Journal of Colloid and Interface Science 457 (2015) 86–95

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

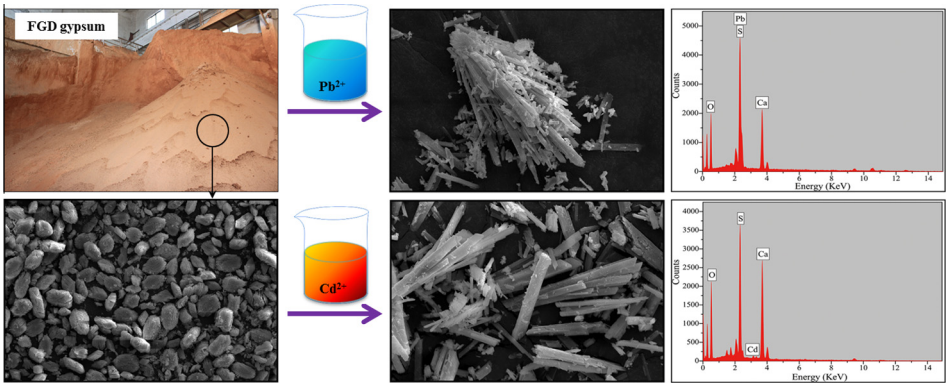
journal homepage: www.elsevier.com/locate/jcis

Recycling flue gas desulphurization (FGD) gypsum for removal of Pb(II) and Cd(II) from wastewater

Yubo Yan, Qiao Li, Xiuyun Sun *, Zhiyuan Ren, Fei He, Yalun Wang, Lianjun Wang *

Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 April 2015
Revised 14 June 2015
Accepted 23 June 2015
Available online 24 June 2015

Keywords:
FGD gypsum
Pb(II)
Cd(II)
Adsorption
Mechanism

ABSTRACT

The present study aims to verify the feasibility of directly reusing the flue gas desulphurization (FGD) gypsum generated from coal-fired power plants to adsorptively remove Pb(II) and Cd(II) from wastewater. The Toxicity Characteristic Leaching Procedure (TCLP) test was conducted to evaluate the leachability of toxic heavy metals from FGD gypsum. The adsorption behaviors of FGD gypsum for Pb(II) and Cd(II) such as pH impact, sorption kinetics, sorption isotherms and sorption thermodynamics were studied in a series of batch experiments. The pH studies indicated that the adsorption of Pb(II) and Cd(II) had their best adsorption amounts both at the pH values from 5.0 to 7.0. The kinetic analysis displayed that the adsorption processes both followed the pseudo-second order model well, and the FGD gypsum provided a higher sorption rate for Pb(II). Equilibrium studies showed that the adsorption of Pb(II) and Cd(II) could be properly described by Langmuir isotherms model, and the predicted maximum adsorption capacities were even greater than some specially prepared adsorbents. The thermodynamic investigation confirmed that the removal of Pb(II) and Cd(II) from aqueous medium could carry out spontaneously, and the higher temperature favored the processes. The instrument analysis techniques were also employed to deeply understand the mechanism involved in Pb(II) and Cd(II) removal by FGD gypsum. Overall, good sorption performance together with cost-effective characteristic makes FGD gypsum potentially attractive material for the Pb(II) and Cd(II) removal in industrial wastewater.

* Corresponding authors.
E-mail addresses: sunxyun@njust.edu.cn (X. Sun), wanglj@njust.edu.cn (L. Wang).

http://dx.doi.org/10.1016/j.jcis.2015.06.035
0021-9797/

1. Introduction

The rapid industrialization and urbanization has undesirably resulted in significant build up in nature water bodies of a wide range of heavy metals, posing a severe threat to environmental ecosystems and public health [1]. Lead (Pb) and cadmium (Cd), widely generated from battery manufacturing, mining operations, tanneries, petroleum refining, ceramics, metal finishing, explosive manufacturing, electroplating, photography, pigments and painting [2–4] have been listed as Priority Pollutants by the US Environmental Protection Agency (USEPA) due to their bioaccumulation in ecosystems and persistence in nature. Long term exposure to Pb(II) can damage the central nervous system, reproductive system, hemopoiesis, heart and blood vessels, kidney and liver of human beings [5]. Contrasting with Pb(II), Cd(II) possesses highly toxicity, chronic exposure to it even at low level can lead to bone lesions, cancer, lung insufficiency and hypertension, etc. [6]. Therefore, it is urgently and universally required to develop appropriate technologies to efficiently remove Pb(II) and Cd(II) from wastewater.

During the past decades, tremendous efforts have been proposed in response to heavy metal contamination, such as flocculation, chemical precipitation, evaporation, reverse osmosis, ultrafiltration, adsorption, ion exchange and electrodialysis [7–9]. Among these, adsorption has been identified as one of the most promising and frequently used techniques because of its easy operation, high efficiency and less residue production. Various novel materials including iron-coated zeolite [10], carbon nanotubes [11], functionalized graphene oxide [12], magnetic chitosan [13], γ-Fe_2O_3 nanotubes [14], etc. have been prepared and successfully applied in the heavy metals adsorption. However, the large quantity consumed in the real wastewater treatment restricts their widespread applications. This problem induced the search of available low-cost materials as alternative adsorbents for the purpose.

In China, more than 90% of coal-fired power plants adopt the wet limestone flue gas desulphurization (FGD) process to control the emissions of sulphur dioxide due to its high desulphurization performance, reliability and low utility consumption [15], thus a great deal of the by-product (FGD gypsum) is produced from such process. According to the data from China Association of Environmental Protection Industry (CAEPI), almost 43 million tons of FGD gypsum was produced in 2010 [16]. As the second largest solid waste in coal-fired power plants, how to efficiently reuse it gradually became a hot topic. American Coal Ash Association (ACAA) [17] reported that over 7.0 million tons of FGD gypsum was recycled for the production of gypsum wallboard, accounting for about 63% of total emissions in 2006. Chandara et al. [18] used the waste FGD gypsum to replace natural gypsum as set retarders in Portland cement, and obtained the ideal values in flexural and compressive strength. Hua et al. [19] found that a new type of road sub-base material (a mixture of FGD gypsum, water glass and slaked lime) reflected excellent mechanical properties and soundness durability. Apart from its use in construction industry, some attention has also been paid to the utilization of FGD gypsum to increase soil pH and reduce subsoil acidity and mechanical impedance for agricultural purpose [20–22].

Up to now, little research has been conducted to reuse FGD gypsum as an adsorbent for wastewater treatment, especially for wastewater contaminated by heavy metals. Hence, the primary objectives for this research were (i) to test the feasibility of using FGD gypsum to remove Pb(II) and Cd(II) from wastewater, (ii) to systematically evaluate the adsorption properties including pH effects, sorption kinetics, sorption isotherms and sorption thermodynamics, (iii) to investigate the mechanisms of Pb(II)/Cd(II) removal by FGD gypsum in depth.

2. Materials and methods

2.1. Materials preparation

FGD gypsum used for this study was collected from Huarun power plant, Nanjing, China. Prior to use, the sample was subjected to conventional pretreatment processes. Briefly, it was washed thoroughly with Milli-Q water to remove any solute salt and dirt, dried at 80 °C for 3 days to a constant weight and screened with a 200 mesh sieve to obtain fine powder (adsorbent). The major composition of the adsorbent was identified as CaO (40.1 wt.%), MgO (0.18 wt.%), SiO_2 (2.12 wt.%), Fe_2O_3 (0.29 wt.%), Al_2O_3 (1.23 wt.%) and SO_3 (55.9 wt.%).

$Pb(NO_3)_2$, $Cd(NO_3)_2{\cdot}4H_2O$, NaOH and HNO_3, purchased from Sinopharm Chemical Reagent Co., Ltd, China, are all analytical grade. Simulated wastewaters with 1000 mg/L were prepared by dissolving appropriate amounts of $Pb(NO_3)_2$ and $Cd(NO_3)_2{\cdot}4H_2O$ in Milli-Q water. The required concentrations in subsequent experiments were prepared by diluting the stock wastewaters.

2.2. Experimental procedure

Batch adsorption experiments were carried out by exposing 0.1 g FGD gypsum to 100 mL single-metal wastewater in 250 mL Erlenmeyer flasks. To study the effect of pH on adsorption, the initial pH values of wastewaters were adjusted from 2.0 to 7.0 with 0.1 M NaOH and 0.1 M HNO_3 solutions at 20 °C. Kinetics studies for both Pb(II) and Cd(II) were performed by varying contact time from 10 to 300 min. Six initial concentrations (50, 100, 150, 200, 250 and 300 mg/L for Pb(II); 20, 50, 70, 100, 150 and 200 mg/L for Cd(II)) were chosen for investigating the adsorption isotherms. Adsorption thermodynamics of two metals were conducted in the range of 20–40 °C. All mixtures were shaken at 200 rpm in an air bath oscillator. After shaking, the mixtures were separated by 0.22 μm membrane filter and the filtrates were analyzed for the residual concentration of Pb(II) and Cd(II). The adsorbed amount of Pb(II) and Cd(II) per unit weight of FGD gypsum at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 and C_t (mg/L) are the initial concentration of Pb(II) and Cd(II) at time t, respectively, V (L) is the volume of wastewater and m (g) is the weight of FGD gypsum.

2.3. Analytical techniques

The chemical composition of FGD gypsum was analyzed by X-ray fluorescence spectrometer (XRF) (XRF-1800, Shimadzu, Japan). The concentration of heavy metals in solution was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Optima 7000DV, PerkinElmer, USA). The mineralogical compositions of FGD gypsum before and after adsorption were determined by X-ray diffraction (XRD) (D8 Advance, Bruker, Germany) with Cu Kα radiation (40 kV and 40 mA). The morphology of FGD gypsum before and after adsorption was observed by scanning electronic microscope coupled with energy dispersive spectroscopy (SEM-EDS) (Quanta 250FEG, FEI, USA). Zeta potential of FGD gypsum was measured by Zetasizer (ZetaPALS, Brookhaven Instruments, USA) with 0.01 M KCl solution as a background electrolyte.