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Efficient removal of lead from aqueous solution by urea-functionalized magnetic biochar: Preparation, characterization and mechanism study

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A novel urea-functionalized magnetic biochar (MBCU) was prepared, characterized and evaluated for removal of lead (II) from aqueous solution. The results of SEM, BET, XPS, FTIR, VSM and Zeta-potential exhibited a successful fabrication of MBCU. The magnetism magnitude of magnetic biochar could simultaneously affect the adsorption and recovery efficiency of lead (II) on magnetic biochar. Hence, the optimum mass ratio range of MBCU was determined to be 1.7:1–2.3:1, which could guarantee high removal (> 73.14%) and recovery (> 78.35%) efficiency. The experimental results indicated that the adsorption isotherm and kinetics were well described by the Sips model and pseudo-second-order model, respectively. The maximum adsorption capacity of lead (II) on MBCU was 188.18 mg/g at 323 K. Five-cycle reusability tests demonstrated MBCU could be effectively recovered and repeatedly used with a small adsorption loss (< 20%). Mechanism study demonstrated that the adsorption process involved in electrostatic interaction, ion exchange and complexation. The unique features of its outstanding adsorption performance, reusability and separation efficiency suggested that the magnetic biochar can be potentially applied in elimination of lead (II) from wastewater.

1. Introduction

Due to the rapid development of industrialization, water pollution by heavy metals is a global issue owing to its high toxicity, carcinogenicity, wide sources and non-biodegradable properties. Most seriously, it can cause continuous threat to the environment and human health and has become more serious than ever before [1,2]. Among these heavy metals, lead deserves special attention, because it's highly toxic to human beings even in small quantity [3]. Lead can be easily accumulated in various industrial wastewaters, then assimilated and concentrated in body system, causing anaemia, chills, diarrhea and dysfunction of the kidney [4,5]. Removal lead from aqueous environments is important and urgent to ensure purified and recycled water.

Several methods for lead removal from wastewater have been investigated, including chemical precipitation [6], ion exchange [7], filtration [8], electroplating [9], reverse osmosis [10], and adsorption [11]. Among these methods, adsorption has been considered to be the most promising one because of its easy operation, high efficiency and low cost, which can be used for removal lead at a low content. The widely successful application of adsorption largely depends on the efficient development of adsorbent, thus diverse materials have been designed and conducted as adsorbents to eliminate lead from wastewater in both academic research and industrial application [12]. While the activated carbon, ion-exchange resins, natural clay has impeded the wide application of adsorption owing to its expensive produce cost [13,14]. Biochar is black carbon which is the pyrolytic product of biomass under oxygen-limited condition. Biochar, as adsorbent, has been received increasing interest because of its several potential environmental applications in soil amendment, carbon sequestration and contaminant remediation [15,16]. Biochar could immobilize many kinds of contaminants including organic pollutants and heavy metals [17,18]. Hence, biochar shows a great potential in the wastewater treatment.

However, the powered biochars are difficult to be separated from the aqueous solution due to the small particle sizes and lower density, which restricts its further practical industrial application in the wastewater treatment process. A system which can capture the heavy metal ions with great competence and then to isolate them out with ease is essential [19]. Maybe the magnetic biochar could achieve the goal. Introducing magnetic compounds to the biochar enables the magnetic biochar to be effectively separated by magnetic separating technique. It is well known that Fe_3O_4 process rapidly magnetic responsibility when the external magnetic field is applied. However, the magnetization of the biochar partially reduced its heavy metal adsorption efficiency due to the biochar's surface pores becoming plugged with iron oxide particles. In literatures, many efforts have been devoted to removing

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contaminates from aqueous solution by magnetic biochars, which was fabricated from various raw materials. For example, the magnetic biochar derived from peanut hull was applied to eliminate chromium (VI) from wastewater [20]. The waste marine macroalgal biomass was used as the precursor to fabricate magnetic biochar for removal cadmium, copper and zinc [21]. But the application of palm fiber biochar remains limited. The widespread and low-cost palm fiber is a common nature vegetable fiber with large elastic modulus, high strength, highly developed porous and regenerative nature. Hence, the palm fiber may be the ideal resource to produce biochar. Lu et al. has testified the pristine biochar for removal of lead, but achieved adsorption capacity is still unsatisfactory [22]. Thus the functional modification of biochar is required to improve the adsorption capacity and selectivity [23]. The urea NH_2CONH_2 is extensively found in natural products and is an attractive functional moiety. The groups-nitrogen and oxygen of urea can offer multitude of bonding potentials owing to its electron pair, which plays a key role in adsorption of heavy metals.

To overcome the aforesaid challenges, we prepared a novel magnetic palm fiber biochar via magnetic and functional modification for elimination of lead (II) in aqueous solution. The biochar derived from palm fiber was used as the support to load Fe_3O_4 nano-particles on the surface, then the composites were coated a layer of 3-Triethoxysilylpropylamine, which could immobilize the Fe_3O_4 nano-particles sites on the surface of biochar. In order to further increase the adsorption sites and selectivity to lead, the magnetic biochar was modified with urea containing amino groups. The magnetic modified biochar was characterized by SEM, BET, FTIR, XPS, VSM and Zeta potential. The effects of pH, contact time, and initial concentration of lead on the removal of lead (II) from the aqueous solution by the magnetic biochar were investigated. This work will provide an alternately low cost, high adsorption and separation efficiency adsorbent for detoxification of lead from wastewater.

2. Experimental and methods

2.1. Chemicals and material

$FeSO_4 \bullet 7H_2O$ and $FeCl_3 \bullet 6H_2O$ were purchased from Sinopharm Chemical reagent Company. 3-Triethoxysilylpropylamine (TSA), epichlorohydrin (EC), urea and other chemicals were purchased from Honghua Reagent Co. Ltd. (Changsha, China). Lead (II) stock solution (500 mg/L) was prepared by dissolving lead nitrate in distilled water and then diluted to appropriate concentrations. All the chemicals used in this study were of analytical grade, and distilled water (18.2 MΩ, 25 °C) from a Milli-Q plus purification system (Millipore) was utilized throughout the experiments for solution preparation and glassware cleaning. About 50 g of palm fiber was purchased from a local market, which is shaped with broom, cut into about 0.5 cm filaments, thoroughly washed with tap water to clear the dust and other adhering impurities, soaked in 1000 mL of 1 mol/L NaOH for 12 h, washed with distilled water for several times and then dried at 323 K.

2.2. Preparation of Fe_3O_4 nano-particles

Fe_3O_4 nano-particles were prepared by chemical co-precipitation of in Fe^{3+}/Fe^{2+} solution. Typically, 2.3967 g of $FeSO_4 \bullet 7H_2O$ and 4.6634 g of $FeCl_3 \bullet 6H_2O$ were dissolved in 150 mL of distilled water in a flask. The mixture was stirred for 30 min under the protection of N_2, then 28%$NH_3 \bullet H_2O$ was gradually added in the flask, until the pH of the mixture was around 10.0. The suspension was vigorously stirred in an oil bath for 5 h at 353 K. The black precipitate was collected by a magnet and then washed with distilled water several times, dried at 323 K for 12 h and then stored in polyethylene bag.

2.3. Fabrication of magnetic biochar (MBCU)

The pretreated palm fiber was converted into biochar by pyrolysis in a muffle furnace at 400 °C with a heating rate of 10 °C/min under the protection of N_2 for 2 h. The pristine biochar was referred to as BC.

The method to synthesize the magnetic biochar (MBC) was based on the previous study by Zhou [24] and it was amended and optimized in this study. As shown in Scheme 1, the procedure was as follows: A certain mass ratio of biochar and Fe_3O_4 nano-particles were mixed in 100 mL distilled water and then 5.0 mL of 3-Triethoxysilylpropylamine (TSA) was later added to the solution. The mixture was stirred in an oil bath for 8 h at 323 K. The magnetic biochar named as MBC was subsequently washed with ethanol and distilled water several times after being separated by a magnet.

Next, 4 mL epichlorohydrin (EC) was dissolved in 100 mL mixed solvent with acetone/distilled water (V:V = 1:1)solution and 2.0 g of MBC was later added to the media for cross-linking, the mixture was constantly stirred for 12 h in an oil bath at 303 K. Then, 4.0 g of urea and 50 mL of 1 mol/L NaOH were added into mixture and stirred in an oil bath at 333 K for 12 h. After being separated with magnet, the materials were subsequently washed with acetone, ethanol and distilled water and finally oven-dried for 24 h at 323 K. The resulting biochar sample was referred as MBCU.

2.4. Characterization of biochar

The surface morphologies of the biochars were analyzed by scanning electron microscopy measurement (JSM-6360LV, Japan). The functional groups of biochars before and after modification were measured by a Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700, USA) using the KBr pellet technique and were examined in the 4000–400/cm region. The BET surface area (S_{BET}, m^2/g), total pore volume (V_T, m^3/g) and average diameter (D_p, nm) for the investigated biochar were determined through N_2 adsorption/desorption isotherms at 77 K using a surface area analyzer (Gemini VII2390, USA). The surface chemical composition was confirmed by the X-ray Photoelectron Spectroscopy (ESCALAB 250Xi, USA). The Zeta potential was measured at different pH using a Zeta potential analyzer (JS94H, China). Magnetic property of the MBCU was determined by magnetization curve using the vibrating sample magnetometer (Lake Shore 7404, USA).

2.5. Batch sorption equilibrium experiments

Batch experiments were conducted to examine the adsorption efficiency of BC, MBC and MBCU for removal lead (II) from aqueous solution. Generally, a certain amount of biochar was mixed with lead (II) solution in a flask. Then the mixture was shaken in a thermostatic shaker at 160 rpm at the investigated temperature for 24 h. After that, the separated solution was drawn out for absorbance measurement with a UV–vis spectrophotometer (UV759S, China).

MBCU adsorbent was used to study the dosage effects on lead removal. The pH values of solution ranging from 2.0 to 8.0 were adjusted by 0.01 mol/L HCl and 0.01 mol/L NaOH solution. The equilibrium adsorption isotherms for lead on MBCU were determined using 0.0400 g biochar with 40 ml lead solutions of different concentrations ranging from 25 to 300 mg/L in a batch of conical vessels. The adsorption kinetic experiments were conducted at different time intervals, ranging from 5 to 120 min, with 100 mg/L lead solution at pH 6.5.

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