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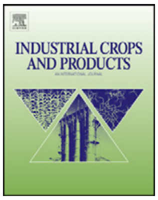

Cr(VI) removal from water using cobalt-coated bamboo charcoal prepared with microwave heating

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ABSTRACT

Bamboo charcoal-based, cobalt-coated adsorbent (Co-MBC) was developed by $Co(NO_3)_2$ and HNO_3 simultaneous impregnating treatment assisted with microwave irradiation. The virgin and modified bamboo charcoals were characterized by means of XRD, SEM-EDS, FT-IR, BET and point of zero charge (pHpzc) measurement. The results showed that Co-MBC exhibited higher surface area of 263 m^2/g and pore volume of 0.27 cm^3/g than those of the virgin bamboo charcoal (MBC). As an adsorbent, Co-MBC showed an excellent adsorption capability for Cr(VI), the adsorption process followed the Langmuir isotherm model well, the adsorption kinetic followed pseudo-second order model. The adsorption of Cr(VI) onto Co-MBC was spontaneous and exothermic in nature, and the addition of Co^{2+} was advantageous to the spontaneous process, and the ion exchange mechanism played an significant role.

The regeneration shows that the Co-MBC has good reuse performance and the hexavalent chromium was recycled.

1. Introduction

In recent years, the toxicity and the effect of heavy metals which are dangerous to public health and environment are attracting more attention (Baniamerian et al., 2009). Among them, Cr(VI) has been classified as a top-priority toxic pollutant by the USEPA, as well as the Chinese EPB, due to its high solubility and toxicity to living organisms (Raji and Anirudhan, 1998; Costa, 2003). Soil and water contamination of Cr(VI) arises from various industries including mining operation, metal plating, leather tanning, water cooling, and pigment manufacturing (Katz and Salem, 1994). In China, Cr(VI) is a common contaminant in the surface water and groundwater resulting in deterioration of drinking water quality. For example, in Huan County, Gansu Province, China, the concentration of Cr(VI) in more than 30% of well and cellar waters, which are the only drinking waters for the local people, is higher than the permissible limit 0.05 mg/L (Wang et al., 2011). Since Cr(VI) is considered as a common teratogenic, mutagenic, and carcinogenic chemicals, the presence of Cr(VI) ions in the environment is posing serious problems and causing great public concern, which significantly motivates the investigation and development of new and improved materials to address the problems (Wang et al., 2011; Zhou et al., 2008).

Various methods have been used for treating Cr(VI) containing wastewater, including electro-chemical precipitation, oxidation/reduction, ion exchange, membrane ultra filtration, and adsorption (Terry, 2004; ölmez, 2009; Alguacil et al., 2003). Among them, activated carbon adsorption seems to be an attractive choice for chromium removal both for its removal efficiency and for the rapid adaptation to pollutant loading alteration (Fang et al., 2007; Di Natale et al., 2007). However, commercially available activated carbons may be expensive and, for this reason, the production of low cost, disposable sorbents for chromium removal is worth considering. Recently, agricultural by-products have received an increasing attention for the production of activated carbons due to their low-cost, renewability and wide prevalence. Many adsorbents have been developed for Cr(VI) removal such as olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal used, hazelnut shell, coconut shell charcoal, banana peel, and green alga (Mohan and Pittman, 2006; Ahmedna et al., 2004; Yang and Lua, 2003; Zhang et al., 2004; Zielke et al., 1996). Bamboo belongs to the grass family which is an enduring, versatile and renewable material (Liu et al., 2010a). It can be carbonized in a furnace at high temperature in the absence of oxygen to produce carbon chars. In order to develop an innovative processing system which can significantly increase the value of the utilization of bamboo, manufacturers have studied the use of bamboo charcoal for the removal of pollutants from liquid solutions (Wang et al., 2008). In China, bamboo is widely planted and spread, and it is estimated that the throughput of bamboo charcoal (BC) has been approximately 40,000 tons a year (Wang et al., 2011). However, its utilization has not been fully explored.

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Therefore, BC used as a potential adsorbent for the removal of toxic pollutants from waters will enlarge its application and help to deal with the emergent wastewater treatment challenge in China.

In general, carbon adsorption is not nearly effective at removing metals and inorganic pollutants as it is in removing organic compounds. In fact, the low adsorption capacity of Cr(VI) on carbon has restricted its wide application (Hezami and Capart, 2005). Recent researches have placed emphasis on surface modification of carbons to enhance Cr(VI) removal from wastewater (Arenillas et al., 2005). Adsorption of Cr(VI) by metal oxides such as iron oxides and aluminum oxide has been demonstrated and shown as a promising method for chromium removal (Liu et al., 2010b; Wei et al., 2009; Ajouyed et al., 2010; Mak et al., 2011). In our previous study (Wang et al., 2011), we used bamboo charcoal as a low cost supporting material for iron oxide coating by a novel and simple synthetic approach. The approach is based on hypotheses that BC is a good microwave absorber, which receives microwave energy directly through dipole rotation and ionic conduction. As a consequence, bulk temperature of the iron-impregnated BC rises rapidly and uniformly under microwave irradiation, the pyrolysis process will promote ferric species to cross-link with various functional groups in a dispersive way on the BC. The Cr(VI) removal capability of Fe-BC was investigated and compared by the batch and column adsorption experiments. The results suggest that Fe-BC is a potential adsorbent for Cr(VI) removal from drinking water. However, as compared with other adsorbents, its adsorption capacity is still unsatisfactory.

As we know that adsorption of metal ions on adsorbent from aquatic environments is governed by both the electrostatic and nonelectrostatic interactions, coming mainly from the surface charges generated on adsorbent and the specific surface area and pore structure (Ajouyed et al., 2010; Lee, 2012). As a typical transition metal oxide, cobalt oxide not only has good electrochemical characterization, but also is an effective activation agent for preparation of activated carbons (Tian et al., 2011; Shen et al., 2006). Therefore, as a continuation of our previous work, the present study is trying to develop a new cobalt-impregnated BC for effective removal of Cr(VI) from water. The adsorbent is characterized by scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), and nitrogen adsorption analyses for Brunauer–Emmett–Teller (BET) specific surface area. The influence of several operating parameters, such as pH, temperature and ionic strength on the adsorption of Cr(VI) are investigated in batch system.

2. Experimental

2.1. Materials

All chemicals and reagents used were of analytical grade. Standard stock Cr(VI) solution (1000 mg/L) was prepared by dissolving $K_2Cr_2O_7$ in de-ionized water and desired solutions were prepared by dilution of the stock solution. $Co(NO_3)_2{\cdot}6H_2O$ was employed as a precursor for cobalt oxide incorporation into the pores of granular-size porous BC.

The BC used in the present investigation was obtained from Suichang Mingkang Charcoal Enterprise Co. Ltd. (Zhejiang, China) with a particle size of 1–2 mm. Before usage, the original charcoal was thoroughly washed in boiling de-ionized water until circum-neutral pH of the supernatant, then ultrasonicated for 0.5 h, oven dried in thin layers at 378 K for 24 h and kept in desiccator for use.

2.2. Preparation of cobalt-containing adsorbents

A proportion of 10 g of the BC sample and 50 mL 29% (w/v) $Co(NO_3)_2{\cdot}6H_2O$ solution were mixed followed by adding 50 mL of 9 M nitric acid. The resulting mixture was ultrasonicated for 2 h for thorough mixing and aged at room temperature for 24 h. Subsequently, the slurry was subjected to centrifugal separation. The recovered residue was set on a quartz boat which was then inserted into a modified microwave heating apparatus, and heated with continuous output 640 W power and a frequency of 2.45 GHz for 5 min under a nitrogen flow of 10 mL/min. It is important to remark that the manufacturing conditions used here were optimized according to the resultant material's characteristics, in particular cobalt oxide contents, specific surface area and porosity development. After cooling, the solid product was washed with de-ionized water until the filtrates were close to neutral. Subsequently the product was dried at 333 K for 24 h and then kept in a desiccator for use (designed as Co-MBC). Additionally, the BC impregnated with de-ionized water was prepared under same procedure for comparison (designed as MBC).

2.3. Surface characteristics of the adsorbents

Surface area and porous size distribution of Co-MBC and MBC samples were measured by nitrogen adsorption and desorption analysis (Micrometritics, ASAP 2020). Crystal structures of samples were determined by performing X-ray diffraction (XRD) on D8 ADVANCE X-ray diffraction spectrometer (Bruker, German). Surface morphologies were examined by a scanning electron microscope (SEM, Hitachi S4700) with the working distance of 5–12 mm and an accelerating voltage of 20 keV. The SEM was equipped with an energy dispersion spectrometer (EDS) and it was used to perform the analysis of chemical constituents of the adsorbents. Infrared absorption spectroscopy (IR) spectra were measured at room temperature on a Fourier transform infrared (FTIR) spectroscopy (Nicolet Instrument Corporation, USA) using the KBr Pellet technique.

2.4. pH point of zero charge

The point of zero charge was carried out using the pH drift method (Yang et al., 2004). For this purpose, 50 mL of a 0.01 M NaCl solution was placed in a 100 mL glass flask. The pH was adjusted to a value between 2.0 and 11.0 by addition of HCl or NaOH, and 0.15 g of adsorbents were added to the solution, shaking for 48 h, the final pH was measured and plotted against the initial pH. The pH at which the curve crossed the line, $\mathrm{pH_{initial}} = \mathrm{pH_{final}}$, was taken as the point of zero charge, $\mathrm{pH_{pzc}}$.

2.5. Adsorption experiments

Adsorption of Cr(VI) on MBC and Co-MBC were studied by batch experiments. Series of experiments were carried out using 0.1 g adsorbents into 150 mL flasks and contacted with 50 mL of desired concentration of Cr(VI) solutions. All batch reactors were placed on a shaker at 150 rpm under controlled temperature. The pH of the solutions was regulated by micro-additions of 0.2 M H_2SO_4 and 0.1 M NaOH.

Adsorption kinetics were studied at 298 K with an initial Cr(VI) concentration of 50 mg/L. At predetermined time intervals, one of the flasks was picked out for the analysis of Cr(VI) concentration. The amount of Cr(VI) adsorbed onto the adsorbent q_t (mg/g) was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where C_0 and C_t (mg/L) are initial and final concentrations of Cr(VI) at time t in the solutions, respectively; W (g) the amount of the adsorbent and V (L) the volume of Cr(VI) solution.