Bioresource Technology 247 (2018) 370–379

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Polyethylene imine modified hydrochar adsorption for chromium (VI) and nickel (II) removal from aqueous solution

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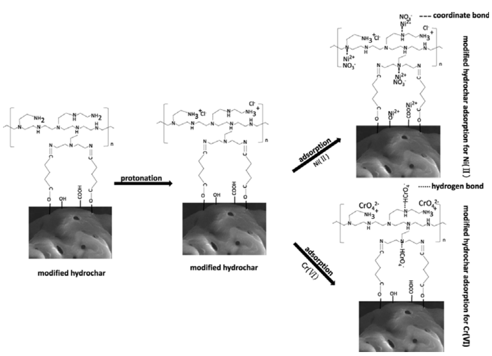
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydrochar
Chromium
Nickel
Polyethylene imine
Adsorption

ABSTRACT

An adsorbent hydrochar was synthesized from corn cobs and modified with polyethylene imine (PEI). The hydrochars before and after modification were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis. FTIR and XPS revealed that the PEI was grafted onto the hydrochar via ether and imine bonds formed with glutaraldehyde. The maximum adsorption capacities for Cr(VI) (33.663 mg/g) and Ni(II) (29.059 mg/g) on the modified hydrochars were 365% and 43.7% higher, respectively, than those on the unmodified hydrochar. A pseudo-second-order model described the adsorption of Ni(II) and Cr(VI) on all the adsorbents. The adsorption of Cr(VI) was endothermic, spontaneous, increased disorder, and obeyed the Langmuir model. By contrast, the adsorption of Ni(II) was exothermic, spontaneous, decreased disorder, and obeyed the Freundlich model. XPS confirmed that the adsorption sites and mechanisms for Ni(II) and Cr(VI) on the modified hydrochars were different.

1. Introduction

The agricultural industry produces large quantities of biomass waste, such as straw, which imposes critical burdens on the environment (Doula et al., 2016). In China, the annual production of waste crop straw is approximately 0.7 billion tons, of which 70% is rice straw,

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http://dx.doi.org/10.1016/j.biortech.2017.09.107
Received 24 June 2017; Received in revised form 11 September 2017; Accepted 15 September 2017
Available online 20 September 2017
0960-8524/

wheat straw, and corn stalk (Liu et al., 2013). Sustainable management of waste straw is required for environmental, financial, and social reasons.

Biochemical conversion to biogas or compost, and thermochemical conversion by pyrolysis and hydrothermal treatment have been considered for waste straw. Recently, hydrothermal treatment has attracted attention as a promising treatment technology. Hydrothermal processing is divided into three separate processes, depending on the operating conditions (Elliott et al., 2015). At temperatures above 647 K, gasification reactions dominate and the process is defined as hydrothermal gasification, resulting in the production of a synthetic fuel gas. At intermediate temperatures between 520 and 647 K, the process is defined as hydrothermal liquefaction and produces a liquid fuel known as biocrude. Biocrude is similar to petroleum crude and can be upgraded to the whole distillate range of petroleum-derived fuel products. At temperatures below 520 K, hydrothermal processing is known as hydrothermal carbonization. The solid product from hydrothermal carbonization, called hydrochar, has rich surface chemistry, interesting nanostructures (e.g., spheres and nanowires), abundant oxygen-containing functional groups, and a large porous structure (Hu et al., 2010). Hydrochar shows potential as a sorbent for wastewater treatment and has received much attention (Liu et al., 2010, 2016). Many researchers have used hydrochar for adsorption of organic contaminants (Li et al., 2016), such as Congo red and 2-naphthol, and nutrient elements (Takaya et al., 2016), such as phosphate and ammonium.

Several recent studies have focused on removal of heavy metals, such as antimony, cadmium, and lead, by hydrochar adsorption (Han et al., 2017; Petrovic et al., 2016). Heavy metal pollution is a very serious problem that affects the survival of all living organisms and can have a number of adverse effects on the human body (Ma et al., 2014). Chromium (Cr) is a ubiquitous natural element, and mostly exists in the environment as trivalent (Cr(III)) and hexavalent (Cr(VI)) chromium. Hexavalent chromium is more toxic than trivalent chromium, and can enter the human body through the skin, inhalation, or oral intake. In the body, it is transferred by the blood to the kidneys and liver, and can cause DNA damage and is carcinogenic (Yi et al., 2017). Nickel (Ni) is also ubiquitous in the environment, and can enter the human body by the same pathways as hexavalent chromium. After entering the body, it penetrates all organs and accumulates in various tissues and causes tissue damage, which may cause neurotoxicity, hepatotoxicity, nephrotoxicity, gene toxicity, reproductive toxicity, and increase the risk of cancer (Guo et al., 2016). Therefore, chromium and nickel have been designated as top-priority toxic pollutants by the United States Environmental Protection Agency. Hydrochar is considered an economic and efficient adsorbent for removal of chromium and nickel from aqueous solutions. Anaerobically digested sludge and pulp and paper industry sludge have been used as feedstocks for hydrochar synthesis for a preliminary investigation of the hydrochar adsorption capacity for hexavalent chromium and other heavy metal ions (Alatalo et al., 2013). Xue et al. (2012) examined the effect of H_2O_2 treatment on hydrothermally produced biochar (hydrochar) from peanut hulls for the removal of nickel and other heavy metals from aqueous solutions. However, several factors hampered the adsorption efficiency of hydrochar for chromium and nickel removal.

Polyethylene imine (PEI) contains many primary and secondary amine groups in its linear polymer chains, and shows strong adsorption performance for heavy metal ions (Ma et al., 2014). PEI can combine with Cr(VI), Cu(II), Zn(II), and Cd(II) by electrostatic interactions or complexation (Pang et al., 2011a,b). Previous studies have found that PEI modification of adsorbents, such as silica gel, granular sludge, and mesoporous silica improves the efficiency of chromium and nickel adsorption (Ghoul et al., 2003; Sun et al., 2011; Thakur et al., 2017).

In this study, PEI-modified hydrochar was prepared and used to adsorb Cr(VI) and Ni(II) from aqueous solutions. The PEI-modified hydrochar was synthesized under acidic conditions (acid-hydrochar) or alkaline conditions (alkali-hydrochar). The hydrochars were characterized and their adsorption efficiencies and regeneration were investigated.

2. Materials and methods

2.1. Materials

PEI (MW 10,000) was purchased from Aladdin Industrial Corporation (Shanghai, China). Corn cobs were supplied by China Agriculture University (Beijing, China). Other reagents used were of analytical grade and were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Synthesizing hydrohcar and modification of hydrochar with PEI were performed according to established methods (Ma et al., 2014; Li et al., 2016).

Hydrochar was prepared from the corn cobs using hydrothermal treatment. Kibbling corn cobs (40 g) was loaded into a 300-mL hydrothermal reactor with 240 mL of ultrapure water. The reactor was then closed tightly and heated to 573 K for 0.5 h. Then, the reactor was cooled to room temperature in the air. The reaction mixture was filtered and the solid was retained. The solid was washed three times with 400 mL of ultrapure water each time, and dried in an oven at 378 K for 24 h.

Before modification, the hydrochar was treated with an acidic or alkaline solution. The hydrochar (20 g) was mixed with 200 mL of 1 M HCl or 3 M KOH, and agitated at 200 rpm for 1 h at room temperature to remove any impurities contained in the hydrochar. Then, the hydrochar was washed with ultrapure water until the pH was around 7.0, dried at 378 K for 12 h, and stored in desiccator before use. After treated hydrochar was added to 100 mL of 10% (w/v) PEI/methanol solution, and agitated at 200 rpm and 303 K for 18 h. Then, the hydrochar was immediately transferred to a 200 mL 1% (w/v) glutaraldehyde solution for cross-linking. The solution was agitated at 200 rpm and 303 K for 30 min. Finally, the modified hydrochar was washed with ultrapure water and labeled as acid-hydrochar or alkali-hydrochar.

2.2. Methods

Adsorption experiments were performed using a batch equilibration technique. Stock solutions (2000 mg/L) of Cr(VI) and Ni(II) were prepared by dissolving analytical grade $K_2Cr_2O_7$ and $NiCl_2{\cdot}6H_2O$ in ultrapure water.

To study the kinetics of the adsorption process, 0.05 g of one of the hydrochars (unmodified, acid-hydrochar, or alkali-hydrochar) was mixed with 20 mL of $NaNO_3$ solution (pH 5.5, 0.01 M) containing either 20 mg/L Cr(VI) or 50 mg/L Ni(II). The mixture was then agitated on a reciprocating shaker at 298 ± 0.5 K, 308 ± 0.5 K, or 318 ± 0.5 K at 200 rpm. Samples were removed at desired intervals and filtered using filter paper. The filtrates were analyzed for residual Cr(VI) or Ni(II) in the solution. Finally, the adsorption kinetics for Cr(VI) and Ni(II) were studied with the unmodified hydrochar, acid-hydrochar, and alkali-hydrochar and fitted to three kinetic models as follows.

The linear equation of a pseudo first order model can be expressed as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (1)$$

The linear equation of a pseudo second order model can be expressed as follows:

$$\frac{t}{Q_t} = \frac{1}{Q_e^2 k_2} + \frac{t}{Q_e} \quad (2)$$

The Webber-Morris model (W-M model) can be expressed as follows:

$$Q_t = k_{id} t^{1/2} + C \quad (3)$$