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$ZnCl_2$-activated biochar from biogas residue facilitates aqueous As(III) removal

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ABSTRACT

Biochars prepared from biogas residue using different chemical activators were investigated for their As(III) adsorption properties. The results indicated that the original biochars did not exhibit significant As(III) adsorption. However, $ZnCl_2$-activated biochar, which possessed the largest specific surface area, 516.67 cm^2/g, and exhibited a perfectly porous texture, showed excellent performance in a 500 μgL^{-1} solution of As(III). Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy were utilized to identify the mechanism of As(III) adsorption by $ZnCl_2$-activated biochar. Adsorption was found to occur mainly through ligand exchange of the hydroxyl in Zn-OH to form Zn-O-As(III), as well as through porous adsorption. As a low-cost adsorbent, the adsorption process was well fitted using a pseudo-second-order model, with an $R^2 > 0.993$. The adsorption process was fast, requiring nearly 90 min to reach adsorption equilibrium. Batch adsorption experimental results indicated that $ZnCl_2$-activated biochar has a maximum adsorption capacity of 27.67 mg/g at pH 7.0, and the adsorption process followed the Freundlich isotherm model well, with an $R^2 > 0.994$. In addition, the current work demonstrated the efficiency of using $ZnCl_2$-activated biochar adsorbent to treat As(III)-contaminated water.

1. Introduction

Arsenic is a toxic trace element that has been linked to numerous types of skin, bladder, and lung cancers [1]. Naturally occurring and anthropogenic sources of arsenic in the environment include geothermal regions, arsenic-bearing sulfide deposits, poultry litter, and industrial wastes [2]. The bioavailability and mobility of arsenic is dependent on the arsenic species. The most prevalent arsenic species are arsenite (As(III)) and arsenate (As(V)) [3]. Arsenite is generally found under reduced conditions and near-neutral pH, while arsenate is predominant under well-oxidized conditions. As(V) is less soluble and toxic than the reduced As(III) [4]. In regions of India and Bangladesh [5], high arsenic concentrations in the groundwater, above the The World Health Organization limit of 10 μgL^{-1}, result in the exposure of millions of people to contaminated drinking water [6]. Luis et al. estimated that 19.6 million people in China are drinking arsenic-contaminated groundwater [7]. Therefore, developing economical, effective and reliable treatment techniques to ensure that this limit is met is critical and urgent.

Different methods have been developed to remove arsenic from wastewater. Chemical oxidation, precipitation, adsorption, ion exchange, reverse osmosis and membrane separation have all been applied to reverse arsenic pollution [3]. Among these methods, the adsorption of arsenic onto select adsorbents is one of the more efficient strategies due to its technical and because a wide range of adsorbents is available [8]. Meanwhile, numerous types of absorbents, such as biological materials, agricultural products/by-products, industrial by-products/wastes, and mineral oxides, have been developed with a key focus on maintaining low-cost and high efficiency [9–16]. Among these adsorbents, biochars, a carbon-rich solid prepared from crop residues, sludge, wood wastes, manure, and biogas residues under high-temperature and nitrogen atmosphere pyrolysis, shows outstanding thermal stability and favorable physicochemical properties [17]. Therefore,

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biochars have been developed for the treatment of many pollutants, including heavy metals. Biogas residues is a common low-grade biomass that has been increasingly used on a large scale to achieve sustainable anaerobic digestion [18]. More importantly, biogas residues mainly consist of hemicellulose, lignin and ash, which are suitable for the production of biochars [19].

Several researchers have focused on the use of biochars for arsenic adsorption. For example, Liu et al. adopted Fe_3O_4-loaded activated carbon prepared from waste biomass [20] and Agrafioti et al. produced Ca- and Fe-modified biochar to remove As(V) [21]. Additionally, Dobrowolski et al. created Ni-loaded activated carbon for As(V) removal [22]. However, reports regarding the use of biochars to adsorb As(III) from sewage are scarce. As arsenite predominately exists as uncharged H_3AsO_3 in the pH range of water, it cannot be effectively removed by adsorption [23]. However, the activation of prepared biochar using different activators is an efficient method of facilitating As(III) adsorption. Activated biochar uptakes arsenite mainly through metal-ligand surface interactions and porous attraction [24]. Baig et al. adopted magnetic Kans grass biochar [4] and Vinh et al. utilized Zn-loaded biochar [25] to remove As(III). However, the adsorption efficiencies of these metal-activated biochars were not notable, and their adsorption mechanisms were not clear. Thus, the current study focused on enhancing As(III) adsorption capacity and uncovering adsorption mechanisms.

In this paper, biochars were derived from pig manure slurry for the removal of As(III) from aqueous solution. The biochars were activated by KOH, NaOH, $AlCl_3$, $FeCl_3$ and $ZnCl_2$. The following key aims were addressed: (1) characterize the composition of $ZnCl_2$-activated biochar; (2) analyze the adsorption kinetics and equilibrium isotherms of As(III); and (3) detail the mechanisms underlying As(III) removal. The results from this study demonstrate the development of a low-cost and effective As(III) removal agent, as well as an environmental way to treat biogas residue.

2. Materials and methods

2.1. Source of raw materials

Biogas residue from pig manure was provided by Chengdu, Sichuan. The biogas residue was air-dried in an oven at 105 °C and subsequently milled and sieved prior to carbonized treatment. Samples were stored in centrifuge tubes for further analysis and study. All the chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. As(III) stock solution was prepared by dissolving measured amounts of $NaAsO_2$ in deionized water for a concentration of 1000 mg/L. The stock solution was precisely diluted to achieve different arsenic concentrations. All solution preparations in this work used deionized water.

2.2. Preparation of biochar

A specific amount of activator was dissolved in deionized water, an equivalent weight of biogas residue (2–5 mm in diameter) was added, and the solution was stirred for 30 min. The mixtures were then dehydrated in an oven at 105 °C for approximately 24 h. The dried mixtures were pyrolyzed at 700 °C and maintained at 700 °C for 2 h in a tubular furnace (SK2-1-12, Tianye, China) under a 100 mL/min N_2 gas flow rate until the reactor temperature cooled to room temperature. The pyrolyzed mixtures were filtered and rinsed with distilled water three times, dried in an oven at 105 °C for approximately 5 h, and weighed to calculate yield. Then, the samples, now referred to as activator-activated biochars, were stored in a desiccator until further analysis.

2.3. Adsorption of As(III)

Different impregnated biochars were exposed to different arsenic concentrations to select the most effective activator and define the best adsorption capacity. For example, NaOH-activated biochar (NaOH-BC), KOH-activated biochar (KOH-BC), $ZnCl_2$-activated biochar ($ZnCl_2$-BC), $AlCl_3$-activated biochar ($AlCl_3$-BC), $FeCl_3$-activated biochar ($FeCl_3$-BC) and pristine biochar (BC) were evaluated under the same conditions. Each solution of different arsenic concentration was adjusted approximately pH 7.0, and each adsorbent was kept at 2 g/L at room temperature.

The adsorption kinetics of $ZnCl_2$-activated biochar were measured using 150 mL conical flasks containing 100 mL of a 40 mg/L As(III) solution and 0.2 g adsorbent. The initial pH of the batch experiment was adjusted to 7.0 ± 0.2. The pH value was regulated using either 0.1 mol/L HCl or 0.1 mol/L NaOH. Then, the flasks were sealed and shaken in an orbital shaker water (25 ± 1 °C) for 150 min at a rate of 180 rpm to reach adsorption equilibrium. The amount of time required to reach equilibrium varied widely between different biochars. Aliquots of 2 mL were taken from the flask at predetermined intervals, and a 0.2-μm membrane filter (Millipore) was used to separate sorbent and filtrate. The arsenic concentration in the filtrate was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). Each experiment was conducted in duplicate, and the results are reported as average values.

Adsorption isotherm experiments were run at the concentration ranges from 5 to 150 mg/L. Each conical flak contained 30 mL arsenic solution, to which 0.06 g biochar was added. Then, the flasks were stirred for approximately 24 h to reach equilibrium. Next, previously published procedures were used to determine the adsorbed As(III) concentrations in the mixed solutions. The percentage solute removal and specific amount of arsenic adsorbed were respectively calculated using Eqs. (1) and (2):

$$\text{Percentage arsenic removal} \quad q = \left(1 - \frac{c_e}{c_0}\right) \times 100\% \tag{1}$$

$$q_e = \frac{V\,(c_0 - c_e)}{m} \tag{2}$$

where q (%) is the percentage arsenic removal, q_e (mg/g) is the adsorption capacity equilibrium, V is the volume (L) of arsenic solution and m is the mass (g) of adsorbent used. c_0 and c_e (mg/L) are the initial and equilibrium concentration of the solution, respectively.

2.4. Analytical methods

The C, H, O and N contents of the biogas residue and biochars were analyzed using an elemental analyzer (Vario EL III, Elementar, Germany). A muffle furnace was used to measure the ash contents of biochars under an air atmosphere at 600 °C for 6 h. The thermal stability of each sample was analyzed using thermo-gravimetric analysis (TGA) with temperature ranges between 30 °C and 900 °C under an air atmosphere. The structural properties of each sample before and after reaction were measured by Fourier transform infrared spectroscopy (Nicolet 6700, Thermo Electron, USA). The surface area of each biochar was determined using the Brunaure-Emmet-Teller (BET) method, and pore structures were determined using an ASAP 2020 with N_2 as the adsorbent at −195.74 °C. All samples were degassed at 300 °C 2 h before being measured. Scanning electron microscopy (SEM) was used to visualize the surface structures of the samples, and electron dispersive X-ray (EDX) spectroscopy was used for qualitative analysis of elemental composition (ZEISS SIGMA, Germany). X-ray photoelectron spectroscopy (XPS) was applied to characterize the properties of the elements before and after reaction. Samples were compressed into a thin pellet for XPS analysis. In order to prevent As(III) oxidation, $ZnCl_2$-activated