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Biomass based activated carbon obtained from sludge and sugarcane bagasse for removing lead ion from wastewater



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HIGHLIGHTS

• Bagasse modified municipal sewage sludge based adsorbent.

• HNO₃ modified adsorbent to promote its adsorb-ability of Pb²⁺.

 \bullet The adsorption capacity of Pb^{2+} increases to more than 50 mg/g.

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1. Introduction

ABSTRACT

Sewage sludge and bagasse were used as raw materials to produce cheap and efficient adsorbent with great adsorption capacity of Pb^{2+} . By pyrolysis at 800 °C for 0.5 h, the largest surface area (806.57 m²/g) of the adsorbent was obtained, enriched with organic functional groups. The optimal conditions for production of the adsorbent and adsorption of Pb^{2+} were investigated. The results of adsorb-ability fitted the Langmuir isotherm and pseudo-second-order model well. The highest Pb^{2+} (at pH = 4.0) adsorption capacity was achieved by treating with 60% (v/v) HNO₃. This is a promising approach for metal removal from wastewater, as well as recycling sewage sludge and bagasse to ease their disposal pressure.

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Sewage sludge is an inevitable by-product of wastewater treatment possesses. The amount of sewage sludge has been increasing during recent years due to urbanization and industrialization, which can lead to potential environmental problems (Chen et al., 2012; Wang et al., 2013). Besides, it has been estimated that approximately 30–60% of operating costs of sewage treatment plants are related to sludge treatment activities (Siddiquee and Rohani, 2011). Therefore, the management of sewage sludge is of great importance for both economy and the environment.

Enriched with organic matter and microorganisms, sludge can be turned into porous adsorbent material by chemical, physical, or physicochemical activation methods under high-temperature and oxygen-free conditions (Werle and Wilk, 2010). However, the adsorption capacities of such sludge-based adsorbents are usually low due to the inherent property of sludge. Therefore, accessory materials such as agricultural and forestry wastes such as leaves, husks, peels, pits and stems have been added to sludge to enhance the adsorption properties of sludge-based adsorbents (Sharma et al., 2013). China is one of the largest cane sugar producers, with plantation area of sugar cane ranked third in the world. After the extraction of sucrose from sugar cane, the huge amount of bagasse has become a challenge for treatment and disposal. A recent review indicated that bagasse-based adsorbents are efficient in removing heavy metals from wastewater (Homagai et al., 2010; Velazquez-Jimenez et al., 2013). Thus, bagasse could serve as an additive for the production of sludge-based adsorbents to enhance its adsorption capacity. By recycling sludge and bagasse into useful adsorption materials with great economic benefit, their disposal pressure can be partially eased.

In this study, sludge is combined with bagasse to produce a low-cost adsorbent for heavy metals with great adsorption capacity. The adsorbent is activated by KOH through pyrolysis and modified with HNO₃ to remove lead from the contaminated water.



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2. Methods

2.1. Chemicals

All chemicals were analytical reagents. All solutions were prepared using deionized water. The pHs of working solutions were adjusted with 10% (wt/wt) NaOH and 10% (v/v) HNO_3 .

2.2. Preparation of raw materials

The dewatered sludge with an initial moisture content of 79.84% was collected from Binhe Wastewater Treatment Plant (WWTP) in Shenzhen, China. The bagasse after extracting sugarcane juice by crushing and squeezing was collected from Haikou, China. Both dewatered sludge and bagasse were dried at 105 °C to a constant weight before they were grounded and sieved to different particle sizes, respectively.

2.3. Preparation of primary adsorbent (bagasse–sludge-based adsorbent–KOH, B–SBA–K)

The dry sludge and bagasse were mixed well in the graphite boat (bagasse/sludge = 1/2; w/w) before adding 3 mol/L KOH solution [(sludge + bagasse)/KOH solution = 1/3; w/w]. The loaded graphite boat was then placed in a 105 °C oven for 15 min. After that, the graphite boat was placed into a horizontal tube furnace for activation, with a heating rate of 10 °C/min. This process was carried out from room temperature (25 °C) to 800 °C under the protection of N₂ (300 mL/min). After remaining at 800 °C for 30 min, the materials were cooled to room temperature under nitrogen atmosphere.

Afterwards, the product was soaked and boiled with 3 mol/L HCl (Velghe et al., 2012) for 1 min. After cooling under room temperature, the product was washed and boiled with deionized water till a neutral pH. Then the product was dried in an oven at 110 °C to a constant weight. Finally, B–SBA–K was grounded and sieved through a 200 mesh sieve.

2.4. Preparation of acid-bagasse-sludge-based adsorbent-KOH (Acid-B-SBA-K)

 HNO_3 can be used as an oxidizing agent to modify acidic functional groups on the surface of B–SBA–K in order to enhance its adsorption capacity to Pb^{2+} . Therefore, B–SBA–K was soaked in 60% HNO_3 and heated for 6 h at 90 °C in a water bath (Song et al., 2010), and finally the adsorbent Acid-B–SBA–K was obtained.

2.5. Characterization of the adsorbents

The iodine numbers of different adsorbents were determined according to China National Standards (GB/T12496.10-1999). To obtain the methylene blue value, 0.1 g of adsorbent was added into 10 mL 1500 mg/L methylene blue. After shaking at 220 rpm and 25 °C for 30 min, the final methylene blue concentration was determined by measuring the light absorbance at 665 nm with a UV–VIS spectrophotometer (MAPADA, Shanghai, China) (Gobi et al., 2011).

The percentages of C, N, H and S in the adsorbent were determined using a CHNS analyzer (PerkinElmer, USA). The specific surface areas were measured using a TriStar II surface area pore analyzer (Micromeritics, USA). The surface topography was analyzed using scanning electron microscopy (Hitachi Limited, Japan). The Fourier Transform Infrared Spectroscopy (FTIR) were recorded using IR Prestige-21 (SHIMADZU, Japan) with a scanning range of 4000–400 cm⁻¹.

2.6. Adsorption experiments

The solution of Pb²⁺ was prepared by diluting lead nitrate with deionized water. In the batch tests, 10 mg of dried adsorbent was added into 5 ml solution of lead nitrate in a 10 ml centrifuge tube. The tubes were shaken vigorously in a thermo-stated shaker at 35 °C (Supplementary data 6) at 180 rpm for 2 h to ensure that equilibrium had been attained (Zhang et al., 2013). Besides, multi-metal ions adsorption was conducted in order to confirm adsorption was best for Pb²⁺. The initial and equilibrium concentrations of the metal ions were measured by ICP-OES (PRODIGY XP, Teledyne Leeman Labs). All experiments were performed in duplicate at least and mean values were presented. The sorption capacity can be calculated based on the mass balance principle (Homagai et al., 2010):

$$Q_e = \nu(c_t - c_0)/m \tag{1}$$

In which Q_e is the capacity of metal ion adsorbed onto the adsorbent, c_t (mg/L) and c_0 (mg/L) are the equilibrium and initial concentrations of Pb²⁺ in solution, whereas v (L) and m (g) are solution volume and mass of adsorbent, respectively.

The removal percentage of Pb²⁺ was calculated as follows:

$$R = (c_0 - c_t)/c_0 \times 100\%$$
⁽²⁾

where *R* is the removal percentage of Pb^{2+} (%), c_0 and c_t are the initial and equilibrium concentrations of Pb^{2+} (mg/L).

Blank tests without adsorbent were performed to confirm that metal precipitation or adsorption on the pH electrode or on the walls of tubes did not interfere with metal sorption (Chen et al., 2014).

In this study the equation of Langmuir and Freundlich isotherms were applied.

Langmuir equation is as follows:

$$q_e = Q_m b C_e / (1 + b C_e) \tag{3}$$

where $C_e(mg/L)$ and $q_e(mg/g)$ are the equilibrium concentrations of Pb²⁺ in the liquid and solid phases, respectively; Q_m and b are Langmuir constants. Q_m is the maximum metal uptake (mg/g), whereas b is adsorption equilibrium constant (L/g) and related to the energy of adsorption.

Freundlich equation is as follows:

$$q_e = k_f C_e^{1/n} \tag{4}$$

In which $q_e (mg/g)$ and $C_e (mg/L)$ are the equilibrium concentrations of Pb²⁺ in the adsorbed and liquid phases. k_f and n are the Freundlich constants, indicating the adsorption capacity and adsorption intensity. Eq. (4) can be transformed as:

$$\log q_e = \log k_f + \log C_e/n \tag{5}$$

The Freundlich constants k_f and n can be calculated from the intercept and slope of the linear plot.

The pseudo-first order model and pseudo-second-order model were used to analyze the adsorption kinetics. The non-linear pseudo-first order model is expressed as:

$$q_t = q_e (1 - e^{-k_1 t}) \tag{6}$$

Eq. (6) can be linearized in logarithmic form as:

$$\ln[(q_e - q_t)/q_e] = -k_1 t \tag{7}$$

The pseudo-second-order model equation is:

$$q_t = q_e^2 k_2 t / (1 + q_e k_2 t) \tag{8}$$

Eq. (8) can be linearized in logarithmic form as:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \tag{9}$$

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