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Enhanced removal of Cr(VI) from aqueous solution by supported ZnO nanoparticles on biochar derived from waste water hyacinth

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HIGHLIGHTS

- Effect of carbonization temperature on the characteristics of biochar was examined.
- . The biochar derived from water hyacinth was modified by ZnO nanoparticles.
- . Higher than 95% removal efficiency of Cr(VI) was achieved even at natural pH.
- Possible mechanisms involved in the Cr (VI) adsorption by ZnO/BC were investigated.

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ABSTRACT

Biochar derived from waste water hyacinth was prepared and modified by ZnO nanoparticles for Cr(VI) removal from aqueous solution with the aim of Cr(VI) removal and management of waste biomass. The effect of carbonization temperature (500–800 °C), ZnO content (10–50 wt%) loaded on biochar and contact time (0.17–14 h) on the Cr(VI) removal were investigated. It was found that higher than 95% removal efficiency of Cr(VI) can be achieved with the biochar loaded 30 wt% ZnO. The adsorption kinetics of the sorbent is consistent with the pseudo-second-order kinetic model and adsorption isotherm follows the Langmuir model with maximum adsorption capacity of 43.48 mg g^{-1} for Cr(VI). Multiple techniques such as XRD, XPS, SEM, EDX and FT-IR were performed to investigate the possible mechanisms involved in the Cr (VI) adsorption. The results show that there is precipitation between chromium ions and Zn oxide. Furthermore, the ZnO nanoparticles acts as photo-catalyst to generate photo-generated electrons to enhance the reduction of Cr(VI) to Cr(III). The as-prepared ZnO/BC possess good recyclability and the removal ratio remained at about 70% in the fifth cycle, which suggests that both contaminants removal and effective management of water hyacinth can be achieved by the approach.

1. Introduction

Chromium (Cr) is one of the most toxic heavy metals, which is widely exists in industrial wastewater from electroplating, petroleum refining, alloy manufacturing and battery production. Cr exists mainly as Cr(III) and Cr(VI) in the natural environment, among which Cr(VI) is much more poisonous, soluble and mobile than Cr(III). Cr(VI) could cause poisonous and harmful effects on humans and animals (Modenes et al., 2017). Therefore, it is very imperative to treat Cr-contaminated wastewater prior to their disposal into environment. There are many methods, including ion-exchange, chemical precipitation, membrane filtration and adsorption have been explored to remove toxic metal ions from water. Among these techniques, adsorption is frequently employed because the operation is simple, low cost and a great variety of adsorbents are available (Kong et al., 2016; Mazaheri et al., 2017).

Biochar derived from biomass, especially from waste biomass, is recognized as one of the most available adsorbents due to their specific properties such as large surface area, highly porous structure and enriched surface functional groups (Lonappan et al., 2016). The conversion of waste biomass into biochar is gaining

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increased attention due to its potential in resource reuse and waste management. Water hyacinth (*Eichornia crassipes*), as one of the worst aquatic plants and the most aggressive invasive species, has resulted in a serious problem in subtropical monsoon climate zone due to its rapid spread and uncontrolled growth (Malik, 2007). In order to achieve effective management of the problematic invasive species, several literature have reported the conversion of water hyacinth into biochar followed by application in the treatment of wastewater (Zhang et al., 2015, 2016; Xu et al., 2016). These results indicate that the conversion of water hyacinth into biochar could serve as a "win-win" strategy for both contaminants removal and effective management of the highly problematic invasive species.

Furthermore, to enhance the adsorption capacity of biochar, the chemical or physical modification of biochar has also been investigated. Zhang et al. (2016). prepared magnetite-modified water hyacinth biochar for arsenate removal and found that 100% As(V) was depleted by magnetite-modified biochar compared to 8.9% by no Fe-modified biochar. Zhu et al. (2016). found that the loaded bismuth on the wheat straw biochar served as the adsorption site, which played an important role in arsenic and phosphorus adsorption. Li et al. (2016b). synthesized MgO decorated magnetic biochar for phosphate recovery from aqueous solution. In addition, CuS nanorods (Sharifpour et al., 2018) and Mn doped Fe_3O_4 nanoparticles (Asfaram et al., 2015) loaded on activated carbon were also synthesized and used for simultaneous ultrasound-assisted adsorption of dye and metal ion from aqueous solution. These results strongly highlight that the adsorption performance can be significantly improved by loading adscititious composition onto the biochar. Ghaedi' s group also focus on the preparation of molecularly imprinted nanoparticles and their application in the adsorption of hydrochlorothiazide (Arabi et al., 2017a) and hippuric acid (Arabi et al., 2017b) from aqueous solution. Moreover, the adsorbing material relating to zinc nanostructures have also aroused increasing interest. CuO–ZnO composite nanofibers (Malwal and Gopinath, 2017), ZnO microspheres (Lei et al., 2017), Al-doped ZnO rods (Chouchene et al., 2017) and ZnO nanorods (Ansari et al., 2016) exhibited excellent adsorption capacity for dyes. In particular, ZnO loaded on activated carbon and ZnO thin films showed effective adsorption for Pb(II) (Kikuchi et al., 2006) and Cu(II) (Bagheri et al., 2014) removal, respectively. MWCNT-ZnO quantum dot nanocomposite was also applied in Cd(II) adsorption (Mallakpour and Behranvand, 2017). These researches suggest it may be feasible to load ZnO nanoparticles on water hyacinth biochar for efficient Cr(VI) removal. But unfortunately, to our best knowledge, there are very few papers focus on the preparation of biochar from water hyacinth and modification with zinc nanostructures for Cr(VI) removal from aqueous solution.

Therefore, in this work, the preparation of biochar generated from water hyacinth and modification by ZnO nanoparticles for Cr(VI) removal was investigated. The effect of carbonization temperature, ZnO content and contact time on the Cr(VI) removal were examined. Furthermore, multiple techniques such as XRD, XPS, SEM and FT-IR were performed to investigate the possible mechanisms involved in the Cr (VI) adsorption by water hyacinth biochar modified by ZnO nanoparticles.

2. Materials and methods

2.1. Preparation of biochar and ZnO/BC

The biochar samples (BC) used in this study were obtained by slowly pyrolyzing the sun-dried water hyacinth biomass (collected from Lake Dianchi in Kunming, China) under argon atmosphere at 500, 550, 600, 650, 700, 750 and 800 °C for 2 h with the heating rate of 3 °C min^{-1}. After BC was obtained, the BC was purified with 15% nitric acid solution under stirring at 40 °C for 4 h, followed by washing with deionized water and then the neutralized material was dried at 105 °C for 12 h. The purified BC was used as adsorbent for Cr(VI) removal without further activation.

The BC modified by ZnO nanoparticles (ZnO/BC) was prepared by impregnation the purified BC powder into $Zn(NO_3)_2$ aqueous solutions. After addition of the metal salt, the adsorbent was dried at 105 °C for 12 h, and then the precursor was calcinated at 380 °C for 3 h under N_2 atmosphere to obtain ZnO/BC. Subsequently, the sample was naturally cooled to ambient temperature to obtain the finally adsorbent. The ZnO content on ZnO/BC was designed as 10, 20, 30, 40 and 50 wt%.

2.2. Characterization of biochar and ZnO/BC

The adsorbing material, including BC and the BC modified by ZnO nanoparticles (ZnO/BC) were characterized by Field emission scanning electron microscopy (FE-SEM-EDX, Nova Nano SEM 450) equipped with an energy dispersive X-ray spectroscopy (EDX) and Nitrogen physical adsorption-desorption isotherms (Micromeritics Tristar II 3020) conducted at −196 °C. The adsorbents were characterized by powder X-ray diffraction (XRD, D/Max 2200, Rigaku) equipped with Cu K_α radiation (1.5406 Å) and a graphite monochromator and X-ray photoelectron spectrum (XPS, ULVAC PHI 5000 Versa Probe-II equipment). Fourier transform infrared spectroscopy (FT-IR) spectra of adsorbents were recorded with a Nicolet 6700 FT-IR spectrophotometer.

2.3. Batch adsorption studies

All the batch adsorption experiments were conducted in a 150 mL glass bottle at natural pH and natural light with the concentration of Cr(VI) fixed at 100 mg L^{-1}. Cr(VI) solution was prepared by dissolving $K_2Cr_2O_7$ in deionized water. In all experiments, 50 mL Cr(VI) solution with a concentration of 100 mg L^{-1} was mixed with 0.2 g adsorbent and the mixture was shaken in a water bath shaker at 25 °C and 100 rpm. After the desired contact time, the mixture was withdrawn and subsequently vacuum filtered. The filtrate was collected to determine the Cr(VI) concentration by an ultraviolet spectrophotometer at 540 nm with the 1,5-diphenylcarbazide method. The post-adsorption adsorbents were collected and dried at 105 °C overnight for characterization. Additional, to get a comparable results for modified BC and bare BC, the respective batch adsorption studies are conducted under the same conditions.

In this work, the sorption% (removal efficiency) and adsorption capacity were used to evaluate the performance of adsorbing material. The removal efficiency of Cr(VI), percent of sorption%, is calculated from Equation (1):

$$\text{percent of} = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

The adsorption capacity Q_t (mg g^{-1}) of Cr(VI) on adsorbent was calculated according to Equation (2):

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

where C_0 and C_t are the initial Cr(VI) concentrations (mg L^{-1}) and the Cr(VI) concentrations at contact time t, respectively. V is the volume of solution (mL) and m is the weight of added adsorbent (g). All experiments were performed in duplicate and the data are presented as mean ± deviation.