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Adsorption and cosorption of ciprofloxacin and Ni(II) on activated carbon-mechanism study

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ABSTRACT

Antibiotics and heavy metals often coexist in water bodies due to influxes of various pollution sources. The objective of this study was to evaluate the interaction between Ni(II) and ciprofloxacin (CIP) concerning their adsorption and cosorption onto activated carbon as a function of time, solution pH and initial concentration. Adsorption of Ni(II) and CIP on activated carbon was strongly dependent on solution pH, indicating an electrostatic attraction mechanism. Cosorption of Ni(II) and CIP also strongly depended on solution pH. The presence of CIP suppressed Ni(II) adsorption, especially at low pH, due to the competition of CIP with Ni(II) for adsorption sites. The presence of Ni(II) in the aqueous solution increased the adsorption of CIP onto activated carbon at pH between 3.4 and 6.5, because the positively charged complexes of Ni–CIP with greater sorption affinity to activated carbon than CIP itself form in this pH range.

1. Introduction

Antibiotics have been used for several decades as medicine for human and animals. The primary drug elimination mechanisms of antibiotics from organisms are via urine and feces, so essentially all antibiotics taken are ultimately excreted, whether unchanged or in metabolite form [1,2]. These residues could threaten surface water and even groundwater as a result of leaching from agricultural fields [3]. Many studies showed that CIP residues were widespread in wastewater and surface water with high concentrations [4–6] and were poorly removed by sewage treatment plants due to the bacteria-inhibiting effect. As a synthetic antibiotic, ciprofloxacin (CIP) is categorized as the second generation of fluoroquinolones and has the strongest antimicrobial activity. The presence of CIP in aqueous solution, even in low concentrations, can result in the development of antibiotic resistant bacteria. Therefore its removal from water has become an increasingly important concern. Even so, there are few researches dealing with the elimination of CIP, when compared with other antibiotics.

As a naturally occurring element, nickel is 5th most abundant element. It is found in rock or soil or sediment. It is largely present in the wastewaters coming from industrial production processes such as mining, smelting, galvanization, batteries manufacturing and metal finishing [7,8]. The presence and accumulation of Ni(II) in industrial effluents have a toxic or carcinogenic effect on living species. World Health Organization (WHO) has set that the maximum amount of nickel in drinking water is 0.1 mg/L. However, the concentration of Ni(II) in many electroplating effluent water is as high as 50 mg/L. Thereby, it is a challenging objective to eliminate Ni(II) ions from wastewaters. The same as CIP, there are few studies dealing with the elimination of Ni(II), when compared with other widely used heavy metal.

As an economical and efficient method, adsorption technique by activated carbon is widely applied to remove antibiotics and heavy metal ions from wastewaters [6,9,10]. Previous studies were conducted to investigate the adsorption of CIP [11] and Ni(II) [8] from aqueous solution by activated carbon separately. As we know, the water body is a complex system where antibiotics and heavy metal often coexist due to influxes of various pollution sources. Little attention has been given to investigate the adsorption of antibiotics on activated carbon in aqueous solution as affected by heavy metals. Similarly, few studies have been reported about the effect of heavy metals on activated carbon in aqueous solution as affected by antibiotics.

The objectives of this study were to investigate the adsorption and cosorption of Ni(II) and CIP on activated carbon in aqueous solution as a function of time, solution pH and initial concentration. Specific focus was on the effect of solution chemistry on the adsorption onto activated carbon, and to explore their interaction mechanisms.

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2. Materials and methods

2.1. Materials

Arundo donax Linn obtained from Nansi lake (Shandong, China) was used as a raw material for activated carbon preparation. CIP hydrochloride used as adsorbate was purchased from Sangon Biotech (Shanghai, China). Its pK_{a1} and pK_{a2} are 6.1 and 8.7 [12]. The cationic form (CIP^+), zwitterionic form (CIP^0) and anionic form (CIP^-) existed in different pH range. The feed solution of Ni(II) was prepared by dissolving exact quantities of analytical grade of $NiCl_2$ $6H_2O$ in deionized-distilled water. All other chemicals were of analytical grade.

2.2. Adsorbent preparation

The preparation procedure was reported in previous study [13]. Briefly, the washed *A. donax* Linn sample was dried in a drying oven. After ground into small particle, the material was impregnated with 45% $H_4P_2O_7$ (w/w) to form slurries. Then, the mixture was mechanically stirred coupled with 10 min sonication and set aside at room temperature for 10 h. The wet sample was transferred into a microwave furnace where the sample was heated (radiation power of 700 W and radiation time of 15 min). After cooling down, the activated carbon obtained was washed several times with tap water, hydrochloric acid and distilled water for removal of residual $H_4P_2O_7$ until the pH of filtrate became constant (at about 7.0). The wet mass was dried, crushed and sieved. Particles with sizes between 0.074 and 0.15 mm (100–200 mesh) were used for experiment.

2.3. Adsorbents characterization

The textural structure including surface area, pore volume and pore size was determined by nitrogen adsorption/desorption isotherms at −196 °C using a surface area analyzer (JW-BK122W, Beijing JWGB Sci. & Tech. Co., Ltd., China). The surface area (S_{BET}) was determined by following the BET equation. The micropore surface area (S_{mic}) and volume (V_{mic}) were obtained with the *t*-plot method. The external volume (V_{ext}) was obtained by deducting of V_{mic} from V_T and the external area (S_{ext}) was S_{mic} from S_{BET} [13]. The zeta potential of AC at different pH and $NaCl_2$ solutions was measured by micro-electrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., China). pH_{pzc} was the pH at which the zeta potential on AC surface was zero. The amount of surface functional groups was determined by Boehm titration method [14].

2.4. Adsorption of CIP onto activated carbon as affected by Ni(II)

The effect of time on CIP adsorption onto activated carbon as effect by Ni(II) was conducted as follows: The CIP solutions of 400 mg/L with and without 20 mg/L of Ni(II) were prepared. Then, the pH of the solutions was adjusted to 6.0 with concentrated HCl or NaOH. A series of carbons (0.050 g) were weighed into 150 mL conical flasks to contact with 50 mL of CIP solutions. The flasks were then completely wrapped with aluminum foil and placed in a temperature-controlled oscillator (SHA-B, Shanghai) at a preset temperature of 25 °C and a shaking speed of 125 rpm. In adsorption progress, samples were withdrawn at a predefined time and the supernatant was taken to determine the residual liquid-phase CIP concentration with UV–visible spectrophotometry at 275 nm (UV-754, China).

The effect of pH on adsorption of CIP onto activated carbon as affected by Ni(II) was conducted as follows: CIP solutions with and without 20 mg/g of Ni(II) were prepared. After adjusting the pH to different values between 2.6 and 7.4 by concentrated HCl or NaOH, 50 mL of solutions were transferred to 150 mL flasks. Then, activated carbons (0.05 mg) were added. The flasks were then completely wrapped with aluminum foil and placed in a temperature-controlled oscillator (SHA-B, Shanghai) at a preset temperature of 25 °C and a shaking speed of 125 rpm. After equilibrium, the supernatant was taken for analysis.

Equilibrium adsorption experiments of CIP on activated carbon were carried out by adding CIP solution with and without Ni(II) (20 mg/L) to a series of 150 mL conical flasks. The initial CIP concentrations of the solutions were in the range of 200–1200 mg/L. After adjusting the solution pH to 6.0 using concentrated HCl or NaOH, 50 mL of solutions were introduced into flasks to contact with 0.050 g of activated carbon. The flasks were then completely wrapped with aluminum foil and placed in a temperature-controlled oscillator (SHA-B, Shanghai) at a preset temperature of 25 °C and a shaking speed of 125 rpm. Adsorption experiments were maintained for 36 h to ensure equilibrium. The supernatant concentration of CIP was taken for analysis.

2.5. Adsorption of Ni(II) on activated carbon as affected by CIP

The effect of time on Ni(II) adsorption on activated carbon affected by CIP was conducted in the same way as the adsorption of CIP as affected by Ni(II). The suspension pH was adjusted to 6.0. The Ni(II) concentration was 20 mg/L, and the CIP concentration was 0 or 400 mg/L.

The effect of pH on adsorption of Ni(II) onto activated carbon with and without CIP was obtained in the same way as the effect of pH on adsorption of CIP with and without Ni(II). The suspension pH was adjusted from 2.6 to 7.4. The Ni(II) concentration was 20 mg/L, and the CIP concentration was 0 or 400 mg/L.

Adsorption isotherms of Ni(II) on activated carbon were carried out in the same way as the adsorption isotherms of Ni(II) as affected by CIP. The initial Ni(II) concentrations of the solutions were in the range of 20–100 mg/L. The initial solution pH was adjusted to 6.0 by using concentrated HCl or NaOH.

The control test without AC was also carried out and the results suggested that there was no precipitate such as $Ni(OH)_2$ formed in the adsorption progress.

2.6. Analyses

To observe the changes of the position and the intensity of the maximum absorption wavelength, the absorbance of CIP and CIP with Ni(II) solutions at wavelength of 200–700 nm was determined by an UV–visible spectrophotometer (UV2450, SHIMADZU). The results are shown in Fig. S1. As can be seen, the maximum absorption wavelength of CIP was 275 nm, which was consistent with previous studies [12,15]. With the addition of Ni(II), the maximum absorption wavelength still maintained at 275 nm. Thus, the detector wavelength was set at 275 nm. However, the addition of Ni(II) slightly increased the absorbance at maximum absorption wavelength, which was attributed to the formation of complex of CIP–Ni(II). The solution before and after adsorption was recorded to determined the removal rate and adsorption capacity. All adsorption data were collected in triplicate.

The concentration of CIP was analyzed by a UV-754 UV/visible spectrophotometer at the maximum absorption wavelength of 275 nm and Ni(II) by atomic absorption spectrophotometer (Beijing Purkinje General Instrument Co., China).

3. Results and discussion

3.1. Activated carbon characterization

The results of pore structure analysis are present in Table S1. The pore structure of AC was well developed with BET surface area