Chemical Engineering Journal 280 (2015) 275–282

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Sponge-like polysiloxane-graphene oxide gel as a highly efficient and renewable adsorbent for lead and cadmium metals removal from wastewater

Guiyin Zhou [a], Chengbin Liu [a,c,*], Yanhong Tang [b,*], Shenglian Luo [a,c,*], Zebing Zeng [a,c], Yutang Liu [d], Rui Xu [a], Lin Chu [a]

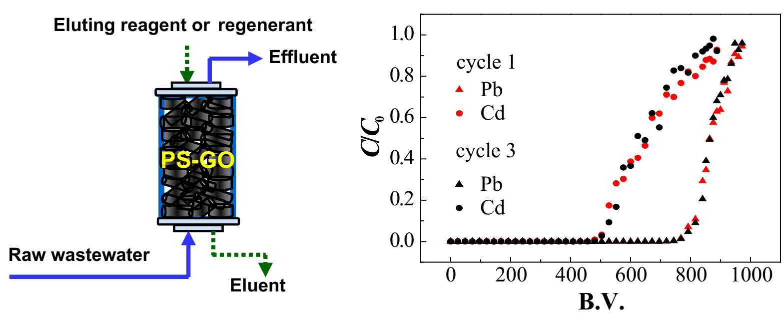
[a] State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, PR China
[b] College of Materials Science and Engineering, Hunan University, Changsha 410082, PR China
[c] Hunan Provincial Key Laboratory for Cost-effective Utilization of Fossil Fuel Aimed at Reducing Carbon-dioxide Emissions, Hunan University, Changsha 410082, PR China
[d] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China

HIGHLIGHTS

- The PS-GO gel was prepared by simple preparation process with low cost.
- This adsorbent exhibited high adsorption capacity and excellent reusability.
- This adsorbent showed efficient removal of heavy metals from industrial effluent.
- "Zero" amount of sludge was produced after fixed-bed column sorption.

GRAPHICAL ABSTRACT

A sponge-like polysiloxane-graphene oxide (PS-GO) gel adsorbent has been prepared by simple one-step sol-gel method. The adsorbent shows high heavy metal adsorption capacity and excellent reusability.



ARTICLE INFO

Article history:
Received 12 April 2015
Received in revised form 6 June 2015
Accepted 8 June 2015
Available online 15 June 2015

Keywords:
Gel adsorbent
Heavy metals removal
Sorption capacity
Regeneration
Reusability

ABSTRACT

Low cost, high adsorptivity, fast regeneration and excellent reusability are strongly recommended for a qualified adsorbent used in removing heavy metals from practical wastewater. A sponge-like polysiloxane-graphene oxide (PS-GO) gel adsorbent for removing lead and cadmium from wastewater has been prepared by simple one-step sol-gel method. The maximum sorption capacity of Pb(II) achieves as high as 256 mg/g. PS-GO gel adsorbent exhibits an excellent reusability because of its remarkable mechanical strength and highly efficient desorption/regeneration. In the static treatment process, after five cycles, Pb(II) in actual industrial effluent at 3.225 mg/L could be reduced to below 0.01 mg/L, still holding over 99% removal efficiency. Significantly, in the dynamic treatment process using a fixed-bed column packed with PS-GO gel, the treatment volume of wastewater is as high as 720 bed volume (BV) (8143 mL) for Pb(II) and 480 BV (5429 mL) for Cd(II) with producing only 11.31 mL eluent in each cycle. It should be stressed that the in situ regeneration of PS-GO gel adsorbent in fixed-bed column is operationally feasible and the treatment technology has the advantage of producing "zero" amount of sludge. This work has taken a key step closer to the treatment of actual heavy metals wastewater based on adsorption technology in large scale.

* Corresponding authors at: State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, PR China (C. Liu and S. Luo). Tel./fax: +86 731 88823805.
E-mail addresses: chem_cbliu@hnu.edu.cn (C. Liu), tangyh@hnu.edu.cn (Y. Tang), sllou@hnu.edu.cn (S. Luo).

http://dx.doi.org/10.1016/j.cej.2015.06.041
1385-8947/

1. Introduction

The treatment of heavy metal wastewater has been a difficult issue. There are various traditional techniques for the treatment of heavy metal pollution, including reduction, chemical precipitation, membrane filtration, ion exchange, and electrochemical treatment. However, these methods have been found to be limited by cost, complexity, efficiency or secondary waste. Among them, precipitation technique has been applied on a large scale to the treatment of heavy metal wastewater [1–3], but there is no avoiding the fact that the subsequent processing of toxic sludge treatment is a thorny problem. Adsorption technology is considered as a practicable alternative due to batch and continuous processes and suitable chemistry [4,5]. Various adsorbents including polymers [6–8], clay minerals [9,10], oxides [11–13], carbon materials [14–16], and biosorbents [17,18], have been studied to remove heavy metal ions from aqueous solutions. From a practical point of view, there is still a major drawback to the application of such materials for treating wastewater. Because the treatment of wastewater is usually conducted in a suspension of adsorbents, it requires an additional separation step to remove them from solution. Removing adsorbent materials, especially those with nanostructures, from a large volume of water involves further expense. Furthermore, metal-adsorbed adsorbents with nanostructures are difficult to separate, probably producing toxic sludge. Therefore, low cost, high adsorptivity, easy separation, good reusability, and "zero" sludge are strongly recommended for a qualified adsorbent used in removing heavy metals from practical wastewater [19]. However, there has no breakthrough progress as yet.

In the present study, a novel polysiloxane-graphene oxide (PS-GO) gel adsorbent was prepared by simple one-step sol-gel method. The relationship among the adsorbent structure feature, adsorption characteristics, separation, regeneration, recycling and actual wastewater treatment was studied. The sponge-like porous gel adsorbent exhibits remarkable mechanical strength, high adsorption capacity, rapid separation, fast regeneration and excellent reusability. The static and dynamic treatment processes using the novel adsorbent can quickly and effectively remove heavy metal ions, especially Pb(II), from actual industrial wastewater.

2. Experimental

2.1. Synthesis

Graphene oxide (GO) was prepared by oxidizing natural graphite powder. Detailed processes are described in the Supporting Information (SI). In a typical preparation procedure of PS-GO gel, 0.40 mL of 3-aminopropyltriethoxysilane (APTS) and 0.40 mL of dimethyldiethoxylsilane (DDS) were added under stirring into a mixture containing 4 mL of 5 mg/mL GO aqueous, 0.2 g of sodium dodecylsulfonate and 0.8 g of urea. The above mixture was transferred into a closed vessel for gelation and aging at 90 °C for 6 h to get a wet gel. The gel was washed with water/ethanol (volume ratio 1:1) and then dried to obtain PS-GO gel. The preparation procedure is illustrated as Scheme 1.

2.2. Characterization

The morphologies of the samples were determined by scanning electron microscopy (SEM, Quanta 200). The structure of the samples was characterized by Fourier transform infrared spectra (FTIR, Nicolet 5700), Raman spectra (Labram-010), and X-ray diffraction spectra (XRD, M21X). The Brunauer–Emmett–Teller (BET) surface area of sample was measured by BELSORP-MINI II. Compression test of PS-GO gel was performed on a universal testing machine (HZ-1007C) with compression/decompression rate of 1 mm/min. The sample zeta potentials in different pH solutions were analyzed by a Zetasizer (Malvern 3000). The functional group changes of PS-GO gel before and after adsorbing metal ions were determined by X-ray photoelectron spectroscopy (XPS, Al–Kα 1063).

2.3. Adsorption kinetics and isotherms

Analytical grade lead nitrate and cadmium nitrate were employed to prepare the Pb(II) and Cd(II) stock solutions, respectively. The pH values of Pb(II) and Cd(II) solution were 5.0 ± 0.1 and 6.0 ± 0.1, respectively. After adsorption process, the adsorbent was separated by being picked up with a tuck net. All the experimental data were the average of triplicate determinations with 4% relative errors. The sorption efficiency of metals was calculated from the difference between initial concentration (C_0) and equilibrium concentration (C_e) (Sorption % = $(C_0 - C_e)/C_0 \times 100\%$, and $Q_e = (C_0 - C_e)/V \times m$, where Q_e (mg/g) is the quantity of adsorbed metal ions at equilibrium, V is the suspension volume, and m is the mass of PS-GO gel). The concentrations of metal ions in aqueous solution were measured by an atomic absorption spectrometer (Hitachi Z-2000).

2.4. Selective adsorption experiments

For the selective adsorption experiment, a mixed solution contained Pb(II), Cd(II), Cu(II), Zn(II), Mn(II) and Ni(II) ($C_{initial}$ = 40 mg/L, 20 mL) and the pH value of the solution kept 5.0 ± 0.1. The adsorption process on PS-GO gel (20 mg) was conducted for 2 h at 303 K.

2.5. Static adsorption of heavy metals from industrial effluent

PS-GO gel with different dosage (1–4 g/L) was used to remove the metal ions in the actual industrial effluent from Shuikoushan smelting plant located in Hengyang, Hunan province, China. The treatment process was carried out in 20 mL wastewater under pH 5.0, room temperature (~298 K) and 15 min of sorption time.

The recycling experiments of removing metal ions from actual industrial effluent using PS-GO gel adsorbent were conducted with each cycle of 15-min sorption time using 3 g/L adsorbent dosage. After each cycle, the metal-adsorbed adsorbent was eluted with 0.1 M HCl solution and regenerated with 0.1 M NaOH solution.

2.6. Pb(II) and Cd(II) removal using PS-GO gel column

The flowchart of the simulated wastewater treatment in one small-scale column is shown in Scheme 2. The pH of the simulated wastewater was adjusted to 5.0. The simulated wastewater contains several metal ions of Pb, Cd, Ca, Mg, K and Na with the concentrations of 20, 10, 25, 25, 50 and 50 mg/L, respectively. The simulated wastewater was pumped through the column with 11.31 mL bed volume (BV) at a flow rate of 2.26 mL/min with an empty bed contact time (EBCT) of 5 min which was determined by the requirement of effluent concentration. When achieving saturation adsorption of Pb or Cd on PS-GO gel in each cycle, the metal-adsorbed PS-GO gel was in situ eluted with 0.1 M HCl solution and regenerated with 0.1 M NaOH solution. The effluent samples were collected and analyzed by an atomic absorption spectrometer. The column parameters are summarized in Table 1.