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Conversion of waste FGD gypsum into hydroxyapatite for removal of Pb^{2+} and Cd^{2+} from wastewater

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ABSTRACT

Flue gas desulfurization (FGD) gypsum, a familiar waste generated from coal-fired power plants, was successfully transformed to hydroxyapatite (FGD-HAP) by hydrothermal method. The obtained FGD-HAP was characterized by XRD, FTIR, TEM and BET methods and investigated as adsorbent for removal of Pb^{2+} and Cd^{2+} from wastewater. Batch experiments were performed by varying the pH values, contact time and initial metal concentration. The result of pH impact showed that the adsorption of two ions was pH dependent process, and the pH 5.0–6.0 was found to be the optimum condition. The achieved experimental data were analyzed with various kinetic and isotherm models. The kinetic studies displayed that the pseudo-second order kinetic model could describe adsorption processes well with high correlation coefficient, and the Langmuir isotherm model provided the best fit to the equilibrium experimental data. The maximum adsorption capacities calculated from Langmuir equation were 277.8 and 43.10 mg/g for Pb^{2+} and Cd^{2+}, respectively, which can compete with other adsorbents. The thermodynamic parameters revealed the adsorption processes were endothermic and spontaneous in nature. In binary adsorption, the amount of Cd^{2+} adsorbed on FGD-HAP decreased by 46.0% with increasing concentration of Pb^{2+}, which was higher than that of Pb^{2+}(21.7%), demonstrating the stronger affinity between FGD-HAP and Pb^{2+}. The highest amount of Pb^{2+} and Cd^{2+} desorbed from saturated FGD-HAP by EDTA solution confirmed the FGD-HAP was a promising alternative adsorbent in treatment of toxic Pb^{2+} and Cd^{2+} wastewater.

1. Introduction

With the rapid industrial development, the increasing levels of heavy metals are discharged into surface waters. Pollution by heavy metals, such as Pb^{2+} and Cd^{2+}, has drawn much international attention due to their non-biodegradability, persistence in nature, accumulation in the food chain and toxicity even at low concentration [1]. Pb^{2+} and Cd^{2+} are commonly presented in wastewater through their intensive industrial application, for example, mining operations, tanneries, metal plating, ceramics, metal finishing, electroplating, battery manufacture and painting [2]. Consequently, it is necessary to reduce such poisonous heavy metals before wastewater discharge. Conventional technologies for heavy metals removal from wastewater include chemical precipitation, reverse osmosis, electrocoagulation, ion exchange, evaporation and membrane filtration [3,4], etc. Many of them, however, either not effective enough or are too expensive [5]. Adsorption, compared with above approaches, is considered as a most promising technique for removal of heavy metals from wastewater because of its high removal efficiency, easy operation and less residue production.

During the past decade, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) has attracted particular interest in treating heavy metal wastewater due to its high sorption capacity, low water solubility and high stability under oxidizing and reducing conditions [6–10]. Currently, utilization of hydroxyapatite or its nanocomposites to immobilize metal ions from aqueous solution is still a research hotspot. Zhao et al. [11] synthesized three-dimensional HAP nanosheet-assembled microspheres as adsorbent for removal of Pb^{2+}, Cd^{2+} and Cu^{2+}. Yang et al. [12] prepared Fe_3O_4@HAP nanocomposite for adsorbing Pb^{2+}, Y^{3+}, Eu^{3+} and Sb^{3+}. Aliabadi et al. [13] reported that Chitosan/HAp composite nanofiber had high sorption capacity for Pb^{2+} (296.7 mg/g), Ni^{2+} (213.8 mg/g) and Co^{2+} (180.2 mg/g). They also confirmed that Chitosan/HAp composite

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nanofiber possessed an effective regenerability. On the other hand, Minh et al. [14] used calcium carbonate as low cost Ca source to synthesize HAP for adsorbing Pb^{2+}. Kongsri et al. [15] converted waste fish scale to nanocrystalline HAP for selenium adsorption.

Generally, Ca-contained reagent or Ca-contained biowaste is primarily selected as Ca sources for preparation of HAP. However, little research focused on the Ca-contained industrial waste. Flue gas desulfurization (FGD) gypsum, a common waste from the wet flue gas desulfurization process in coal power plants, is mainly composed of $CaSO_4{\cdot}2H_2O$, which can be an ideal Ca source. China Association of Environmental Protection Industry (CAEPI) reported over 43 million tons FGD gypsum was produced in 2010 [16]. A considerable portion of FGD gypsum is dumped directly, such disposal not only occupy a large amount of land resources but also cause serious dust pollution and groundwater pollution. Thus, finding an appropriate method to transform waste FGD gypsum into useful materials may be an economically valuable solution to this problem.

Up to now, no report has ever been published regarding conversion of waste FGD gypsum into hydroxyapatite and then application for adsorbing heavy metals. Therefore, the objectives of this work were (1) to assess the feasibility of preparing HAP (FGD-HAP) using waste FGD gypsum as Ca source, (2) to thoroughly characterize the FGD-HAP by XRD, TEM, FTIR and BET methods, (3) to firstly evaluate the FGD-HAP's adsorption properties (pH effects, adsorption kinetics, isotherms, thermodynamics and competitive adsorption) and regenerability toward Pb^{2+} and Cd^{2+}, (4) to deeply investigate the mechanisms involved in adsorption process.

2. Materials and methods

2.1. Materials

The FGD gypsum was obtained from Huarun power plant, Nanjing, China. The sample was washed thoroughly with Milli-Q water and then dried at 100 °C for 24 h. The 200 mesh sieve was used to collect FGD gypsum with particle size smaller than 0.04 mm. The components of screened sample were analyzed by energy dispersive X-ray fluorescence (XRF) (LAB CENTER XRF-1800, Shimadzu, Japan) and the results were listed in Table 1. $Pb(NO_3)_2$, $Cd(NO_3)_2$, $(NH_4)_2HPO_4$, $NH_3{\cdot}H_2O$, NaOH and HNO_3, purchased from Nanjing Chemical Reagent Company, are all analytical grade. Simulated stock wastewaters with 1000 mg/L were prepared by respectively dissolving appropriate amounts of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ in Milli-Q water. The desired concentrations in experiments were prepared by diluting stock wastewaters.

2.2. FGD-HAP synthesis and characterization

The FGD-HAP powder was synthesized by the following procedures: (i) 2 g FGD gypsum and 100 mL $(NH_4)_2HPO_4$ solution (0.086 mol P/L) was mixed at room temperature. (ii) The mixture was maintained at a pH value 10–11 by adding $NH_3{\cdot}H_2O$ and vigorously stirred for 4 h. (iii) After stirring, the mixture was transferred to Teflon-lined stainless steel autoclave and kept in an oven at 150 °C for 24 h. (iv) The solid obtained from the cooled autoclave was rinsed several times with Milli-Q water and ethanol, then dried at 80 °C for overnight. (v) The dried sample was milled to pass through a 200 mesh sieve and stored in a desiccator for further analysis.

Table 1
Chemical composition of FGD gypsum by XRF.

Composition	Value (wt.%)
CaO	40.1
SiO_2	2.12
Al_2O_3	1.23
Fe_2O_3	0.29
MgO	0.18
SO_3	55.9

The crystalline phases of the FGD-HAP powder were analyzed by X-ray diffraction (XRD) (D8 Advance, Bruker, Germany) with Cu Kα radiation. The surface area and pore volume of material were determined by BET apparatus (ASAP 2020, Micromeritics Instrument, USA), using nitrogen gas as the adsorbate at 77 K. The morphology of sample was analyzed through transmission electron microscopy (TEM). Infrared spectra were obtained using Fourier transform infrared (FTIR) (IR Prestige-21, Shimadzu, Japan) spectroscopy. The zeta potential of powder was measured by a Zeta meter (ZetaPALS, Brookhaven Instruments, USA), using 0.01 M KCl solution as a background electrolyte.

2.3. Batch adsorption experiments

The adsorption experiments of Pb^{2+} and Cd^{2+} were carried out according to batch method. The conical flasks containing 0.05 g FGD-HAP and 50 mL single-component solution at desired concentration and pH were placed in an air bath oscillator with a constant speed of 200 rpm and constant temperature of 20 °C. After adsorption, the mixtures were filtered through 0.22 μm membrane filter and the filtrates were analyzed for residual metal concentration via an inductive coupled plasma atomic emission spectroscopy (ICP-AES) (Optima 7000DV, PerkinElmer, USA). The Pb^{2+} and Cd^{2+} adsorption capacities at time t, q_t (mg/g), are calculated according to:

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

where C_0 and C_t (mg/L) are the single-metal concentration in the initial solution and at time t, respectively; V (L) is the volume of solution, and m (g) is the weight of the sample added to the solution.

For determination of pH impact on adsorption, the pH of was adjusted using 1 M NaOH or 1 M HNO_3 ranging from 2.0 to 6.0 in 200 mg/L Pb^{2+} or 100 mg/L Cd^{2+} wastewater. Adsorption kinetics of Pb^{2+} and Cd^{2+} were both studied in the range of 10–300 min at optimum pH. Adsorption isotherms were investigated in the range of 50–500 mg/L for Pb^{2+} and 20–200 mg/L for Cd^{2+}. Adsorption thermodynamic studies were carried out with 250 mg/L Pb^{2+} and 50 mg/L Cd^{2+} at 20, 30 and 40 °C, respectively.

2.4. Binary adsorption

2.4.1. Preferential adsorption

Preferential adsorption systems were prepared by solubilizing a combination of Pb–Cd in presence of each metal with other metal present in equal concentrations (20, 50, 100, 150 and 200 mg/L).

2.4.2. Competitive adsorption

The competitive adsorption studies of Pb^{2+} and Cd^{2+} in binary system consists of two parts: (i) Effect on the adsorption capacity of Pb^{2+} with Cd^{2+} present in system. In this part, the initial Pb^{2+} concentration remained at 50, 100, 150, 200, 250, 300, 400 and 500 mg/L respectively, while the concentration of Cd^{2+} varied from 50 to 200 mg/L respectively. (ii) Effect on the adsorption capacity of Cd^{2+} with Pb^{2+} present in solution. In this section, the initial Cd^{2+} concentration fixed at 20, 40, 60, 80, 100, 120, 150 and 200 mg/L respectively, whereas the other one ranged from 50 to 200 mg/L respectively.