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Removal of humic acid from aqueous solution by amino-functionalized degreasing cotton

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ABSTRACT

Amino-functionalized degreasing cotton (ADC) was prepared by surface modification and was used as an adsorbent to remove humic acid (HA) from aqueous solutions. The prepared ADC was characterized by scanning electron microscopy and Fourier transform infrared spectroscope. The effect of various parameters such as initial pH, contact time and initial HA concentration was investigated. The studies of adsorption kinetics indicated that the adsorption follows a pseudo-second-order kinetic model. The adsorption isotherm analysis data confirm that experimental data fitted well into both the Langmuir and the Freundlich models. Moreover, the assessment of the reusability of the ADC was tested for five successive cycles revealed no significant decrease of the adsorption capacity.

Keywords: Amino-functionalized; Degreasing cotton; Humic acid; Adsorption

1. Introduction

Humic substances, one of the major components of natural organic matter, are mainly composed of humic acid (HA), fulvic acid and humin, and exist in soil, water and geological organic deposits [1–3]. HA is composed of aliphatic or aromatic organic macromolecules with high content of unsaturated conjugated functional groups, such as double bonds, aromatic rings and oxygen-containing groups including carboxyl, hydroxyl and carbonyl [4]. This leads to the result that the presence of large amounts of HA in natural waters can cause a yellowish to brown colour, and also cause various environmental and health problems. For example, HA can bind with heavy metal ions and other organic substances, facilitating their transportation in the water systems [5], and chlorine used during water purification reacts with HA to form carcinogenic material [6]. Therefore, it is essential to remove HA from drinking water and other process waters.

Various methods, including advanced oxidation [7], membrane separation [8], coagulation [9] and adsorption [10], have been extensively investigated in the treatment of HA from water. Among these existing methods, adsorption technology is one of the most applied methods for the removal of HA from aqueous solutions due to its simplicity, high efficiency, ease in the operation and lack of side effects or secondary pollution [11]. Many adsorbents have been reported in previous literatures, including chitosan [12], zeolite [13], calcium phosphate [14], activated carbon [15] and resin [16]. However, due to the macromolecular feature of humic acid, conventional porous adsorbents, such as resins and activated carbon are generally known not to

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be very effective in adsorbing HA as most of the pores are not usually available for the adsorption of HA [17]. Hence, nonporous adsorbents with larger specific surface areas are of interest for HA removal. Compared with previously reported adsorbents, fibers, including cotton fibers and other artificial polymer fibers, usually possess large external surface area owing to their small diameters. Many kinds of fibers have been studied as adsorbents for the removal of heavy metal ions or other contaminants from aqueous solutions in recent years [18–20].

Degreasing cotton has a better hydrophilic property, large external surface area and flexibility. In addition, there are a lot of hydroxyl groups on the surface of degreasing cotton, which makes it easy to be ammoniated. As an adsorbent, degreasing cotton is environmental and economical; it also can be separated easily from the aqueous solution, which promotes recyclability and reusability. In this study, the degreasing cotton was first reacted with epichlorohydrin by using the modifying agents of diethylenetriamine in the presence of the organic medium of N,N-dimethylformamide. Then, the amino-functionalized degreasing cotton (ADC) was used to investigate the adsorption property to HA. Moreover, the prepared ADC was involved in a batch experiments to evaluate the effects of initial pH, contact time and recyclability as well as the adsorption isotherm models and kinetics.

2. Experiment

2.1. Materials

Humic acid was obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Epichlorohydrin, N,N-dimethylformamide (DMF) and diethylenetriamine (DETA) were purchased from Sinopharm Chemical Reagent Corp. (Shanghai, China). Degreasing cotton was provided by Xuzhou Weicai Hygiene of Material Factory Co. Ltd. (Xuzhou, China).

2.2. Preparation of ADC

ADC was prepared via in situ polymerization [21,22]. The ADC was prepared in a 250 mL beaker with 10 mL of N,N-dimethylformamide and 10 mL epichlorohydrin. A 0.2 g of degreasing cotton was added into the solution with stirring, and the reaction in the beaker was allowed to proceed at 85°C for 1.5 h. After that, 1 mL of diethylenetriamine was added into the above solution drop by drop and stirred for 1 h. Then, the sample was immersed in ethyl alcohol for 30 min without stirring, followed by thorough rinsing with distilled water and drying at 60°C for 5 h. The surface modification mechanism of degreasing cotton has been shown in Fig. 1.

2.3. Characterization

The morphology of the degreasing cotton and ADC can be observed from scanning electron microscopy (SEM) using a JSM-IT300A scanning electron microscope (JEOL Ltd., Tokyo, Japan). Infrared spectroscopy spectra measurement was taken using Fourier transform infrared spectrometer (FTIR, VERTEX 70, Bruker, Germany) in the wave number range of 450~4,000 cm^{-1}. A Zatasizer Nano ZS (ZEN 3600) was used to determine the zeta potentials of the ADC, HA and ADC adsorbed with HA.

2.4. Adsorption experiments

Batch adsorption experiments were conducted at various solution pH values, contact time, initial adsorbate concentrations. The pH of the HA solution was adjusted to the required pH value by adding either 0.1 mol/L HCl or 0.1 mol/L NaOH solution. Adsorption experiments were conducted at room temperature in a 250 mL beaker, equilibrated with a magnetic stirrer. 0.1 g of the prepared ADC was added to 100 mL of a 100 mg/L HA solution for 120 min. Taking into account the many functional groups in HA, one may expect that various interactions took place in adsorption between the carboxylic or phenolic groups of HA and the amine groups of the ADC to form surface complexes [23]. The residual concentration of HA solutions was determined by a UV-2700 UV-visible spectrophotometer at 254 nm. The adsorption capacity Q (mg/g) of HA was calculated using the following equation:

$$Q = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where C_0 is the initial concentration of HA solution (mg/L), C_e is the HA concentration of the supernatant (mg/L), V (mL) is the volume of HA solution, and m (mg) is the mass of the absorbent.

3. Results and discussion

3.1. Characterization of the samples

Fig. 2 shows the SEM surface images of degreasing cotton, ADC and HA-adsorbed ADC. Fig. 2a illustrates that the surface morphology of degreasing cotton was smooth with a diameter of about 10 um. As shown in Fig. 2b, the diameter of the ADC was greater than that of the degreasing cotton, due to the expansion of the cottons during the surface modification reaction. Besides, the ADC appeared much rougher, indicating that the organic monomers were grafted on the surface of the cellulosic backbone. After HA adsorption, it can be seen that a layer of HA was adsorbed on the surface of the ADC (Fig. 2c).

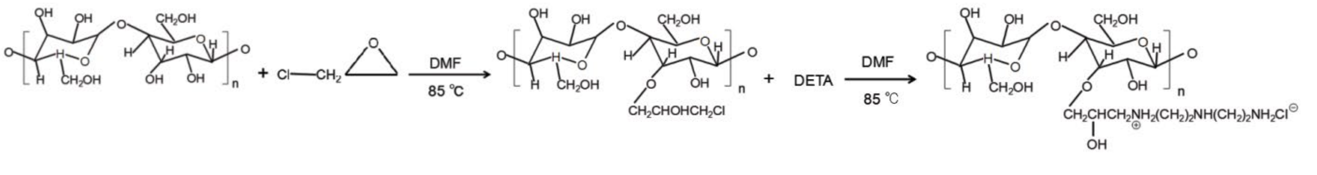

Fig. 1. Proposed surface modification mechanism of degreasing cotton.

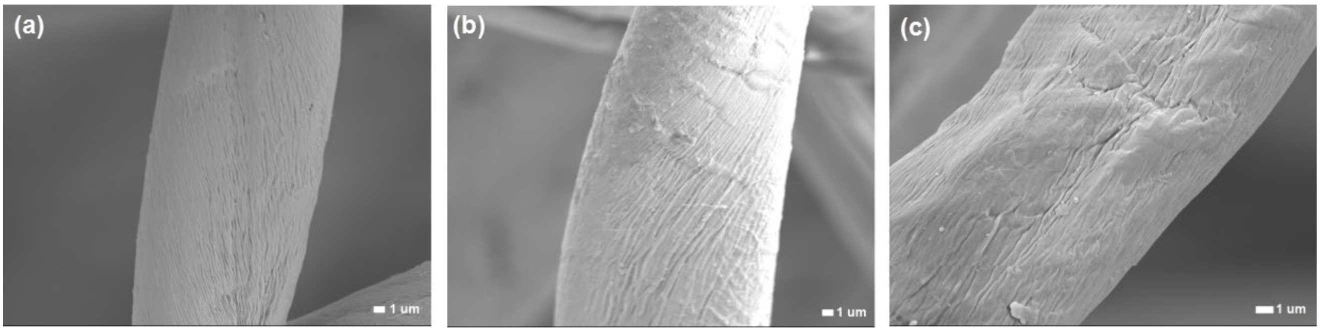

Fig. 2. SEM images of the degreasing cotton (a), ADC (b) and HA-adsorbed ADC (c).

The FTIR spectra of degreasing cotton and ADC are shown in Fig. 3. The spectrum displayed in Fig. 3a shows the characteristic peaks of degreasing cotton, the peak at 3,334 cm^{-1} denotes the stretching vibration of hydrogen bond O–H; the bands at 1,427 and 1,303 cm^{-1} were assigned to CH_2 bending and CH bending, respectively; the peaks of 1,159 and 1,028 cm^{-1} were related to antisymmetric stretching vibrations of the C–O–C bridge and skeletal vibrations involving C–O stretching, respectively [24]. In the ADC spectra displayed in Fig. 3b, the appearance of the characteristic peak at 3,410 cm^{-1} confirmed the insertion of amine groups into the degreasing cotton, and a strong broad band ranging from 3,045 to 3,643 cm^{-1} usually corresponds to the overlapping stretching vibration between $-NH_2$ and –OH, indicating that there are many OH and NH groups on the surface of the degreasing cotton.

The zeta potentials of the ADC, HA and ADC adsorbed with HA as a function of the solution pH values are shown in Fig. 4. The zeta potentials of HA are positive below pH 1.5 and negative above pH 1.5. The negative zeta potentials of HA may due to the deprotonation of carboxylic and phenolic groups in the HA. However, the zero point of zeta potential at pH 1.5 is very closer to the pK_a value of 3 for the carboxylic group but far away from the pK_a value of 9 for the phenolic groups, which suggest that the zeta potentials of HA are dependent upon the carboxylic groups in the macromolecules to a large extent [25]. The ADC has positive zeta potentials below pH 7.2 and negative zeta potentials above pH 7.2, the positive zeta potentials of ADC may be attributed to the protonation of the amino groups. After adsorption equilibrium of HA, the zeta potentials of ADC become lower at all pH values investigated. The zeta potentials are negative at pH above 2.6, indicating the dominance of HA on the surface of the ADC. The significant changes of zeta potentials of the ADC from positive to negative at different pH values before and after HA adsorption suggest that the electrostatic charge interactions play an important role in the adsorption of HA.

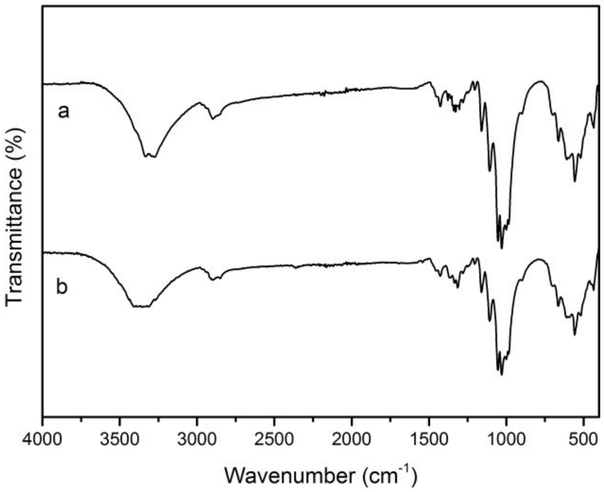

Fig. 3. FTIR spectra of degreasing cotton and ADC.

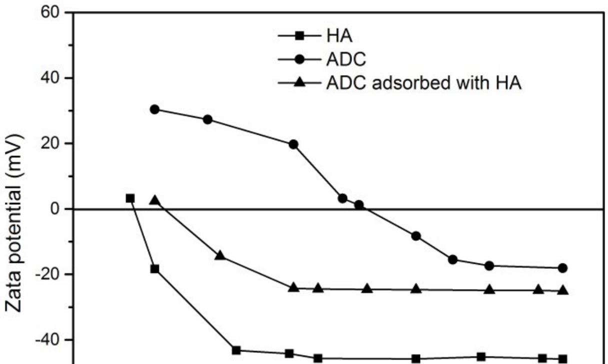

Fig. 4. Zeta potentials of the ADC, HA and ADC adsorbed with HA as a function of the solution pH values.

3.2. Adsorption studies

3.2.1. Effect of the solution pH

Since many adsorbents have pH-dependent adsorption performance, the effect of solution pH on the adsorption of HA on ADC was investigated in the pH range 2–12. As shown in Fig. 5, a decrease in solution pH from 7 to 2 caused a remarkable increase in the HA adsorption capacity for ADC from 6.24 to 36.68 mg/g, while at pH from 7 to 12, the adsorption capacity of HA is obviously low, which indicate that the adsorption can be greatly enhanced in an acidic environment. According to this phenomenon and

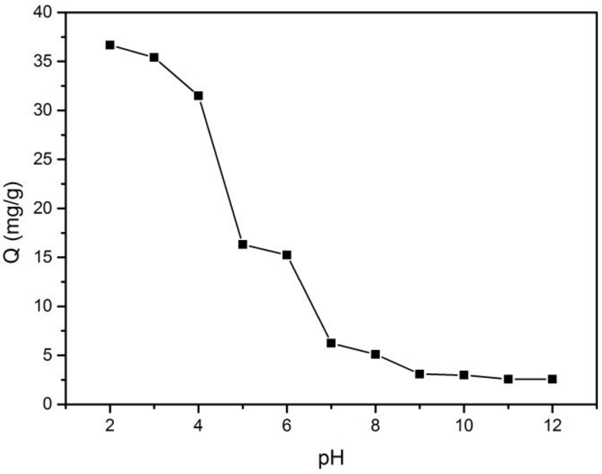

Fig. 5. Effect of solution pH on HA adsorption onto ADC (amount of sorbent 100 mg, at a concentration of 100 mg/L, stirring time of 120 min, at a temperature of 20°C).

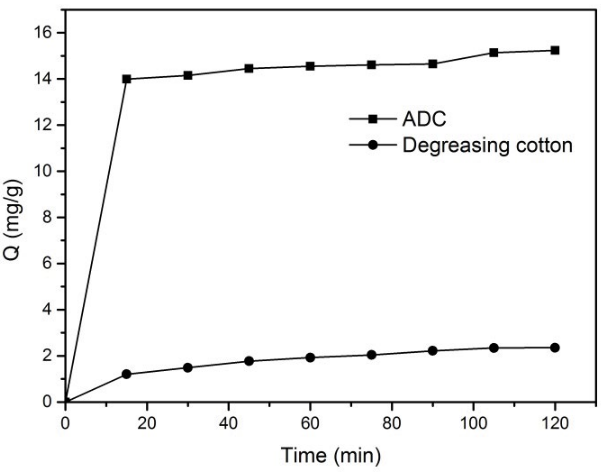

Fig. 6. Effect of contact time on the HA adsorption capacity of degreasing cotton and ADC (amount of each sorbents 100 mg, at a concentration of 100 mg/L, stirring time of 120 min, at a temperature of 20°C, pH = 6).

the analysis of zeta potentials of the ADC, HA and ADC adsorbed with HA, it can be seen that the electrostatic interactions played a very important role in HA adsorption on the ADC because the electrostatic interactions between the ADC and the HA were attractive for pH less than 7.2 but greater than 1.5. In addition, it has been suggested that HA may exist in a spherical structure at lower pH value but may exist in a rather linear or stretched structure at higher pH value [26,27]. This result can lead to less amount of HA adsorbed in the adsorbent at higher pH value.

3.2.2. Adsorption kinetics

In order to determine the HA adsorption properties of degreasing cotton and ADC, adsorption experiments were determined using an initial concentration of 100 mg/L and the results are shown in Fig. 6. It can be found that the degreasing cotton can barely adsorb HA, however, after the surface modification, the adsorption capacity of the ADC has been significantly increased. The adsorption of HA to ADC occurred very fast at the beginning and then achieved equilibrium at about 15 min. The main reason is that the ADC had high density of active adsorption sites on the surface at first, with time, the adsorption process of HA to the surface of the ADC may become attachment-limited due to these active adsorption sites became gradually saturated.

To describe the kinetic mechanism of the adsorption process and potential rate controlling steps such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order models were adopted to analyze the kinetic data using the following equation:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \quad (3)$$

where k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order rate constant and pseudo-second-order rate constant, respectively; q_e (mg/g) is the adsorbed amounts of HA at equilibrium time; and q_t (mg/g) is the amount of HA adsorbed at time t (min).

The pseudo-first-order model and the pseudo-second-order model fitting curves for the ADC are shown in Fig. 7. Comparing the values of R^2 of both models shows that the adsorption mechanism is a better fit to the pseudo-second-order kinetic model, because the R^2 of pseudo-second-order kinetic model is very close to 1. Moreover, the calculated q_e value estimated from the pseudo-second-order model agreed with the experimental value better, suggesting that the adsorption of HA onto the ADC follows a pseudo-second-order reaction model. This indicated that the adsorption process was probably dominated by a chemical adsorption phenomenon which involved valency forces through sharing or exchange of electrons between the adsorbent and the adsorbate [28].

3.2.3. Adsorption isotherm

The adsorption isotherm of HA on ADC at 20°C is displayed in Fig. 8. It was shown that the HA adsorption capacity for ADC increased with increasing the HA equilibrium concentration.

To further investigate the adsorption process, Langmuir and Freundlich models were applied to evaluate the equilibrium adsorption data of ADC, the two equations are expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

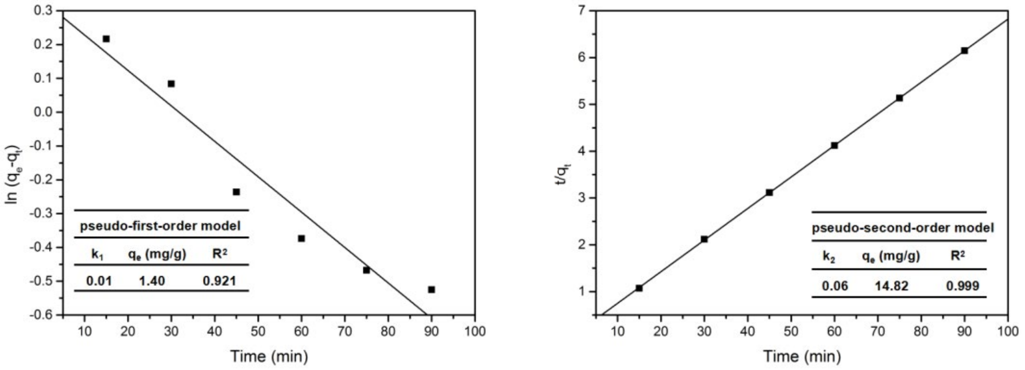

Fig. 7. Pseudo-first-order and pseudo-second-order kinetics for the adsorption of HA onto ADC.

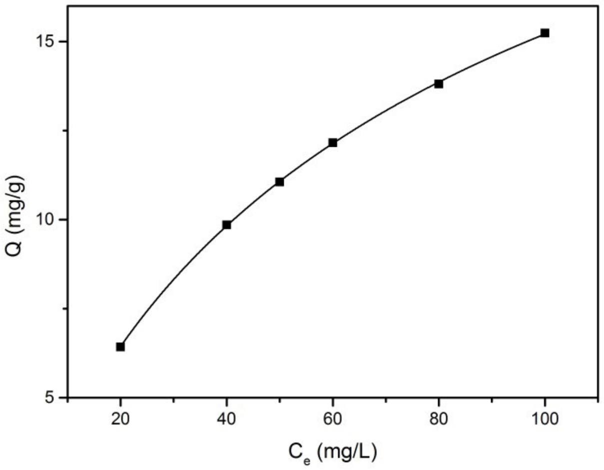

Fig. 8. Adsorption isotherm of HA on the ADC (amount of sorbent 100 mg, stirring time of 120 min, at a temperature of 20°C, pH = 6).

where q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the equilibrium concentration. $q_{\max}$ (mg/g) is the maximum adsorption capacity, and K_L (L/mg) is the Langmuir constant, K_F ((mg/g)/(L/mg))$^{1/n}$ and $1/n$ are the Freundlich constants.

Fig. 9 shows the fitting plots of Langmuir and Freundlich isotherms of HA on ADC. It can be seen that HA adsorption on the ADC can be well described by both the Langmuir and the Freundlich models, and the maximum adsorption capacities of the ADC with the Langmuir model was calculated to be 23.23 mg/g. It is generally known that Langmuir model tends to describe monolayer adsorption and Freundlich model is usually applied to multi-molecular adsorption processes on uneven surface. However, in view of the high negative zeta potentials possessed by HA molecules at pH > 1.5, the adsorption isotherm was probably dominated by a monolayer adsorption process than by a multilayer adsorption one, due to the large electrostatic repulsion between the adsorbed molecules and the molecules to be adsorbed [22].

3.2.4. Regeneration studies of ADC

In order to evaluate the reusability and stability of ADC for the removal HA, regeneration experiments were further conducted. During the regeneration process, the used ADC was desorbed in a 0.1 M NaOH solution for 1 h, and then washed with 0.1 M HCl solution for 1 min, and finally with distilled water for several times. The results were shown in Fig. 10. It can be found that after five adsorption–desorption cycles, the adsorption capacity of ADC was slightly decreased, however, it still remained above 85% of its original capacity, indicating that the ADC has great potential applications for the removal of HA in water treatment.

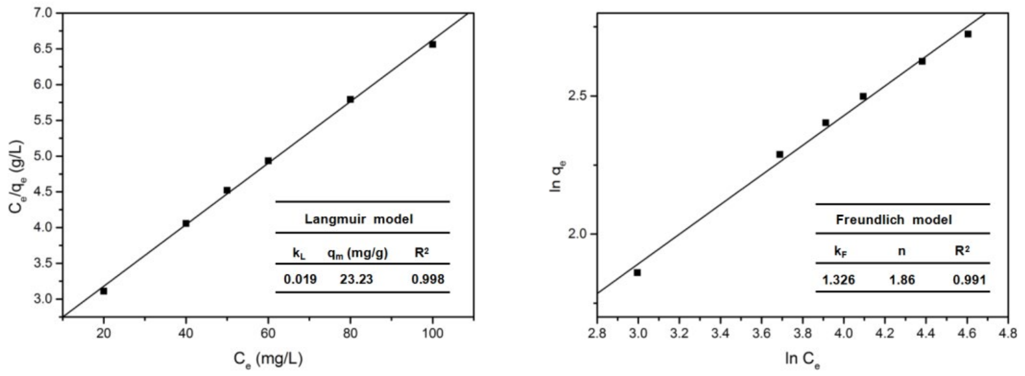

Fig. 9. Curve fitting with the Langmuir and Freundlich model.

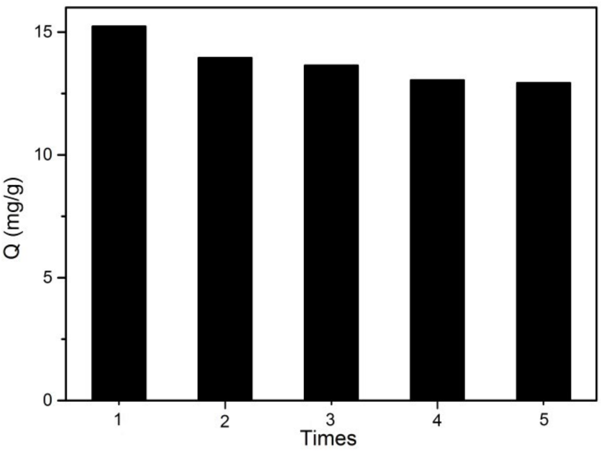

Fig. 10. Five cycles of HA removal efficiency (amount of sorbent 100 mg, stirring time of 120 min, at a temperature of 20°C, pH = 6).

4. Conclusions

In the present study, ADC was synthesized and used to remove HA from aqueous solution. Adsorption of HA onto ADC was pH dependent and significant amounts of HA could be adsorbed under acidic conditions. The higher adsorption capacities at low pH may attribute to the electrostatic interactions between HA and positive surface charge of the sorbent. The kinetic studies demonstrated that the adsorption process follows a kinetic pseudo-second-order kinetic model. Adsorption isotherm studies showed that both the Langmuir and the Freundlich models fitted well with the adsorption equilibrium data. The ADC with adsorbed HA can be regenerated in an NaOH solution and the regenerated ADC can be used five times without significant decrease in its adsorption capacity. These findings indicate that ADC is a promising adsorbent for the removal of HA from aqueous solution.

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