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Adsorption of Pb(II) ions from aqueous solution by surfactant-templated titania aerogels

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ABSTRACT

Titania aerogels were synthesized via sol–gel method by using polyethylene glycol-600 (PEG-600), cetyltrimethylammonium bromide (CTAB), and polyvinylpyrrolidone (PVP) as templates. The obtained aerogels were characterized by N_2 adsorption/desorption, X-ray diffraction, and Fourier transform infrared spectrum, and used for the removal of Pb(II) from aqueous solution. The influences of contact time, the initial concentration of Pb(II), and pH of the aqueous solutions on removal efficiencies were also studied. It was found that titanium dioxide aerogel templated by PEG-600 exhibited higher adsorption capacity than those aerogels without template and templated by CTAB and PVP. Its adsorption capacity was 181 mg Pb(II)/g at pH = 6.5 after 1 h. The adsorption process was described by pseudo-second-order kinetics. The Freundlich and Langmuir models were also used to simulate the adsorption equilibrium. The results indicate that the latter had a better fit with the experimental data. Titania aerogels templated by PEG-600 had great potential for the removal of Pb(II) from aqueous solution.

Keywords: Titania aerogel; Lead (II) ion; Sol–gel method; Surfactant templating; Adsorptive removal

1. Introduction

Heavy metals such as Pb^{2+}, Cu^{2+}, and Cd^{2+} in water are usually considered as serious menaces to the environment and especially to human health. For example, Pb(II) is a potent neurotoxic metal with major concern. The presence of Pb(II) in drinking water, even with low concentrations, may cause diseases such as anemia, hepatitis, nephrite syndrome, etc. [1]. A number of processes such as chemical precipitation, ion exchange, solvent extraction, and adsorption have been designed for the removal of lead from aqueous solution [2]. Among these methods, adsorption is considered to be one of the most efficient and promising methods [3]. A variety of adsorbents such as activated carbon, natural kaolinite clay, zeolites [4–7], polymers [8], and metal–organic frameworks (MOFs) [9] have been reported effective for Pb(II) removal.

Aerogels are high surface area/low density materials consisting of open and highly porous structure derived from the supercritical drying of highly cross-linked inorganic or organic gels. Because of their ultra-low density, high homogeneity, and very high porosities, aerogels have recently attracted great attention in various applications [10]. For example, aerogels have been widely applied as efficient

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adsorbents, which adsorbed organic pollutants from water and as host materials for drug delivery systems [11–14]. So far, very few studies on using aerogels in removal of Pb(II) from water have been reported. To the best of our knowledge, only three aerogels, silica-gel supported hyperbranched polyamidoamine dendrimers [15], carbon aerogel [16], and graphene aerogel [17] have been very recently used to remove Pb(II) from water with low adsorption capacity. On the other hand, titanium dioxide/multiwalled carbon nanotubes (TiO_2/MWCNTs) nanocomposites [18], TiO_2 nanoparticles and bulk particles [19], and TiO_2 nanotubes [20] have been used for the adsorption of Pb(II) from aqueous solution. Among these, titania-based materials, TiO_2/MWCNTs, exhibited maximum adsorption capacity (137 mg/g).

TiO_2 aerogel shows great promise in boosting the dye-loading [21], catalytic/photocatalytic activities [22]. It was generally prepared by sol–gel methods and subsequent supercritical drying process [23], in the course of gelation and pore formation. For the synthesis of aerogels, structure directing agents such as surfactant templating are as important as the preparative parameters for controlling porosity and pore size [24] since the surfactant molecules can reduce the capillary force derived from solvent evaporation and prevent the shrinking and cracking [25]. For example, mesoporous TiO_2-silica aerogels with hierarchical pore structure were synthesized by using triblock polymer pluronic [26]. Triblock polymer pluronic, cetyltrimethylammonium bromide (CTAB), and sodium dodecyl sulfonate were used to synthesize tetraethyl orthosilicate-based wet-gel silica alcogels [27]. Moreover, co-presence of appropriate surfactant effectively suppresses the phase separation and yields transparent aerogels after supercritical drying [28].

In this study, polyethylene glycol-600 (PEG-600), CTAB, and polyvinylpyrrolidone (PVP) were used to synthesize titania-based aerogels. These surfactants were widely used as structure directing agents when building mesoporous structures. They are able to differentiate the titania aerogels from the conventional titania aerogels (without surfactant). The as-prepared titania aerogels were used to remove Pb(II) ions in water.

2. Materials and methods

In the present study, TiO_2 aerogel was used as an adsorbent for the removal of Pb(II) from aqueous solution. TiO_2 aerogel was prepared by surfactant-templated solvent thermal methods (see supporting information).

Powder X-ray diffraction (XRD) data were collected using a Rigaku TTRAX III X-ray diffractometer (Cu Kα irradiation). Nitrogen adsorption/desorption measurements were carried out on a Micromeritics Tristar II surface area and porosity analyzer. UV-Vis diffuse reflectance spectra were measured on a Shimadzu UV-2401PC photometer from 200 to 800 nm. Fourier transform infrared spectrum (FT-IR) measurement was performed on a Thermo Nicolet 8700 FT-IR spectrometer.

In a typical absorption procedure, the adsorption capacities of aerogel were conducted by the following procedure: 30 mg of adsorbent aerogel were added to 50 mL of the Pb(II) solutions with different concentrations under stirring for about 1 h at room temperature. After a specified time, the solid and liquid were separated immediately and analyzed by Metrohm797 volt-ampere polarograph instruments (made in Switzerland) to measure the concentration of Pb(II) in the remaining solution.

The amounts of adsorbed Pb(II) was calculated from the difference between the initial (C_0) and equilibrium (C_e) concentrations (mg/L) in the supernatant after centrifugation. The adsorption percentage was calculated according to Eq. (1):

$$\text{Adsorption percentage (\%)} = (C_0 - C_e)/C_0 \times 100\% \qquad (1)$$

The amount of Pb(II) adsorbed by the adsorbent was taken as the difference between the initial and equilibrium concentrations of Pb(II) in the solutions, and the adsorption capacity (q_e, mg/g) of the Pb(II) adsorbed on to TiO_2 aerogel was obtained from the following equation and used for further adsorption isotherm analysis:

$$q_e = (C_0 - C_e)\,V/W \qquad (2)$$

where V is the volume of Pb(II) solution (L), and W is the weight of adsorbent (g).

The reusability of TiO_2 aerogel mainly relies on the ease with which Pb(II) gets desorbed from used sample. Therefore, 2.0, 1.5 and 0.5 M HCl were used as the recycling agents in this work. Recovery test was carried out for TiO_2 aerogel: 30 mg TiO_2 aerogel, which had been used once was recollected, then soaked and stirred for 1 h in 30 ppm lead solution (50 mL) in order to make sure that the adsorption–desorption equilibrium has been achieved. The filtered TiO_2-PEG aerogel, TiO_2-CTAB aerogel, and TiO_2-PVP aerogel were soaked and stirred for 12 h in 100 mL 2.0, 1.5 and 0.5 M HCl, respectively, then filtered and washed with deionized water to pH ~7, dried at 90°C for 10 h.

3. Results and discussion

Fig. 1 shows XRD patterns of the prepared samples. The XRD pattern of TiO_2-PVP aerogel shows peaks at 2θ values of 25.3°, 37.8°, 48.0°, 53.9°, and 62.7°, which correspond to (101),

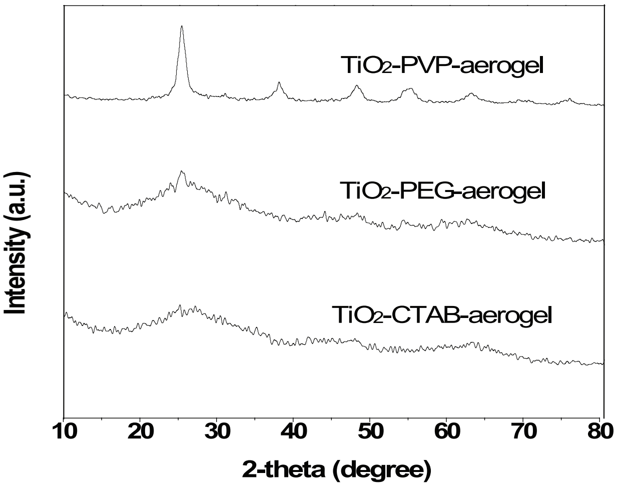

Fig. 1. XRD patterns of the synthesized TiO_2 aerogels.

(004), (200), (105), and (204) crystallographic planes of anatase TiO_2 (joint committee on powder diffraction standards (JCPDS), No. 21-1272). An extra peak at 2θ = 30.8°, which matches with the peaks of brookite TiO_2 (JCPDS, No. 29-1360), implying that solvent thermal process at 245°C under 1,000 KPa partially transform the anatase TiO_2 to brookite [29]. TiO_2-PEG aerogel and TiO_2-CTAB aerogel were amorphous.

Nitrogen adsorption/desorption isotherms for TiO_2 aerogels are shown in Fig. S1. All the three isotherms could be classified as being of type IV according to International Union of Pure and Applied Chemistry classification, which are characteristic of mesoporous material. TiO_2-PVP-aerogel and TiO_2-CTAB-aerogel have very similar hysteresis loop, which could be classified as being H3 type. And the hysteresis loop of TiO_2-PEG-aerogel could be classified to be H4 type. The results suggest that the pore structures of the samples are not intact and the mesopores present in aggregates composed of primary particles, giving rise to pileup pores or cracks and slits. The Brunauer–Emmett–Teller (BET) surface area, average pore volume, and average pore diameter of TiO_2 aerogels are summarized in Table S1 (supporting information). The samples possess high surface areas range from 500 to 700 m^2/g. SEM images of TiO_2-PVP-aerogel are randomly shown in Fig. S2. It can be observed that the bulks are composed of porous TiO_2 particle aggregations.

The relationship between adsorption behavior of Pb(II) on TiO_2 aerogels and contact time was investigated by varying the contact time from 10 to 300 min. The dose of TiO_2 aerogel absorbent was 30 mg, and the initial Pb(II) concentration was 100 pm at pH = 6.5. It was found that the adsorption equilibrium state was reached after 60 min. As shown in Fig. 2, the order of adsorption capacities of the aerogels is TiO_2-CTAB aerogel < TiO_2-PVP aerogel < TiO_2-PEG aerogel. TiO_2-PEG aerogel possesses the highest adsorption capacity of 181 mg/g.

The effect of pH on adsorption capacity was investigated at different pH range from 1.0 to 7.0 and depicted in Fig. 3. It reveals that the adsorption of Pb(II) on TiO_2 aerogels increased quickly with increasing in pH value, and when further increasing pH to 7.0, the adsorption percentage of Pb(II) over TiO_2-PVP aerogel remained around 80%. At high pH, the OH^- on the surface provided the ability of binding Pb(II). However, the decrease of pH resulted in the neutralization of surface charge, and OH^- was displaced from the surface. The adsorption of cations onto TiO_2 therefore decreased quickly. To avoid further precipitation at higher pH values, the optimal pH value for further studies was determined to be 6.5.

Fig. 4 describes the effect of the initial concentration on the adsorption capacity of Pb(II) ions by TiO_2 aerogels. The initial Pb(II) concentration was ranged from 10 to 173 ppm, while the adsorption capacity of Pb(II) increased with increase in initial concentration. For TiO_2-PEG aerogel, the maximum adsorption capacity for Pb(II) on TiO_2 aerogel is about 181 mg/g when initial concentration is 142 ppm. It is suggested that the total available adsorption sites are limited, resulting in a maximum adsorption capacity.

The experimental data for Pb(II) adsorption onto TiO_2 aerogel were analyzed using the Langmuir and Freundlich adsorption isotherm models (shown in Figs. S3 and S4, respectively). The linear Langmuir equation and the Freundlich equation are normally expressed as follows:

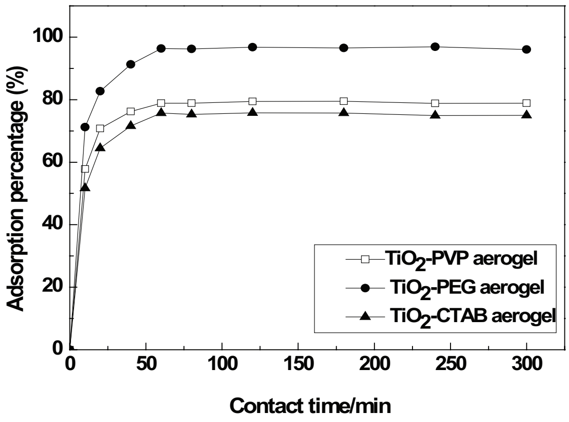

Fig. 2. Effect of contact time on the adsorption percentage of TiO_2 aerogel for Pb(II) (conditions: initial Pb(II) concentration was 100 ppm; adsorbent dose was 30 mg; sample volume was 50 mL; pH value was 6.5).

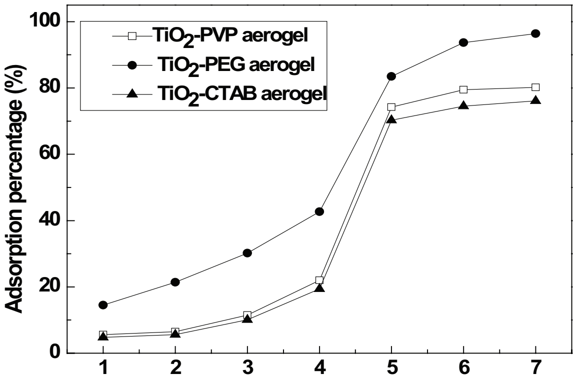

Fig. 3. Effect of pH on the adsorption percentage of TiO_2 aerogel for Pb(II) (conditions: initial Pb(II) concentration was 100 ppm; adsorbent dose was 30 mg; sample volume was 50 mL; contact time was 60 min).

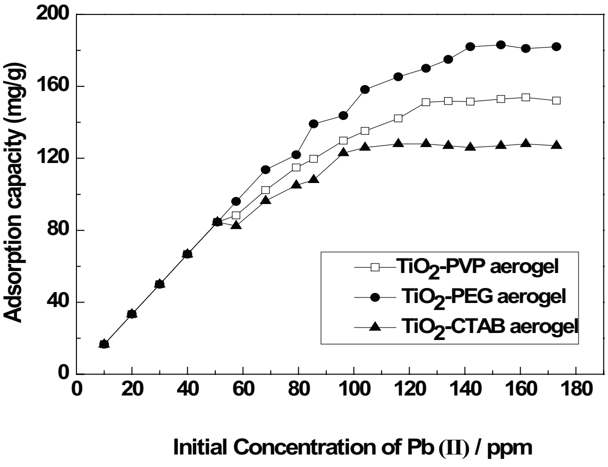

Fig. 4. Effect of initial concentration on adsorption capacity of Pb(II) ions by TiO_2 aerogel (conditions: adsorbent dose was 30 mg; sample volume was 50 mL; contact time was 60 min; pH value was 6.5).

$$C_e/q_e = 1/bq_m + C_e\,(1/q_m) \tag{3}$$

$$\ln q_e = \ln K_F + 1/n\,\ln C_e \tag{4}$$

where C_e is equilibrium concentration in solution (mg/L); q_m and q_e are maximum adsorption capacity (mg/g) and the adsorption capacity at equilibrium (mg/g), respectively. b is the adsorption equilibrium constant (L/mg); K_F and n are the indicator of the adsorption capacity and adsorption intensity.

As presented in Table S2 (supporting information), a high value of the coefficient of correlation indicates better agreement between experimental and predicted data using the Langmuir equation than the Freundlich equation. It is suggested that monolayer sorption took place on the surface of the TiO_2 aerogels.

The comparison of maximum adsorption capacities (q_m) of TiO_2 aerogel for Pb(II) with other adsorbents reported in literatures is given in Table 1. Compared with TiO_2 aerogels without template and other TiO_2 materials reported in literature, TiO_2 aerogels with template had much higher adsorption capacities. In particular, TiO_2-PEG aerogel exhibited highest adsorption capacities (181 mg/g), which is even higher than that of TiO_2/MWCNTs (137 mg/g). Moreover, in comparison to the TiO_2 aerogel templated by PVP, PEG, and CTAB, TiO_2 aerogel without template has a much lower BET surface area (290 m^2/g). Therefore, it could be concluded that employment of surfactants in the synthetic procedures could significantly increase the surface of TiO_2 aerogels. And the surface area should be the main influence factor for adsorption of Pb(II) on TiO_2 aerogels.

To investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, three different kinetic models were used to fit the adsorption kinetic data: the pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion. The pseudo-first-order kinetic model and the pseudo-second-order kinetic model are expressed as follows:

Table 1
Comparison of adsorption of Pb(II) with other absorbents

Adsorbents	$q_{\max}$ (mg/g)	References
TiO_2-PVP aerogel	151	This study
TiO_2-PEG aerogel	181	This study
TiO_2-CTAB aerogel	142	This study
TiO_2 aerogel without template	54	This study
TiO_2/MWCNTs (titanium dioxide/ multiwalled carbon nanotubes)	137.0	[18]
TiO_2 nanoparticles	83	[19]
SiO_2-G0 (silica gel with aminopropyltriethoxysilane)	68	[15]
TiO_2 bulk particles	65	[19]
Activated carbon	43	[30]
Dithizone-modified TiO_2 nanoparticles	23	[31]
Nanometer titanium dioxide immobilized on silica gel	3.2	[32]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

where q_t and q_e are the adsorption capacity (mg/g) of the titania aerogel at a time t and at equilibrium, respectively; k_1 is the pseudo-first-order rate constant (min^{-1}); k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order. The values of k_1 and q_e can be gained from the slopes and intercepts of $\ln(q_e - q_t)$ against the t plot (Fig. S5). The values of q_e and k_2 can be obtained from the slopes and the intercepts of the t/q_t vs. t plots. The plot of t/q_t against t is shown in Fig. S6.

The correlation coefficients for the second-order kinetic model obtained were higher than 0.998 for all TiO_2 aerogels. Besides, the calculated q_e values also agree with the experimental data (181 mg/g) very well for TiO_2-PEG aerogel (Table 1), indicating that the pseudo-second-order kinetic model was valid to predict the behavior of Pb(II) adsorption. A pseudo-second-order is based on the assumption that the rate-limiting step may be chemical sorption, which involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

To gain insight into the adsorption mechanism and rate-controlling steps, which affects the kinetics of adsorption, the intraparticle diffusion model is applied:

$$q_t = k_{\text{ipd}}\, t^{0.5} + C \tag{7}$$

where k_{ipd} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-0.5}$), and C is the intercept.

The Pb(II) adsorption process from aqueous solution onto TiO_2 aerogels involves certain steps: (i) film diffusion; (ii) intraparticular diffusion; and (iii) adsorption on the pore surface. Generally, we think the first step of adsorption, which the film diffusion is a significant rate-controlling step. The third step is supposed to be fast and considered to be negligible [33].

The plot of the experimental data (Fig. S7) showed that the plots are not linear over the whole time range. However, the data points are related by two straight lines. The first sharper portion is attributed to the diffusion of lead through the solution to the external surface of the TiO_2 aerogel (external diffusion), and the second portion describes the equilibrium adsorption, which is called intraparticle diffusion. It deserves to indicate that the second linear plots did not pass by the origin, which notes that the intraparticle diffusion is involved in the adsorption process. However, it is not the only rate-controlling step. Other mechanisms could also control this adsorption process [34].

In order to further confirm the adsorption mechanism of Pb(II) onto TiO_2 aerogel, the changes of characteristic adsorption peaks in adsorbents before and after adsorption were investigated by FT-IR. Fig. S8 shows that the peaks were around 3,400 and 1,625 cm^{-1} in all samples were due to stretching and bending vibrations of –OH groups. The three bands at 1,450 and 1,400 cm^{-1} are attributed to the C–H vibrations derived from the residual organic groups. As to TiO_2-CTAB aerogel, the peaks at 2,920 and 2,866 cm^{-1} could be attributed to vibrations of $-CH_2$ and $-CH_3$ from residuals

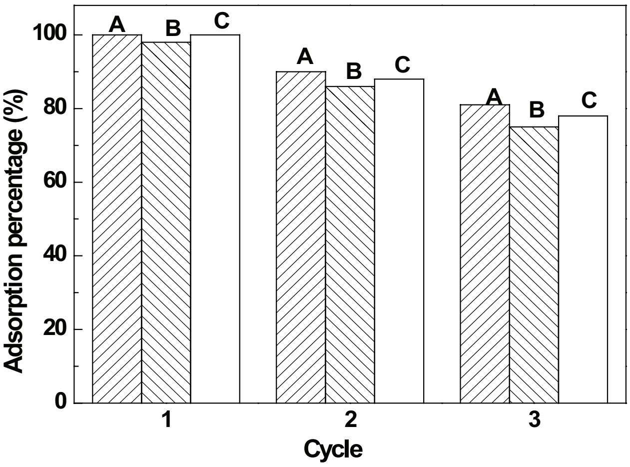

Fig. 5. Pb(II) removal using regenerated TiO_2 aerogels: (A) TiO_2-PEG aerogel, (B) TiO_2-CTAB aerogel, and (C) TiO_2-PVP aerogel (initial lead concentration: 30 ppm; 30 mg TiO_2 aerogels; pH = 6.5; 50 mL solution).

of CTAB. The peak of the hydroxyl groups become weak after adsorbing Pb(II), indicating that the involvement of functional groups like hydrogen in the adsorption process. The possible reason for TiO_2 aerogel with template (PEG, CTAB, and PVP) present higher adsorption capacity is that they possess more hydroxyl groups than TiO_2 aerogel without template.

After desorption, the solids were separated and washed, and then reused in the next cycle of the adsorption experiment. Fig. 5 shows that the amount of Pb(II) adsorbed on TiO_2-PEG aerogel remained relatively constant with each successive cycle ~100% Pb was adsorbed at the end of the first cycle and dropped to 80% at the end of three cycles. This suggests that TiO_2-PEG aerogel can be recycled at least once without losing its activity to a greater extent.

4. Conclusions

In this study, PEG-600, CTAB, and PVP were used as surfactants to synthesize titania-based aerogels. The obtained aerogels have been demonstrated to be able to efficiently remove Pb(II) in standard lead solutions. The adsorption efficiencies were relied on contact time, initial lead ions concentration, and pH. TiO_2 aerogel templated by PEG exhibited higher adsorption capacity than those templated by CTAB and PVP. The maximum adsorption capacity for Pb(II) on TiO_2-PEG aerogel was about 181 mg/g. The Langmuir equation fitted the adsorption equilibrium data over the concentration range used in this investigation better than the Freundlich equation did. In addition, TiO_2-PEG aerogel could be easily recycled without losing its activity to a greater extent. Thus, TiO_2-PEG aerogel is a potential adsorbent for removal of lead ions from aqueous solution.

Acknowledgments

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Supporting Information

Preparation of titania aerogels

0.4 g surfactant was dissolved in 80 mL of N,N-dimethylformamide (DMF). After that, titanium isoporpoxide (TTIP, 10 mL) was added to the dispersion and stirred for 10 min. Subsequently, deionized water of 10 mL was added slowly to the mixture, and the reaction mixture was stirred for another 60 min. Different surfactants including polyethylene glycol-600 (PEG-600), cetyltrimethylammonium bromide (CTAB), and polyvinylpyrrolidone (PVP) have been used. The resulting reaction mixture was transferred to a 500-mL quartz glass-lined autoclave (Parr Instrument Co., USA) and was reacted at 245°C for 1.5 h under N_2 atmosphere to bring the total pressure to 10 bar. After the reaction, the autoclave was cooled to room temperature to obtain the final product. The obtained aerogels by using different templates were denoted as TiO_2-PEG aerogel, TiO_2-CTAB aerogel, and TiO_2-PVP aerogel, respectively.

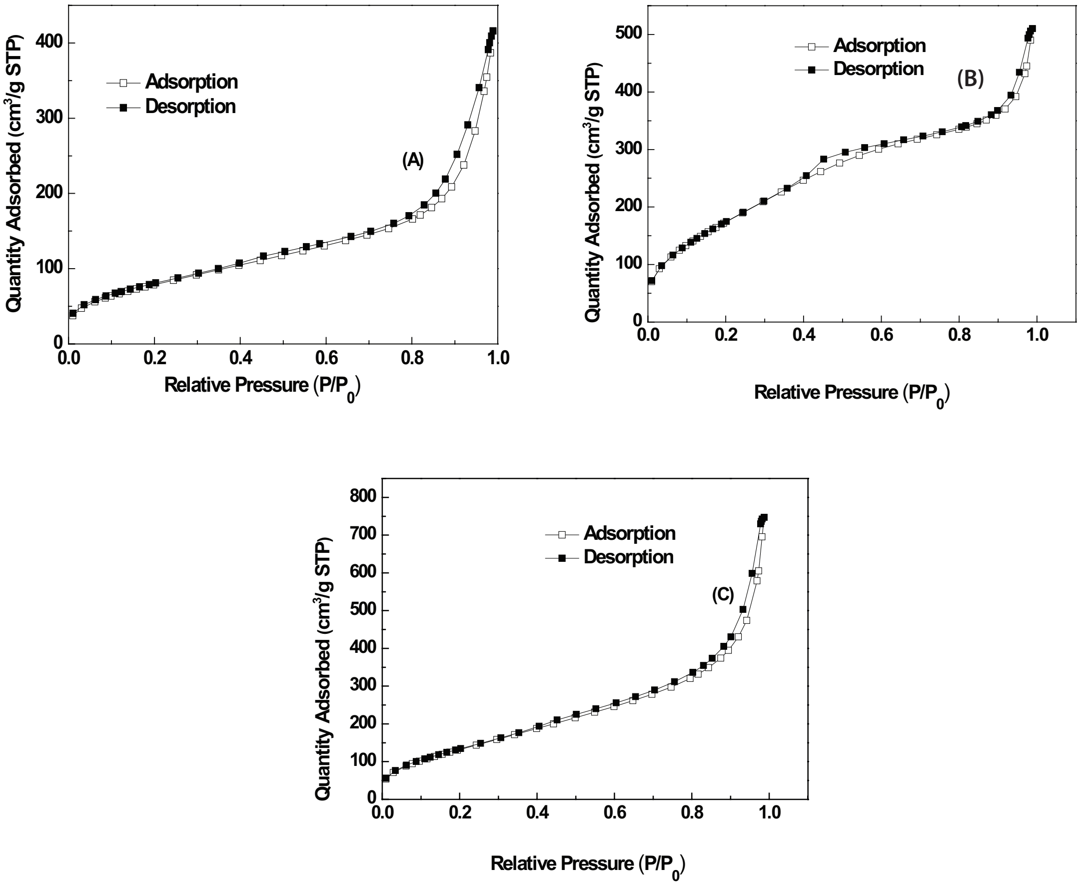

Fig. S1. (A) N_2 adsorption/desorption isotherm of TiO_2-PVP aerogel; (B) N_2 adsorption/desorption isotherm of TiO_2-PEG aerogel; and (C) N_2 adsorption/desorption isotherm of TiO_2-CTAB aerogel.

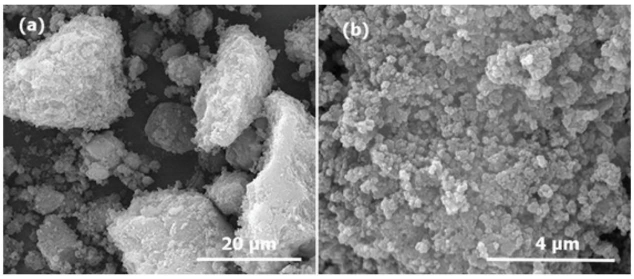

Fig. S2. SEM images of TiO_2-PVP aerogel.

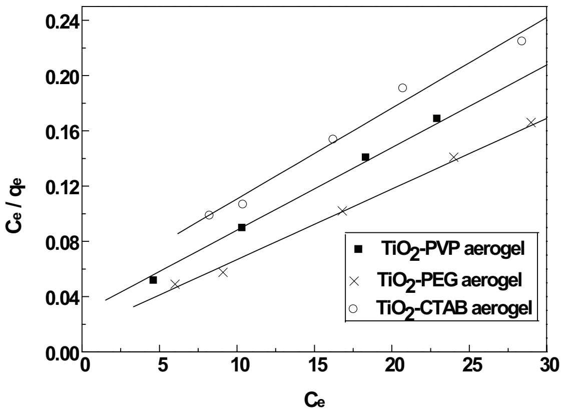

Fig. S3. Langmuir adsorption isotherms for Pb(II) by TiO_2 aerogel.

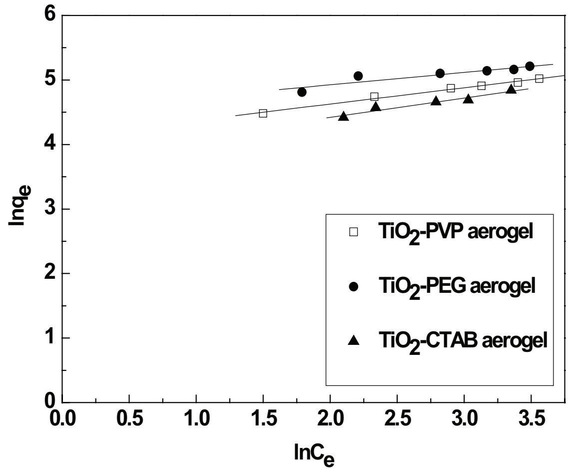

Fig. S4. Freundlich isotherm for Pb(II) by TiO_2 aerogel.

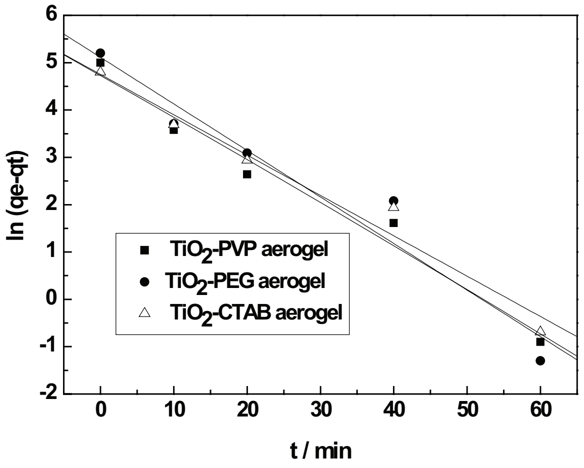

Fig. S5. Pseudo-first-order kinetics plots for the adsorption of Pb(II) onto TiO_2 aerogel.

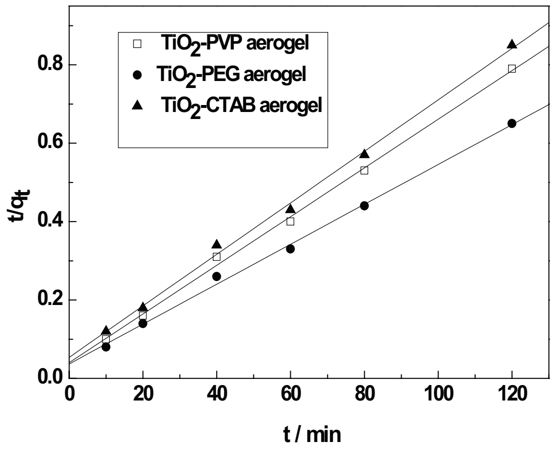

Fig. S6. Pseudo-second-order kinetics plots for the adsorption of Pb(II) onto TiO_2 aerogel.

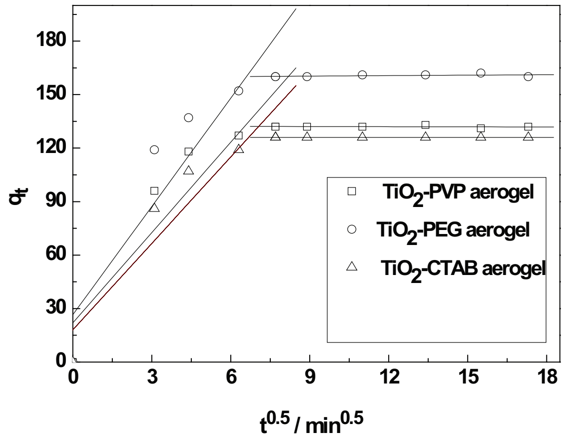

Fig. S7. Intraparticle diffusion model for the adsorption of Pb(II) onto TiO_2 aerogel.

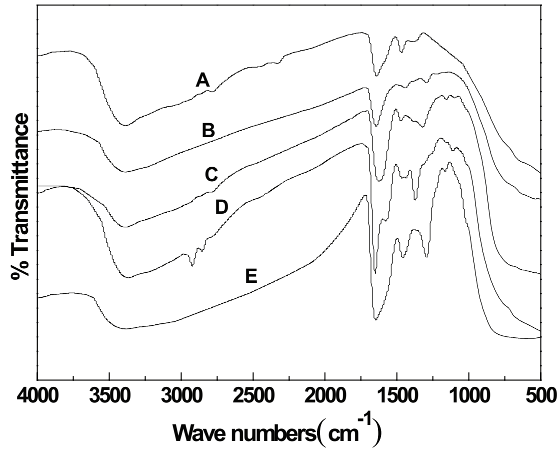

Fig. S8. Fourier transform infrared spectrum (FT-IR) spectra of TiO_2 aerogel before and after adsorption of Pb(II): (A) TiO_2 aerogel without template, (B) TiO_2-PVP aerogel after adsorption, (C) TiO_2-PEG aerogel, (D) TiO_2-CTAB aerogel, and (E) TiO_2-PVP aerogel.

Table S1
Brunauer–Emmett–Teller (BET) surface areas, Barrett–Joyner–Halenda pore volume, and pore diameter

Samples	BET surface areas (m^2/g)	Pore volume (m^3/g)	Pore diameter (nm)
TiO_2-PEG aerogel	675	0.67	3.95
TiO_2-PVP aerogel	597	0.52	7.05
TiO_2-CTAB aerogel	509	0.89	7.04

Table S2
Adsorption constants for the Langmuir and Freundlich isotherm models of TiO_2 aerogel

Adsorbents	Model parameters	Langmuir			Freundlich		
		R^2	q_{max}	b	R^2	K_F	n
TiO_2-PEG aerogel		0.9983	195.0	0.33	0.9185	93.7	5.3
TiO_2-PVP aerogel		0.9982	166.1	0.22	0.9948	61.56	4.0
TiO_2-CTAB aerogel		0.9919	149.8	0.15	0.9734	45.6	3.3