In-situ modification of activated carbon with ethylenediaminetetraacetic acid disodium salt during phosphoric acid activation for enhancement of nickel removal

Yiran Li, Jian Zhang *, Hai Liu

Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

ARTICLE INFO

ABSTRACT

Ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) was employed to in-situ modify activated carbon from *Typha orientalis* during phosphoric acid activation to improve its Ni(II) adsorption capacity. The Ni(II) adsorption capacities of original activated carbon (AC) and Na_2EDTA-modified activated carbon (AC-Na_2EDTA) were evaluated by batch adsorption experiments. The adsorption isotherms of activated carbons conformed to the Langmuir model. The adsorption equilibrium data showed that the calculated maximum Ni(II) adsorption capacities of the samples enhanced from 15.4 mg/g to 27.9 mg/g after modification with Na_2EDTA. The physicochemical properties of AC and AC-Na_2EDTA were characterized by N_2 adsorption/desorption isotherm, Boehm's titration and X-ray photoelectron spectroscopy (XPS) analysis. No obvious differences of AC and AC-Na_2EDTA in nitrogen adsorption/desorption curves and pore size distributions could be observed. However, AC-Na_2EDTA (80.9% and 2.10 mmol/g) exhibited a higher (N + O)/C atomic ratio and total functional groups content than AC (26.2% and 1.35 mmol/g). These results suggested that chemisorption is mainly responsible for Ni(II) adsorption on activated carbon. Based on the results of batch adsorption experiments and XPS analysis, Ni(II) cations were mainly bound with the O-containing and N-containing groups through the mechanisms of cation exchange, electrostatic attraction and surface complexation. Desorption experiments showed maximum Ni(II) recovery in HCl solution.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Nickel (Ni) is a widespread toxic heavy metal in the aqueous environment. For the non-biodegradation and bioaccumulation through the food chain, the severe public health problems caused by nickel pollution have been serious concern [1,2]. The nickel contained effluents derive mainly from industrials such as electroplating, smelting, batteries manufacturing, mining, alloys producing [3–5]. Exposure to significant levels of nickel is associated with dermatitis, gastrointestinal distress, chronic bronchitis, respiratory cancer, cardiovascular and kidney diseases [6,7]. Therefore, it is necessary to effectively remove nickel from industrial wastewater before discharging into aquatic environments. Extensive researches have been reported on developing economical and efficient techniques for Ni(II) removal in wastewater [4,7–10]. Activated carbons with highly excellent adsorption capacity, well-developed porosity and high specific area have been successfully employed as adsorbents for elimination Ni(II) contaminated water [11–13].

It is well known that enhancement of surface functional groups is an effective method to improve the adsorption properties of activated carbons toward heavy metal ions [14–16]. Numbers of researchers have demonstrated that introduction of O-containing functional groups significantly improved the absorption ability of activated carbons for metal species, resulting from the improvement of the electrostatic forces and active sites for complex formation with heavy metal cations [17–19]. The most common modification method is treating carbon samples with oxidizing agents (e.g., HNO_3, H_2O_2, $KMnO_4$, and O_3) and oxy-organics [17–22]. ShamsiJazeyi et al. [17] studied Hg(II) adsorption on nitric acid modified activated carbon. After modifying with nitric acid, more carboxylic acid surface groups were created on activated carbon, and the Hg(II) adsorption capacity increased two times. Chen et al. [18] identified that modification of activated carbon with citric acid caused 140% improvement of copper adsorption capacity, resulting from the surface site density increased by 144%.

In addition, the N-containing functional groups also play a significant role in the field of heavy metal adsorption. The nitrogen atoms of N-containing functional groups could share electron pairs to bind with metal ions. N-containing functional groups can be introduced onto the carbon material surface by either treatment with a nitrogen-containing reagents or activation of nitrogen-rich carbon precursors [13,23–26]. Jia et al. [24] prepared activated carbons with high nitrogen

functional groups concentrations by ammonia treatment or by carbonization of polyacrylonitrile, and their adsorption capacities of heavy metals markedly improved due to these groups acted as surface coordination sites for adsorption. Guo et al. [25] determined that activated carbons prepared with ammonium phosphate activation exhibited about 42%, 21% and 23% higher of Ni(II), Cu(II) and Cd(II) adsorption capacities than the phosphoric acid activated carbon. However, method for simultaneously enhancing both O-containing and N-containing functional groups of carbons has been rarely reported.

Ethylenediaminetetraacetic acid disodium salt (Na$_2$EDTA) is an aminopolycarboxylic acid containing two amine groups and four carboxyl groups, and commonly used as a chelator for its strong metal-complexing property. Ex-situ modification of adsorbents (lignocellulose materials [27], chitosan [28], mesoporous silica [29], and carbon material [30]) by impregnation with Na$_2$EDTA, improved their adsorption capacities for heavy metals ions. However, Na$_2$EDTA is not easily bind on the carbon material's surface, and ex-situ modification is a time consuming and laborious procedure.

Phosphoric acid activation method has been well established for activated carbon preparation from various hydrophyte residues [12,31–33]. Previously, we reported that the activated carbon with in-situ tartaric acid modification during phosphoric acid activation had 60% higher in the O-containing functional groups and 30% higher in the Cr(VI) adsorption capacity than that of the original carbon [34]. No relevant studies have been reported on in-situ modifying activated carbon with Na$_2$EDTA in preparation process. During the phosphoric acid activation, carboxyl groups of Na$_2$EDTA could promote the formation of the O-containing functional groups, and N-containing groups may also introduce onto the resulting activated carbon with amine groups. Thus, in-situ Na$_2$EDTA modification could be a convenient and effective method to improve both O and N contents on activated carbon, eventually further enhancing its heavy metal ions adsorption capacity.

Therefore, the fundamental aim of this research is to explore the feasibility for enhancing Ni(II) adsorption capacity by in-situ modifying activated carbon with Na$_2$EDTA during phosphoric acid activation. The mechanisms for Ni(II) adsorption on the activated carbons were investigated by bath adsorption experiments, N$_2$ adsorption/desorption isotherms, Boehm's titration and XPS analysis of carbons.

2. Materials and methods

2.1. Materials

Typha orientalis (TO) was used as the precursor of activated carbon preparation in this study, and was harvested from a wetland in Jinan, Shandong, China. After washing with distilled water, TO was dried at 105 °C for 24 h, then smashed and screened to 40 mesh particle size by standard sieves (Model Φ200). All chemical reagents used in this study were analytical reagent grade.

2.2. Synthesis of activated carbons

TO (10 g) were adequately mixed with different mounts of Na$_2$EDTA (0–40 mmol), and impregnated with H$_3$PO$_4$ solution (85 wt%) at a ratio of 2.5/1 (g H$_3$PO$_4$/g TO) for 10 h at room temperature. Next, the samples were heated at 500 °C in a muffle furnace for 1 h and then cooled to room temperature. Then, the product was thoroughly washed with distilled water until the pH of filtrate became steady. Finally, the samples were filtered and dried at 105 °C for 10 h, then ground and sieved to 100–200 mesh by standard sieves. The activated carbons with or without Na$_2$EDTA modification are referred to as AC and AC-Na$_2$EDTA-X, where the X is the amount of Na$_2$EDTA added (25, 30, 35 and 40 mmol).

2.3. Characterization of activated carbons

The specific surface area and pore size distribution of activated carbons were determined by N$_2$ adsorption/desorption isotherms at 77 K with a surface area analyzer (Quantachrome Corporation, USA). The specific surface area (S_{BET}) was calculated by Brunauer-Emmett-Teller (BET) method and pore size distribution was determined by Density Functional Theory (DFT) method. Total pore volume (V_{tot}) was determined from the amount of N$_2$ adsorbed at P/P$_0$ = 0.95. Micropore surface area (S_{mic}), external surface area (S_{ext}) and micropore volume (V_{mic}) were obtained via t-plot analysis. Mesopore volume (V_{mes}) was calculated by V_{tot}-V_{mic}. Average pore diameter (D_p) was calculated by $D_p = 4V_{tot}/S_{BET}$ [25].

Boehm's titration method was used to quantify the amounts of functional groups on the carbons [35]. The different types of functional groups were based on the assumptions that NaHCO$_3$ neutralizes carboxyl groups; Na$_2$CO$_3$ neutralizes carboxyl and lactonic groups; NaOH neutralizes carboxyl, lactonic and phenolic groups; and HCl neutralizes all basic groups.

The surface binding state and elemental speciation of activated carbons were analysed by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer PHI 550 ESCA/SAM) with Mg Kα irradiation (1486.71 eV of photons) as X-ray source. All binding energies were referenced to the C 1 s peak at 284.6 eV to compensate for the surface charging effects.

2.4. Adsorption experiments

Batch adsorption experiments were performed by adding 30 mg sample into 50 mL Ni(II) solution to investigate the effect of initial Ni(II) concentration (10–50 mg/L), initial pH (2.0–8.0) and ionic strengths (0–800 mM NaCl) on the adsorption. The initial pH of the Ni(II) solution was adjusted with 0.1 mmol/L HCl or NaOH solution and measured with a pH meter (Model pHS-3C, Shanghai, China). The ionic strengths were adjusted with NaCl solution. The samples were shaken at 120 rmp in room temperature (22 ± 1 °C) for 48 h to ensure that adsorption equilibrium was reached. After equilibrium, the samples were filtered through a 0.45 μm membrane filter. The concentration of Ni(II) in aqueous solution was analysed by a UV–vis spectrophotometer (UV-5100, Shanghai) at wavelength of 530 nm according to the standard methods [36].

Adsorption kinetic experiments were performed to investigate the effect of agitation time on Ni(II) adsorption and deduce the kinetic parameters. The experiments were operated as follows: 0.6 g sample was added into 1000 mL Ni(II) solutions and the mixture was agitated on an electromagnetic stirrer (Model 78-1) at 400 rpm in 22 ± 1 °C. At predetermined time intervals, 20 mL solutions were taken out, and the Ni(II) concentration in solutions was analysed by the abovementioned method.

Duplicate samples were prepared for each experiment. All results were the mean of the duplicate samples with relative error below 5%.

2.5. Desorption experiments

Desorption experiments were carried out immediately after the adsorption experiments. Different concentrations of HCl (25, 50, 75, 100, 125 and 150 meq/L), NaCl and CaCl$_2$ solutions (100, 300, 500, 800, 1000 meq/L) were used to recover Ni(II) from Ni(II)-loaded AC and AC-Na$_2$EDTA. The centrifuged solid residues derived from the adsorption phase were washed with distilled water, then added into 50 mL different solutions and distilled water respectively. The samples were shaken at 120 rmp in room temperature (22 ± 1 °C) for 48 h. After equilibrium, the samples were filtered through a 0.45 μm membrane filter, and the Ni(II) concentration in filtrate was analysed by the above-mentioned method. Duplicate samples were prepared for each