Efficient capture of aqueous humic acid using a functionalized stereoscopic porous activated carbon based on poly(acrylic acid)/food-waste hydrogel

Tao Zhou, Xin Zhao, Shuya Wu, Lianghu Su, Youcai Zhao

1. The State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
2. Shanghai Chengpei Enterprise Management Consulting Co., Ltd., Shanghai 200000, China
3. Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, Nanjing 210042, China
4. Shanghai Institute of Pollution Control and Ecological Security, 1515 North Zhongshan Rd. (No. 2), Shanghai 200092, China

Article history:
Received 8 February 2018
Revised 21 June 2018
Accepted 22 June 2018
Available online 30 June 2018

Keywords:
Stereoscopic porous activated carbon
Humic acid
Food waste
3-aminopropyltriethoxysilane
Adsorption

ABSTRACT
Stereoscopic porous carbons have shown good potential in humic acid (HA) removal. In this work, a novel stereoscopic porous activated carbon (SPAC) was designed and synthesized via the self-assembly of a hydrogel based on food waste during in-situ polymerization, vacuum drying, carbonization, and activation. Then, the SPAC was functionalized with 3-aminopropyltriethoxysilane (APTES) and the adsorption behavior of the modified SPAC (SPAC-NH₂) was studied systematically. The effects of pH, contact time, initial concentration of HA, and adsorbent dose were investigated, showing that optimal HA removal efficiency (>98.0%) could be achieved at an initial HA concentration of 100 mg/L. The experimental adsorption isotherm data was fitted to the Langmuir model with a maximum adsorption capacity of 156.0 mg HA/g SPAC-NH₂. Analysis of the mechanism indicated that the removal of HA was mainly realized through the amidization reaction between the COOH groups of HA and the NH₂ groups of APTES. All of the above results showed that SPAC-NH₂ powder is an efficient, eco-friendly, and reusable adsorbent which is suitable for the removal of HA from wastewater.

© 2018 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Humic acids (HA) are the major components of humic substances, which result from the microbial degradation of biomolecules (Imyim and Prapalimrungsi, 2010). The high affinity of humic substances for complexation with various pollutants (An et al., 2016), such as heavy metals and pesticides, causes the contamination of ground and surface water (Chai et al., 2013; Zhao et al., 2017). Humic substances, mainly containing HA, fulvic acid, and humin (Renou et al., 2008), are typical naturally forming compounds that account for 30-80% of the dissolved organic matters in natural water (Imai et al., 2002). The presence of HA in water is not directly toxic, but it affects the appearance and taste of water, and is very harmful in water treatment processes (Baek et al., 2013).

Many physicochemical and biological methods, such as adsorption, precipitation, ion exchange, and membrane processes (Baek et al., 2013; Lebeau et al., 1998; Wu et al., 2014, 2016; Yan and Bai, 2005; Zhao et al., 2008) have been developed for the removal of HA. Among these techniques, the adsorption process is considered to be effective and economical owing to its high selectivity, radiation stability, and good compatibility.
1. Materials and methods

1.1. Materials

We collected FW from a student canteen of Tongji University, and its pretreatment is described in the Appendix A. Acrylic acid (AA, chemically pure), nitric acid (HNO₃, analytical grade), potassium hydroxide (KOH, analytical grade), potassium persulfate (KPS, analytical grade), N,N’-Methylenebisacrylamide (MBA, chemically pure), (3-aminopropyl)triethoxysilane (APTES, chemically pure), HA (total acidic group content = 9–10 meq/g), and ethanol were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China), and were used without further purification.

1.2. Preparation of poly(acrylic acid)/food-waste hydrogel

Details of the preparation of poly(acrylic acid)/FW hydrogel via cross-linking methods are given in Appendix A Fig. S1.

1.3. Synthesis of SPAC-NH₂

To prepare SPAC, poly(acrylic acid)/food-waste hydrogel particles were chosen as the precursor, and were carbonized in a horizontal tube furnace (Hefei Kejing Materials Technology Co., Ltd., China). Firstly, the poly(acrylic acid)/FW hydrogel particles were heated from room temperature to 400 °C with a heating rate of 10 °C/min, and kept under nitrogen atmosphere for 120 min; the samples were cooled inside the tube furnace in the presence of nitrogen flow. Secondly, the samples were mixed with an equivalent quantity of KOH in a mortar; the mixtures were then heated from room temperature to 600 °C with a heating rate of 10 °C/min, and kept under nitrogen atmosphere for 120 min. Finally, the product was cooled inside the tube furnace in the presence of nitrogen flow, and the porous activated carbon was obtained. Deionized water was used to wash the porous activated carbon until the pH was about 7.0.

The SPAC-NH₂ was prepared as follows. 2.0 g of dried activated carbon was dispersed in 40 mL of acetone in a 50-mL beaker, followed by ultrasonication to disperse the mixture adequately; 10.0 mL of APTES was then added to the above suspension. After that, the beaker was stirred by a magnetic stirrer (HJC-4D, Changzhou Longyue Instrument Manufacturing Co., Ltd., China) for 24 hr at room temperature. Finally, the prepared products were washed with ethanol and dried in an oven, pulverized to pass through a 150-mm mesh sieve, and sealed for future use. A schematic illustration of the synthesis procedure of the SPAC-NH₂ is presented in Appendix A Fig. S2.

1.4. Characterization of samples

The morphologies and microstructures of the samples were characterized using a scanning electron microscopy/energy-dispersive X-ray spectroscopy and mapping system (SEM-EDS, Inspect F, FEI Co., USA). The crystallinity of the SPAC-NH₂ samples was measured using X-ray diffraction (XRD, D8 Advance Sol-X, Bruker Co., USA) with CuKα radiation (1.5418 Å) at 40 kV and 40 mA, and the patterns were recorded in the 2 theta region from 5° to 70°. FT-IR-Nicolet 5700 FT-IR Spectrometer was used for qualitative analysis of the chemical bonds between the functional groups of raw materials and SPAC-NH₂ with a scan range of 500–4000 cm⁻¹ at a resolution of 4 cm⁻¹. The surface area of the samples was determined by N₂ vapor adsorption studies at 77 K using a microporosity system (Micromeritics ASAP 2460). XPS characterization (Kratos AXIS 165) was performed using monochromatic AlKα radiation at a power of 100 W, with high-resolution spectra recorded for the C 1s, O 1s, and N 1s regions. The zeta potential was determined by Zetasizer Nano ZS 90 (Malvern Pananalitical, Britain). Raman spectra were recorded with a Renishaw InVia-reflex confocal laser micro-Raman spectrometer using a 514-nm laser diode for excitation.
1.5. Humic acid adsorption experiments

1.5.1. Batch adsorption experiments

HA solutions were prepared as described by Kim (2015). Briefly, the HA stock solution was prepared by dissolving 1.0 g of HA in 1.0 L of 0.1 mol/L aqueous NaOH, and then it was further diluted with distilled water to the desired concentrations.

Batch-adsorption experiments were performed to determine the adsorption capacity of SPAC-NH2 for HA under different conditions. These experiments were conducted with stirring (150 r/min) at a temperature of 30 °C for a predetermined time. The temperature was maintained using a DNP Series Electric Thermostatic Incubator (DNP-9162, Suzhou Weier Laboratory Supplies Co., Ltd., China). The operational parameters were determined in triplicate.

After adsorption, the concentration of the residual HA in the supernatants was analyzed by UV/vis spectrophotometry (TU-1810, Beijing Purkinje General Instrument Co., Ltd., Beijing, China), and the HA removal efficiency and removal capacity (Qe, mg/g) were calculated, as given in Eqs. (1) and (2), respectively.

\[
\text{HA removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}
\]

\[
Q_t = \frac{(C_0 - C_t)V}{m} \tag{2}
\]

where \(C_0\) (mg/L) and \(C_t\) (mg/L) are equilibrium HA concentrations in aqueous solutions before and after adsorption, respectively. \(V\) (L) is the volume of the aqueous, and \(m\) (g) is the flocculant dosage.

1.5.2. Adsorption isotherm experiment

The adsorption equilibrium experiment for SPAC-NH2 was carried out at 30 °C and pH 6.0. The initial concentration of HA varied from 20 to 500 mg/L. The adsorption isotherm experimental data were fitted by Langmuir and Freundlich models. The Langmuir equation can be expressed as follows:

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_l Q_m} \tag{3}
\]

where \(Q_m\) (mg/g) is the amount of HA adsorbed at equilibrium, \(C_e\) (mg/L) is the residual concentration of HA in solution at equilibrium, \(K_l\) (L/mg) is the maximum adsorption capacity when an adsorbent is fully covered, and \(n\) is a constant related to the affinity of the binding sites.

The Freundlich model is an empirical equation that can be used to describe multilayer adsorption on a heterogeneous surface. It is mathematically described by Eq. (4).

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}
\]

where \(K_F\) ((mg/g)/(L/mg)^{1/n}) and \(n\) are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. \(K_F\) and \(n\) can be determined from the linear plot of \(\ln Q_e\) versus \(\ln C_e\).

1.5.3. Kinetic adsorption experiment

Kinetic adsorption experiments were also carried out at 30 °C and pH 6.0. The initial HA concentration in solution was 250 mg/L. The adsorption kinetics was investigated using two kinetic models, namely pseudo first-order (Eq. (5)) and pseudo second-order models (Eq. (6)).

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{5}
\]

\[
t/Q_t = 1/(k_2 Q_e^2) + t/Q_e \tag{6}
\]

where \(k_1\) (min^{-1}) and \(k_2\) (g/(mg·min)) are the pseudo first-order and pseudo second-order rate constants, respectively; \(Q_e\) (mg/g) is the amount adsorbed at time \(t\) (min), and \(Q_m\) (mg/g) denotes the amount adsorbed at equilibrium.

2. Results and discussion

2.1. Characterization of SPAC-NH2 adsorbent

Various physical and chemical characteristics of SPAC and SPAC-NH2 are given in Table 1. EDS analysis is a very important technique that can be used to confirm the successful modification of the SPAC surface. C, H, N, and Si analyses of the SPAC-NH2 showed an increasing percentage of oxygen, silicon and nitrogen owing to the aminopropyl moiety present on the SPAC surface. Compared with the unmodified SPAC, SPAC-NH2 yielded a smaller surface area and pore volume, which reflected the occupation of small pores of SPAC by APTES.

The FT-IR spectra of APTES, SPAC, and SPAC-NH2 are presented in Fig. 1a. The FT-IR spectrum of SPAC shows two prominent peaks: a broad peak at 3200.0 cm\(^{-1}\) corresponding to the amine group (Zhu et al., 2010). The peak at 1637 cm\(^{-1}\) corresponds to the C=O group and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010). The peak at 1637 cm\(^{-1}\) corresponds to the –OH groups; and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010). The peak at 1637 cm\(^{-1}\) corresponds to the –OH groups; and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010). The peak at 1637 cm\(^{-1}\) corresponds to the –OH groups; and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010). The peak at 1637 cm\(^{-1}\) corresponds to the –OH groups; and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010).

### Table 1 – Physical and chemical characteristics of the stereoscopic porous activated carbon and modified stereoscopic porous activated carbon.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Adsorbent samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPAC</td>
</tr>
<tr>
<td>Color</td>
<td>Black</td>
</tr>
<tr>
<td>EDS analysis</td>
<td>C (wt%)</td>
</tr>
<tr>
<td></td>
<td>O (wt%)</td>
</tr>
<tr>
<td></td>
<td>N (wt%)</td>
</tr>
<tr>
<td></td>
<td>Si (wt%)</td>
</tr>
<tr>
<td>BET analysis</td>
<td>BET surface area (m(^2)/g)</td>
</tr>
<tr>
<td></td>
<td>Total pore volume (cm(^3)/g)</td>
</tr>
</tbody>
</table>

n.d.: not detectable.

The FT-IR spectra of APTES, SPAC, and SPAC-NH2 are presented in Fig. 1a. The FT-IR spectrum of SPAC shows two prominent peaks: a broad peak at 3200.0–3600.0 cm\(^{-1}\), indicating the presence of hydroxyl groups; and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010). The peak at 1637 cm\(^{-1}\) corresponds to the –OH groups; and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010). The peak at 1637 cm\(^{-1}\) corresponds to the –OH groups; and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010). The peak at 1637 cm\(^{-1}\) corresponds to the –OH groups; and a peak at 1558.2, corresponding to the amine group (Zhu et al., 2010).
suggesting that the adsorbates could readily be adsorbed as anionic inner-sphere surface complexes on the positively charged surface of the adsorbents via electrostatic attraction (Park et al., 2017; Zurlinden et al., 2005).

The XRD patterns of SPAC and SPAC-NH₂ are shown in Fig. 1c. SPAC and SPAC-NH₂ showed broad peaks centered at approximately 13.8° and 42.5°, indicating that SPAC and SPAC-NH₂ are typical amorphous substances. The XRD pattern of SPAC HA a broad diffraction peak located at around 2θ = 21.1°, ascribing to the (002) plane of graphitic carbon (An et al., 2017). The defective nature of samples could also be further confirmed using Raman spectra, as shown in Fig. 1d. The Raman spectra of SPAC and SPAC-NH₂ revealed two intense peaks at around 1338.9 and 1589.1 cm⁻¹, which corresponded to the D and G bands of carbon, respectively (Chen et al., 2017). The ratio of the integrated intensities of the D and G bands (I_D/I_G) is often used to indirectly reflect the degree of graphitization of the carbon materials (An et al., 2015). Compared with SPAC (0.789), the peak intensity ratio I_D/I_G of SPAC-NH₂ (0.851) increased slightly, reflecting a lower degree of graphitization and more defective nature. This may be attributed to the heterogeneous porous structure caused by APTES modification. In addition, another weak band was observed at about 2887.1 cm⁻¹, known as 2D, which was indicative of partial graphitization (An et al., 2017).

The microstructures of SPAC and SPAC-NH₂ were investigated by performing SEM analysis. As shown in Fig. 2a, the as-prepared SPAC exhibited a porous, fluffy and hydrogel-like architecture and had a specific surface area of 489.5 m²/g; while after modification (Fig. 2b), the SPAC-NH₂ had a low specific surface area (40.5 m²/g). Meanwhile, a wave-like morphology is clearly observed at the surface of the carbon aerogels, which may be caused by the occupation of pores by APTES. The microstructures and the FT-IR spectra of SPAC-NH₂ showed that the stereoscopic and porous structures would have a high adsorption capacity, and the –NH₂ from APTES modification enhanced the HA adsorption performance. The elemental mapping (EMP) image of the SPAC-NH₂ is shown in Fig. 2c. It can be seen that the elements C, O, N, and Si are nonuniformly distributed for SPAC-NH₂, indicating that the SPAC had been modified successfully by APTES.
Furthermore, from the element mapping (Fig. 2c), a bright mass containing an abundance of O, N, and Si elements was clearly observed, indicating the presence of the hydrolysate of APTES. The mechanism behind the formation of this hydrolysate, that is, ladder-like oligomeric aminosilanes (LAOAs), is discussed in Section 2.3.3.

2.2. Adsorption performance toward HA

2.2.1. Effect of contact time and initial pH

The rates of loading of HA onto SPAC and SPAC-NH₂ were determined by agitating a working standard solution with the adsorbents at pH 6.0 for different contact times. The adsorption efficiencies as a function of the contact time are shown in Fig. 3a. The contact time required to reach adsorption equilibrium was 20 and 15 min for SPAC and SPAC-NH₂, respectively. For SPAC-NH₂, the sharp increase in the removal efficiency during the initial stage may be due to the presence of a sufficient number of available exchange sites, strong chelation, and effective mass transfer. Under the studied experimental conditions, adsorption equilibrium was achieved within about 15 min. In addition, the HA removal efficiencies of SPAC and SPAC-NH₂ were nearly 18.2% and 100.0%, respectively, indicating that the –NH₂ in APTES grafted onto the SPAC played the primary role in HA removal. The initial pH of the solution plays a key role in the adsorption process (El Qada et al., 2006) because of the strong competition between adsorbates and H⁺. The effect of pH was studied in the range of 3.0–10.0 under conditions of HA concentration 100 mg/L, contact time 60 min, and adsorbent dosage 1.0 g/L. The initial pH of the solution was adjusted to the specified value using either 0.1 mol/L HNO₃ or 0.1 mol/L NaOH. As shown in Fig. 3b, consistently high HA removal efficiency (91.9%–99.5%) was observed for pH < 8.0, which decreased from 91.9% to 64.3% as the solution pH increased from 8.0 to 10.0. In the lower pH range, the surface amine groups of the absorbent were protonated to afford primary ammonium ions (Si – R – NH₃⁺), which tended to associate with the abundant deprotonated carboxylic groups (HA – O⁻) (Imyim and Prapalimrungsi, 2010). Meanwhile, in acidic solutions, the solubility of HA gradually declines with decreasing pH, and the self-aggregation of HA in water at low pH may also contribute to the improvement of removal efficiency (Wu et al., 2016). The aim of this research was to use the obtained experimental data for application in the water

Fig. 2 – Scanning electron microscopy photographs images of the SPAC (a) and SPAC-NH₂ (b); elemental mapping (c) of the SPAC-NH₂.
treatment process, where the pH of the water is within the range of 3.0–8.0. Therefore, we decided to use pH 6.0 for further investigations.

2.2.2. Effect of adsorbent dosage and initial humic acid concentration
The effect of the SPAC-NH₂ dosage (0.2–1.5 g/L) on HA removal was determined for conditions of HA concentration 100 mg/L, contact time 60 min, and pH 6.0. As shown in Fig. 3c, the removal efficiency improved with increasing adsorbent dosage from 0.2 to 1.5 g/L, and it reached a maximum of 95.1% at 1.5 g/L SPAC-NH₂. However, the efficiency improvement showed saturation at 1.0 g/L. The improvement of the removal efficiency with increasing SPAC-NH₂ dosage was attributed to the greater surface area and larger number of available adsorption sites of the produced absorbent. Hence, 1.0 g/L was determined as the optimum dosage. According to the results shown in Fig. 3d, the removal efficiency decreased from 99.0% to 31.5% when the initial HA concentration increased from 20 to 500 mg/L. As seen in the figure, the adsorption capacity increased gradually as the initial HA concentration increased up to 300 mg/L; from the results, the equilibrium adsorption capacities were obtained.

2.2.3. Adsorption isotherm
The adsorption isotherm study is important in determining the adsorption capacity and evaluating the commercial potential of an adsorbent (Zhou et al., 2018c). The effect of the initial HA concentration on the adsorption capacity of SPAC-NH₂ was assessed over the range of 20–500 mg/L, and the corresponding results are presented in Fig. 3d. The Langmuir and Freundlich isotherm models were used to describe the data on adsorption of HA from the solution, and the curve fitting results are shown in Fig. 4a.

The obtained isotherm parameters, Qₘ₀, Kₗ, Kₐ, n and the correlation coefficients (R²) are listed in Table 2. The R² value of the linear form of the isotherm equations for HA was much closer to unity for the Langmuir model than for the Freundlich model, suggesting that the adsorption of HA by SPAC-NH₂ was monolayer adsorption. The maximum adsorption capacity of SPAC-NH₂ for HA was calculated as 156.0 mg/g, which was
close to the experimental result (157.6 mg/g). It can be concluded that SPAC-NH2 has good potential for the removal of HA from aqueous solution. In the Langmuir isotherm, R_L (as shown in Table 2) is the equilibrium parameter, which is applied to estimate whether the adsorption is favorable (Xu et al., 2012). The value of R_L indicates whether the adsorption is irreversible (R_L = 0), favorable (0 < R_L < 1), linear (R_L = 1) or unfavorable (R_L > 1) (Hall et al., 1966). In this study, the applicability of the Langmuir isotherm and the R_L values of 0.0036–0.0826 (0 < R_L < 1) indicated that the adsorption process was favorable.

We compared the adsorption capacity of SPAC-NH2 with those of other adsorbents from the literature, as shown in Table 3. It can be seen that the capacities of some adsorbents depend on the type of HA and adsorption conditions. The high adsorption capacity and mild adsorption pH for the removal of HA indicated that SPAC-NH2 appears to be a good candidate for HA adsorption.

2.2.4. Adsorption kinetics
To study the adsorption kinetics of HA on SPAC-NH2, an initial HA concentration of 100 mg/L was prepared. The uptake rate of HA was found to be rapid for the initial period (0–15 min), and it then became slow and constant as the contact time increased (15–60 min).

The two kinetics models are shown in Fig. 4b. The results of the kinetic constants and correlation coefficients (R^2) are listed in Table 4. A higher correlation coefficient (R^2 = 0.996) was achieved for the pseudo-first-order model, which showed that the adsorption of HA onto SPAC-NH2 was fit better by the pseudo-first-order model.

2.3. Mechanism of SPAC-NH2 for removal of humic acid

2.3.1. XPS analysis
To analyze the adsorption mechanisms of HA on SPAC-NH2, HA-loaded SPAC-NH2 was prepared at a pH of 6.0. In this experiment, XPS was further used to characterize the surface states of SPAC-NH2 before and after HA adsorption. Fig. 5 shows the presence of characteristic C 1s, O 1s, N 1s, and Si 2p peaks. HA-induced adsorption increased the contents of carbon (from 70.05% to 77.39%) and decreased those of oxygen (from 20.44% to 18.18%) and nitrogen (from 9.51% to 4.43%) after HA adsorption, which was attributed to the amidization reaction between the COOH groups of HA and the NH2 groups of APTES.

Fig. 5b–d show the high-resolution C 1s, O 1s, and N 1s XPS spectra. High-resolution carbon C 1s spectra yielded information on the relative abundance of carbon atoms in different

| Table 2 – Isotherm parameters for HA adsorption onto SPAC-NH2. |
|-----------------|-----------------|-----------------|-----------------|
|                | Q_m,exp (mg/g)  | Langmuir model  | Freundlich model |
|                 | Q_m,cal (mg/g)  |                  |                 |
| R_L = 1/(1 + K_L C_0) |                  |                 |
|                  | K_L          | R^2            | R_L            |
| 157.6           | 156.0       | 0.555         | 0.954         | 0.0036–0.0826 | 80.90   | 7.79  | 0.816 |

| Table 3 – Adsorption capacity of various adsorbents toward humic acid. |
|-----------------------------|-----------------------------|-----------------------------|
| Adsorbent                  | Adsorption capacity (mg/g)  | Reference                  |
| Modified rice husk ash     | 8.2                         | Imyim and Prapalimunrungs  |
| Activated carbon from      | 21–45                       | Johns et al. (1993)         |
| rice husk                  |                             |                             |
| Chitosan                   | 28.9                        | Ngah and Musa (1998)        |
| Fly ash                    | 84                          | Wang et al. (2008)          |
| Chitosan hydrogel beads    | 0.6                         | Yan and Bai (2005)          |
| TiO2/graphene composite    | 52                          | Ye et al. (2017)            |
| APTES modified palygorskite | 71.43                       | Wang et al. (2017)          |
| PA-NH2                      |                             |                             |
| SPAC-NH2                   | 156.0                       | This study                  |
molecular environments (Fig. 5b). Before adsorption, the XPS spectra of SPAC-NH₂ show peaks at 284.5, 286, and 289 eV for the C 1s region corresponding to C-Si, sp² hybridized carbon in the aromatic rings, and carbon-bonded as C-N (C-O), respectively (Castillo et al., 2016), indicating the successful modification of SPAC with APTES. After adsorption, a new peak appeared located at 287.8 eV, which corresponds to carbon bound to amide (O-C-N), confirming the introduction of HA. Fig. 5c depicts high-resolution O 1s core-level spectra of SPAC-NH₂ before and after adsorption of HA. The peaks at 532.7 and 531.8 eV that appeared after the adsorption of HA corresponded to O-C≡N and C≡O oxygens, respectively (Castillo et al., 2016; Lu et al., 2008), and that at 530.2 eV was attributed to adsorbed OH groups and/or water molecules (Morales et al., 2006). In addition, the strong peak at ~531.2 eV was attributed to Si–O–Si units, reflecting the hydrolysis of APTES. The high-resolution scans of N 1s spectra of SPAC-NH₂ are shown in Fig. 5d. The strong peak at about 399 eV was attributed to amine nitrogen (N=C), while the weaker peak at about 400 eV was attributed to amide nitrogen (N=C=O) (Zhou et al., 2015). However, after the adsorption of HA, the ratios of the N 1s peak integral intensities corresponding to the N=C=O group increased compared with the previous values, which indicated the adsorption of HA.

2.3.2. SEM and FT-IR analysis

In order to further study the adsorption mechanisms, the morphology and functional groups of the adsorbent after adsorption were characterized using SEM and FT-IR. Fig. 6a shows the microstructure of SPAC-NH₂ after adsorption of HA. It can be seen that the surface and pores were occupied by HA. From Fig. 6b, compared with the raw SPAC-NH₂, a new peak appeared at 1396.2 cm⁻¹, which was attributed to the vibrations of COO groups from HA.

### Table 4 – Kinetic model parameters for HA adsorption onto SPAC-NH₂.

<table>
<thead>
<tr>
<th>Qₑ,exp (mg/g)</th>
<th>Pseudo first-order</th>
<th>Pseudo second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Qₑ (mg/g) K₁ R²</td>
<td>Qₑ (mg/g) K₂ R²</td>
</tr>
<tr>
<td>100.0</td>
<td>101.9</td>
<td>0.187</td>
</tr>
<tr>
<td></td>
<td>0.966</td>
<td>116.1</td>
</tr>
<tr>
<td></td>
<td>0.0021</td>
<td>0.970</td>
</tr>
</tbody>
</table>

Fig. 5 – X-ray photoelectron spectroscopy before and after the adsorption of HA. Low-resolution (a) and high-resolution C 1s (b), O 1s (c), and N 1s (d). Spectra feature of the C 1s region (280–294 eV), N 1s region (393–405 eV), and O 1s region (526–538 eV).
2.3.3. Mechanism for the removal of humic acid

Based on the above analysis, the main mechanism of HA removal in the presence of SPAC-NH₂ may be the association between HA − O⁻ and Si − R − NH₃⁺. In order to verify the enhancement mechanism, the proposed schematic drawing illustrating the removal of HA is shown in Fig. 7. The detailed reaction can be summarized as follows: (1) First, during the modification process of SPAC, the hydroxyl groups from SPAC interacted with APTES, resulting in dehydration condensation. Then, the surface of SPAC was modified with −NH₃⁺, which associated with −COO⁻ from HA through hydrogen bonds and coordination bonds; (2) Due to the porosity and adsorptivity of SPAC, the interaction between HA and SPAC also contributed to the HA removal; (3) A portion of APTES was adsorbed by the SPAC and did not form Si − R − NH₃⁺. This part of APTES was hydrolyzed to the corresponding silanol and ethanol upon contact with the HA solution, with the subsequent condensation and self-assembly of silanol units affording ladder-like oligomeric aminosilanes (LAOAs) (Zhou et al., 2018a). Then, the water-soluble HA was adsorbed onto the LAOAs because the HA − O⁻ moieties tended to associate with an equivalent number of Si − R − NH₃⁺ units on the LAOA surface, which contributed to further HA removal. The

Fig. 6 – Scanning electron microscopy images of the SPAC-NH₂ after adsorption (a); FT-IR analysis of SPAC-NH₂ before and after adsorption (b).

Fig. 7 – Schematic illustration of the HA removal mechanism of SPAC-NH₂.
hydrolysis, condensation, and self-assembly of APTES in the HA solution took place as shown in Appendix A Fig. S5.

3. Conclusions

A unique stereoscopic porous activated carbon with an –NH₂ functional group was successfully designed and synthesized for the capture of HA. The adsorption experiments confirmed that the adsorption capacity of SPAC-NH₂ powder for HA depended upon the pH and initial HA concentration of the solution. Batch experiments confirmed that the HA removal efficiency depended on the pH and initial HA concentration. An HA removal efficiency of over 92% was achieved in aqueous solutions containing 100 mg/L of HA, with optimal conditions corresponding to an SPAC-NH₂ dosage of 1.0 g/L, aqueous solutions containing 100 mg/L of HA, with optimal efficiency depended on the pH and initial HA concentration. The Langmuir isotherm model was able to fit the equilibrium adsorption data and yielded a maximum adsorption capacity of 156.0 mg/g, and the adsorption processes were favorable. This study demonstrated the potential and viability of SPAC-NH₂ particles for the removal of HA from contaminated water. In addition, it is necessary to evaluate the utilization of the HA-loaded adsorbent, which consists of organic mass and can play an important role in soil fertility and plant nutrition. The effect of the HA-loaded adsorbent on plant growth will be explored in further research.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51678419), and the Fundamental Research Funds for the Central Universities (No. 22120170266).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.06.019.

REFERENCES


