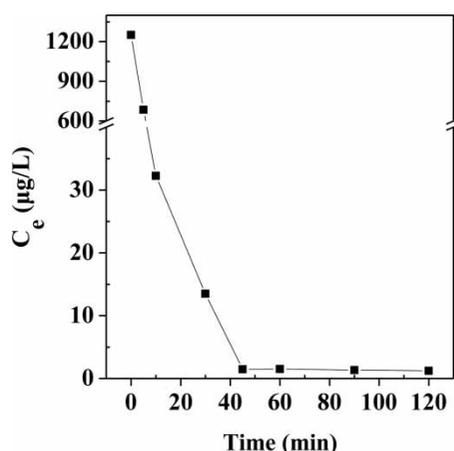

Figure 1 | SEM morphology of active silica.

Figure 2 | Kinetics of Pb^{2+} on the active silica (M_S was 1 g, V_0 was 1,000 mL, C_{0-Pb} was 1.25 mg/L, pH_0 was 5.0 ± 0.2).
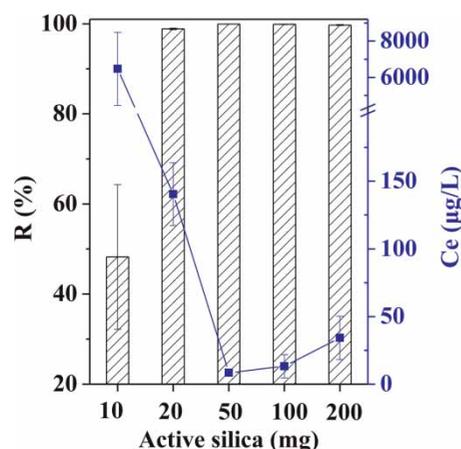

Figure 4 | Effect of sorbent dose on the removal of Pb (V_0 was 50 mL, C_{0-Pb} was 12.5 mg/L, pH_0 was 5.0 ± 0.2).
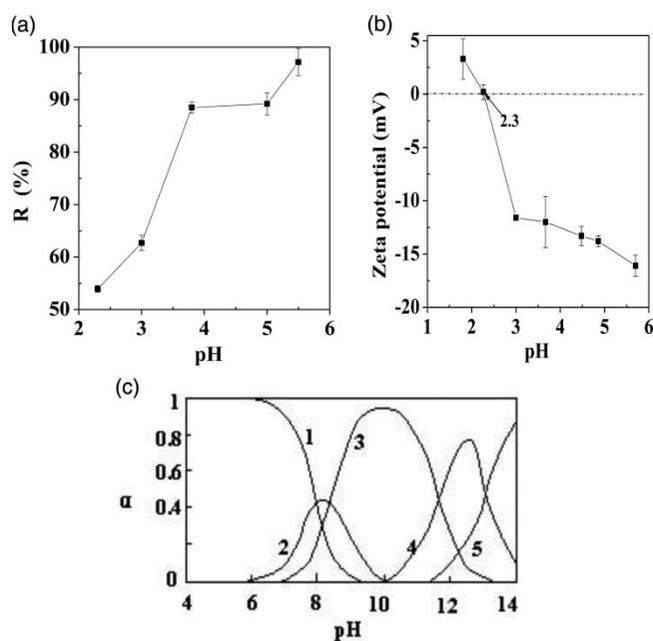

Figure 3 | Effect of pH value on removal efficiency of Pb^{2+} on active silica (a), Zeta potential of active silica (b) (V_0 was 50 mL, M_S was 50 mg, C_{0-Pb} was 12.5 mg/L) and the relationship between pH values and Pb formation (c) (cited from http://gzhx.cooco.net.cn/testdetail/8192/) (1 Pb^{2+}, 2 $Pb(OH)^+$, 3 $Pb(OH)_2$, 4 $Pb(OH)_3^-$, 5 $Pb(OH)_4^{2-}$).

removal efficiency of Pb increased rapidly from 48 to 98.9% with the increase in dosage of active silica from 10 to 20 mg. When the mass of active silica continued to rise from 50 to 200 mg, the removal of Pb kept constant at approximately 99.9%. It was observed that the residual concentration of Pb^{2+} in aqueous solution after sorption treatment with 50 mg active silica was the lowest, which was below 50 μg/L and had met the requirement of water quality standard from World Health Organization (Sharma & Lee 2013).

However, the Pb^{2+} residual concentrations became a little higher with the further increase of sorbent dose to 100 and 200 mg. The result indicated that extra sorbent dose had a negative influence on the removal of Pb^{2+}. When the sorbent doses increased, active silica might tend to agglomerate into larger particles because of direct inter-particle interactions, which might lead to a decrease of effective sorption sites. Based on the discussion, the sorbent dose was adopted as 50 mg in the next sorption isotherm.

Sorption isotherm and mechanism

It can be observed from Figure 5 that the removal efficiency of Pb^{2+} decreased dramatically from more than 99% to less than 20% with the increase of initial concentration of Pb. The residual concentration of Pb^{2+} in the aqueous solution after sorption could reach μg/L level as the C_{0-Pb} was below 50 mg/L. The result indicated that the active silica was effective for the low concentration of lead, whereas it was almost invalid for the high concentration of lead. The maximum sorption amount of Pb on active silica reached approximately 90 mg/g as shown in Figure 5. The sorption capacity of active silica for Pb was lower than some modified sorbents such as aminated resin (201 mg/g) and acrylamide-modified nanocomposite (476 mg/g), whereas the uptake ability was much higher than some pristine activated carbon (27 and 63 mg/g) (Boudrahem *et al.* 2009; Niu *et al.* 2010; Sharma & Lee 2013; Wan *et al.* 2014).

Non-linear isotherm is shown in Figure 5. However, the traditional non-linear models such as the Langmuir/Freundlich models could not fit the experimental data of Pb^{2+} sorption on active silica (fitting results not displayed due
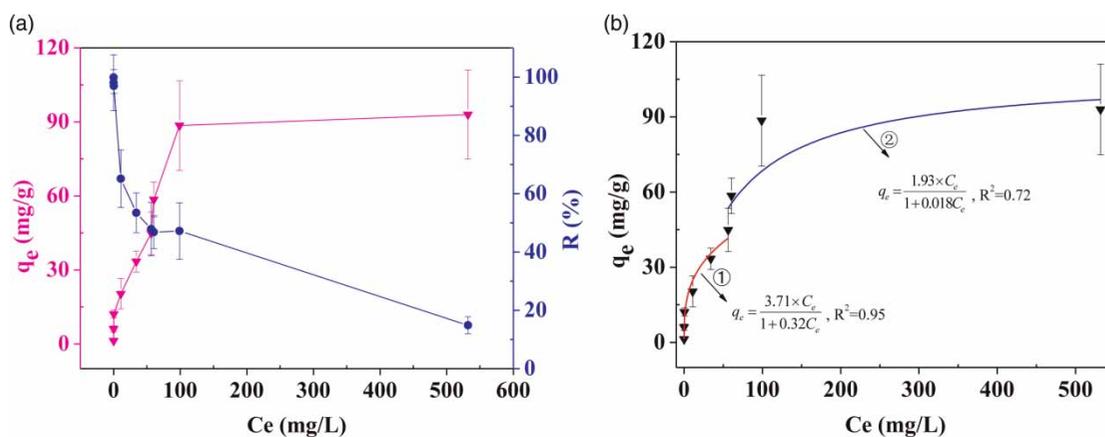
Figure 5 │ Sorption capacity and removal efficiency of Pb on active silica (a); stepwise adsorption model (b) (V_0 was 50 mL, M_S was 50 mg, pH_0 was 5.0 ± 0.2).

to $R^2 < 0.5$). An & Huang (2012) developed the stepwise adsorption model to fit the sorption of phenanthrene on fly ash. In this study, two sections were observed from the sorption isotherm, and each section represented one Langmuir isotherm, which are displayed in Figure 5(b). According to previous reports, the multisite Langmuir model was useful for sorbents with more heterogeneous surface (An & Huang 2012). Therefore, it was reasonable to assume that the surface sites of active silica were not identical and there existed various binding energies with different affinity. The stepwise isotherm was attributed to the multisites based on the monolayer sorption process by electrostatic attraction between positive Pb ions and negative surface of active silica. The special curly lamellae of active silica provided various active sites with different affinity. At the low concentration of Pb ions, all the unoccupied sites were in excess and the Pb preferred sites with high affinity. The sorption of Pb on the high energy sites became saturated and the excess Pb was forced to bind other sites with low affinity when the Pb amount increased.

CONCLUSION

In general, the active silica owned better sorption amount and removal efficiency of Pb, especially for low concentration of Pb. The Pb^{2+} removal on active silica was dependent on pH and the sorbent dose. The increase in pH value and sorbent dose promoted the Pb^{2+} removal. The maximum sorption amount reached approximately 90 mg/g, which was better than some pristine activated carbon. More sorption properties of active silica including

for typical organic pollutants would be further investigated in the future study.

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