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Modified activated carbons with amino groups and their copper adsorption properties in aqueous solution

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ABSTRACT

Activated carbons were prepared by two chemical methods and the adsorption of Cu (II) on activated carbons from aqueous solution containing amino groups was studied. The first method involved the chlorination of activated carbon following by substitution of chloride groups with amino groups, and the second involved the nitration of activated carbon with reduction of nitro groups to amino groups. Resultant activated carbons were characterized in terms of porous structure, elemental analysis, FTIR spectroscopy, XPS, Boehm titration, and pH_{zpc} . Kinetic and equilibrium tests were performed for copper adsorption in the batch mode. Also, adsorption mechanism and effect of pH on the adsorption of Cu (II) ions were discussed. Adsorption study shows enhanced adsorption for copper on the modified activated carbons, mainly by the presence of amino groups, and the Freundlich model is applicable for the activated carbons. It is suggested that binding of nitrogen atoms with Cu (II) ions is stronger than that with H^+ ions due to relatively higher divalent charge or stronger electrostatic force.

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1. Introduction

Activated carbon is a conventional porous adsorbent with unique physical properties such as relatively large surface area, high porosity, and variable pore size distribution and also contains oxygen functional groups, which have significant influences on the adsorption properties of this material [1–5]. Activated carbon has recently attracted great attention in water and wastewater treatment processes due to its cost effectiveness, abundance, and suitable adsorptive properties [6–9]. Chiefly, one of the most important reasons for suitability of this adsorbent in such applications is its high ability towards organic substance removal, which makes it suitable for water purification [10–12]. However, this adsorbent has lower sorption affinity towards inorganic substances.

Heavy metals are among the most toxic pollutants entering the environment in vast quantities through wastewaters of different industrial plants such as mining operations, electronics, tanneries, electroplating and petrochemical industries, as well as textile mill plants [13–15]. Specially, copper is commonly used in electric and electroplating industries and agricultural poisoning [15] and can be found in the wastewater effluents of these industries. When present with high concentrations in the human body, Cu (II) ions can cause liver and kidney damages. The legislation limits for discharge of copper are recommended to be less than $2 \text{ mg} \cdot \text{L}^{-1}$ by the World Health Organization [15].

There are many processes for treatment of Cu (II) from contaminated wastewaters, including chemical precipitation, membrane filtration, reverse osmosis, ion exchange, and adsorption. Among various treatment technologies, activated carbon adsorption is commonly used due to its easy operation, porous surface structure and harmlessness to the environment. However, in general, activated carbons are more effective for the adsorption of organic compounds rather than metal ions and inorganic pollutants, so developing methods for modification of activated carbons towards these materials should be considered.

Usually, original activated carbons contain some functional groups (mostly oxygen groups), and several techniques have been used to improve their structure by introducing other heteroatom-containing functional groups. For example, many investigations have been carried out on activated carbon to introduce functional groups, and it is expected to improve the adsorption of adsorbent towards specific adsorbate [16–19].

Amination of activated carbon, as one of the ways for modification of its structure, has been investigated in several researches, through the reaction with NH_3 at elevated temperatures [20,21], but amination through chemical reaction at low temperature has been rarely reported [22,23]. Considering the limited researches about using these kinds of activated carbons for copper removal, the amination of activated carbon and its influence on copper adsorption capacity are investigated in the present work. In this context, it is attempted to modify the surface of activated carbon by two methods, both introducing amino groups on activated carbon at low temperature. The first innovative method is based on the chlorination of activated carbon and then substitution

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of chloride groups with amino groups. The second method has been reported elsewhere [24], based on nitration of activated carbon and reduction of nitro groups to amino groups.

Eventually, the adsorption capability of the modified adsorbents towards Cu (II) in aqueous phase is determined in the batch mode. Kinetic and equilibrium experiments are carried out in order to determine and compare the rate and capacity of Cu (II) adsorption and provide reasonable mechanisms involved in the copper adsorption by the newly designed sorbents.

2. Materials and Methods

2.1. Activated carbon sample

Commercially activated carbon (prepared from Norit) with $425 \text{ kg} \cdot \text{m}^{-3}$ apparent density and 15 mm particle size (D50) was used as the carrier adsorbent for introduction of nitrogen groups, denoted as SAE. SAE was dried at 90°C for 24 h after washing with 10% HCl and deionized water separately in a Soxhlet apparatus for 24 h to remove impurities.

2.2. Amination of activated carbon

2.2.1. First method: Chlorination of activated carbon and substitution of chloride groups with amino groups

Fig. 1 shows the mechanisms of surface modification by the two methods. In the first method, amino groups are introduced to the activated carbon surface in a three-step procedure. The first step involves the oxidation of carbon to increase oxygen functional groups. 10 g of carbon was oxidized with 100 ml of nitric acid ($5 \text{ mol} \cdot \text{L}^{-1}$) at 84°C for 5 h. Then the mixture was filtered and washed with deionized water in a Soxhlet apparatus till neutral pH was attained. The second step involves the chlorination of activated carbon and transformation of oxygen groups into chloride groups. 10 g oxidized activated carbon was treated with 25 ml concentrated thionyl chloride at 84°C and refluxed for 24 h. Then the mixture was filtered and washed with deionized water in the Soxhlet apparatus till neutral pH was attained. In the final step, chloride groups were substituted into amino groups by another reaction; 10 g of chlorinated carbon along with 50 ml of aqueous ammonia (28%) was placed in a 1000 ml flask and refluxed for 24 h. Then the mixture was filtered and washed with deionized water in the Soxhlet apparatus till neutral pH was attained. It is necessary to note that after each step, the product was dried at 90°C . This carbon sample is hereafter abbreviated to ACN1.

2.2.2. Second method: Nitration of activated carbon and reduction of nitro groups to amino groups

The second method for the amination of activated carbon includes two stages. The first step involves a reaction for the nitration of activated

carbon. At 0°C (an ice bath), 50 ml of concentrated ($18 \text{ mol} \cdot \text{L}^{-1}$) sulfuric acid (H_2SO_4) was added slowly to 50 ml of concentrated ($15.7 \text{ mol} \cdot \text{L}^{-1}$) nitric acid (HNO_3). Then, 10 g activated carbon was slowly added to this acid mixture and stirred for 50 min in the ice bath. The mixture was filtered and washed with deionized water in the Soxhlet apparatus. The product was then dried at 90°C . The second step was the reduction of nitrobenzene to aniline by FeCl_2 . Reduction of nitrated activated carbon proceeded in a 1000 ml flask containing 100 ml of hydrochloric acid, 2 g of powdered iron, and 8 g of carbon with stirring at 80°C for 24 h. The aminated activated carbon obtained was dried at 90°C after the separation of additional powdered iron with magnet and washing with deionized water in the Soxhlet apparatus. This carbon sample is hereafter abbreviated to ACN2.

3. Characterizations

3.1. Point of zero charge measurements

Point of zero charge for produced carbons was measured according to the method suggested by Noh and Schwarz [25], which requires recording of the equilibrium pH after shaking of suspensions of carbon samples in distilled water for 24 h. The initial pH of the suspensions was selected in the range of 2–11. The fixed equilibrium value of pH was taken as the pH_{zpc} .

3.2. Boehm titration

The method introduced by Boehm [26] was used for the determination of the amount of acidic functional groups available on the activated carbon surface. In this method, 0.5 g activated carbon sample was weighed into three 100 ml conical flasks. Then 30 ml of aqueous solutions of sodium hydrogen carbonate ($0.1 \text{ mol} \cdot \text{L}^{-1}$), sodium carbonate ($0.1 \text{ mol} \cdot \text{L}^{-1}$), and sodium hydroxide ($0.1 \text{ mol} \cdot \text{L}^{-1}$) was added into the flasks. Suspended solutions were kept at 20°C for 24 h. After filtration, 10 ml of withdrawn aliquots of products was titrated with $0.1 \text{ mol} \cdot \text{L}^{-1}$ hydrochloric acid. The amount of acidic surface functional groups such as carboxylic groups and phenolic hydroxyl groups was calculated using the titration data.

3.3. Elemental analysis

Elemental analysis of the produced samples was performed by an elemental analyzer (model Carlo Erba 1106). The sample was weighed accurately on an aluminum foil and put into the instrument. Prior to the flash combustion process, the system was purged with helium carrier gas. Flash combustion was then performed at 2073 K, and the gaseous combustion products were quantified using a thermal conductivity detector. Results were obtained as percentages of carbon, hydrogen, and nitrogen, and the oxygen content was determined by difference.

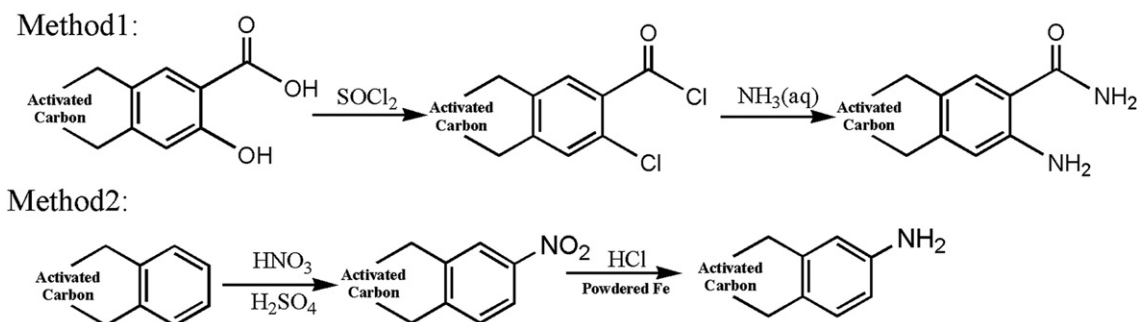


Fig. 1. Synthesis of aminated activated carbon by two different methods.

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