



# Effect of the chemical structure of anion exchange resin on the adsorption of humic acid: Behavior and mechanism



Chendong Shuang, Jun Wang, Haibo Li, Aimin Li, Qing Zhou \*

State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Nanjing 210023, PR China

## ARTICLE INFO

### Article history:

Received 2 April 2014

Accepted 7 September 2014

Available online 16 September 2014

### Keywords:

Anion-exchange resin

Humic acid

Adsorption

Polystyrenic resin

Polyacrylic resin

## ABSTRACT

Polystyrenic (PS) anion-exchange resin and polyacrylic (PA) anion-exchange resin were used to investigate the effect of resin chemical structure on the adsorption of humic acid (HA). Due to the rearrangement of HA to form layers that function as barricades to further HA diffusion, PS resin exhibited 12.4 times slower kinetics for the initial adsorption rate and 8.4 times for the diffusion constant in comparison to that of the PA resin. An HA layer and a spherical cluster of HA can be observed on the surface of the PS and PA resins after adsorption, respectively. The considerable difference in HA adsorption between the PS and PA resins was due to the difference in molecule shape for interaction with different resin structures, which can essentially be explained by the hydrophobicity and various interactions of the PS resin. A given amount of HA occupies more positively charged sites and hydrophobic sites on the PS resin than were occupied by the same amount of HA on the PA resin. Increased pH resulted in an increase of HA adsorption onto the PA resin but a decrease in adsorption onto PS resin, as the non-electrostatic adsorption led to electrostatic repulsion between the HA attached to the resin and the HA dissolved in solution. These results suggest higher rates of adsorption and higher regeneration efficiency for interaction of HA with more hydrophilic anion exchange materials.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

Anion-exchange resin (AER) has been widely used in water purification for the removal of many anionic pollutants, such as reactive dyes, natural organic matter, perfluorooctane sulfonate, bromide, chromium, and arsenic [1–6]. AERs with higher surface areas and/or more functional groups can offer more active sites for interactions, and the macropores or high water content of some resins can provide open channels for the diffusion of larger molecules, alleviating the size exclusion effect often observed in adsorption. Thus, several studies have suggested that AERs with high surface area, large exchange capacity, high water content, and porous structures are ideal for adsorption [7–9].

Commercial AERs are typically classified into two categories according to their chemical structure: those with a polystyrenic (PS) matrix and those with a polyacrylic (PA) matrix. PS-AERs have a strong affinity for anionic organics with hydrophobic groups because of their hydrophobic interaction [10,11]. By contrast, PA-AERs exhibit a greater capacity for natural organic matter, perfluorooctane sulfonate (PFOS), and chromium than the PS-AERs

[13,12–14]. Furthermore, PA-AERs are more resistant to fouling with higher regeneration efficiency because of their hydrophilic structure [14,15]. Thus, the chemical structure of the resin matrix also has significant effects on the adsorption performance, in addition to the above-mentioned factors. The hydrophilicity of the PS-AERs can be modified by functional moieties. The adsorption capacities of polar organics on the PS-AERs can be significantly increased by the introduction of polar moieties as a result of multiple interactions between the modified PS resin and the adsorbate [16–19]. In our previous study of the PA-AERs for the adsorption of humic acid (HA), the improvement in hydrophilicity due to the effect of incorporated  $\text{Fe}_3\text{O}_4$  greatly enhanced both the adsorption and regeneration performances [20].

Although the sorption behaviors of PS-AER and PA-AER exhibit significant differences, the differences of behavior and mechanism are not well understood, greatly limiting the selection, optimization, and preparation of the anion-exchange resin for dissolved organic matter (DOM) removal in water purification, as a large portion of DOM components are complex, with both hydrophilic and hydrophobic properties, such as humic acid (HA). HA is a significant portion of the DOM derived from the degradation of biomass, and causes environmental problems, including its undesirable color and the production of disinfection byproducts. Given that the HA molecule contains carboxylic and phenolic groups

\* Corresponding author. Fax: +86 25 89680377.

E-mail address: zhouqing@nju.edu.cn (Q. Zhou).

connected with aliphatic and aromatic carbons, it generally displays flexible and amphiphilic properties. HA can be adsorbed onto many materials through electrostatic attraction, hydrophobic interactions, hydrogen bonding and/or ligand exchange [21,22]. AER is an effective adsorbent for the negatively charged HA molecule; thus, it is necessary to understand the effect of the resin structure on its adsorption. In this work, a commercial HA produced by the decomposition of dead plants was chosen as the model adsorbate for investigation of the differences in the behavior and mechanism of adsorption on the PS-AER and the PAAER.

## 2. Experimental

### 2.1. Chemicals

PS-AER (201) and PA-AER (213) in chloride form were provided by the Jiangsu Jinkai Resin Chemical Co., Ltd., Yancheng, Jiangsu, China. All inorganic chemicals of analytical grade were purchased from Sinopharm Chemical Reagent Company, China. HA, produced via the decomposition of dead plants by Alfa Aesar Company, was purchased from J&K Chemical, Ltd. HA was dissolved in aqueous solution for 24 h with vigorous stirring, and then filtrated through a cellulose acetate membrane with a pore diameter of 0.45  $\mu\text{m}$ .

### 2.2. Characterization

Basic information about the AERs, including the structure, functional group, type, moisture, and ion exchange capacity, were provided by the manufacturer (Jiangsu Jinkai Resin Chemical Co. Ltd., China). The BET surface area and pore diameter of AERs were determined using an automatic analyzer (Micromeritics ASAP-2010C, USA) with  $\text{N}_2$  as the adsorbate. Zeta potential analysis (Malvern Nano-ZS90, UK) was used to characterize the surface charge of both the AERs and the HA. The morphology of the AER bead surface was imaged using scanning electron microscopy (SEM, S-3400N II, Hitachi, Japan). The samples were dried under vacuum at 323 K for 8 h before the above-mentioned characterization. The HA concentration was indicated via the total organic matter (TOC) content, measured by a TOC analyzer (OIA1088, USA). The pH values were tested with a pH meter (Sanxin MP551, China).

### 2.3. Adsorption

Both PS and PA anion-exchange resins were used in the adsorption study. For the adsorption kinetics, two 500 mL flasks with 200 mL of 200 mg/L HA aqueous solution were shaken with 0.100 g resin at 293 K under constant stirring at 150 rpm. The HA concentration in the solutions following different adsorption times was measured. Isotherms at three different temperatures (278, 293, and 308 K) were collected for different initial concentrations of HA at 130 rpm for 50 h. To investigate the effect of pH on adsorption, 50 mL of 50 mg/L HA solution and 0.100 g resin were shaken in a series of 100 mL conical flasks at pH 2–10 for 50 h. 1 M HCl and 1 M NaOH were used to adjust the pH. The degree of adsorption of HA ( $q_t$ , in mg/g) was calculated using the following equation:

$$q_t = V(C_0 - C_t)/W \quad (1)$$

where  $V$  (L) and  $W$  (g) are the volume of the solution and the weight of the resin, respectively;  $C_0$  (mg/L) and  $C_t$  (mg/L) are the initial concentration and concentration at time  $t$  (min), respectively;  $q_t$  and  $C_t$  can be replaced by  $q_e$  and  $C_e$  to represent the adsorption capacity and HA concentration at adsorption equilibrium, respectively.

### 2.4. Regeneration

A series of parallel adsorption experiments was carried out at 293 K with 50 mL of 50 mg/L HA solution and 0.100 g resin with shaking for 50 h. The resin beads were then filtrated and collected for regeneration. 10 mL of aqueous NaCl (10%, w/w) with different amounts of NaOH (1%, w/w) was used for regeneration at 293 K under shaking for 5 h. Regeneration efficiency (RE, %) was calculated by the following Eq. (2), where  $V_d$  (L) is the volume of the desorption solution and  $C$  is the HA concentration of the desorption solution after regeneration.

$$\text{RE} (\%) = V_d \cdot C / (W \cdot q_e) \quad (2)$$

All adsorption and regeneration experiments were repeated three times, the first of which is in duplicate. The average values were used with an error smaller than 5%.

## 3. Results and discussion

### 3.1. Properties

The essential physicochemical properties of the employed AERs are listed in Table 1. The exchange capacity, moisture, porosity, and surface area of the two AERs are similar, with the greatest difference between these two AERs being the structure of the polymeric matrix. The similar amounts of quaternary ammonium groups suggest no apparent difference between the resins with regards to zeta potential (Fig. 1), which is also apparently uninfluenced by the variation of pH from 2 to 10. For the adsorbate, HA, the ionization of molecular carboxyl, or/and phenolic hydroxyl groups results in its electrostatic negativity, allowing for its easy adsorption onto AERs via electrostatic attraction [23]. The surface charge of HA becomes more negative as the pH increases from 2 to 8 because of the increased ionization of the carboxyl groups. However, the surface charge became less negative when the pH increased beyond 8, which can be explained by the corresponding change in the HA molecule. At pH > 8.0, both the carboxylic and phenolic hydroxyl groups can be ionized to a great extent. These ionized groups increase the electrostatic repulsion, which may lead to the disaggregation of the HA molecule, reducing the size of the agglomerate. As we reported previously, ionized carboxylic groups contribute the majority of the surface charge of the HA molecule [24], while the carboxylic groups are generally only ionized at pH values higher than 8.0. Therefore, the surface charge of the HA molecule decreases with pH increasing beyond 9.0, as the carboxylic groups distributed among the HA molecules become accessible upon HA disaggregation. This interpretation is typically used to explain the dependence of HA molecule size on pH [25,26].

### 3.2. Adsorption kinetics

Fig. 2 shows the HA adsorption kinetics for both resins. The amount of adsorbed HA increases quickly with time at the initial stage, and then gradually reaches equilibriums. Obviously, the PA resin displays greater adsorption than does the PS resin. To further analyze the adsorption kinetics, the pseudo-first-order equation and pseudo-second-order equation were applied in modeling of the HA adsorption onto the adsorbents. The models are expressed as follows.

$$\text{Pseudo-first-order equation: } Q_t = Q_e(1 - \exp(-k_1t)) \quad (3)$$

$$\text{Pseudo-second-order equation: } Q_t = (k_2tQ_e^2)/(1 + k_2tQ_e) \quad (4)$$

$$h_0 = k_2Q_e^2 \quad (5)$$

Download English Version:

<https://daneshyari.com/en/article/6997669>

Download Persian Version:

<https://daneshyari.com/article/6997669>

[Daneshyari.com](https://daneshyari.com)