Synthesization, characterization and adsorption properties of sulfonic cellulose

Wenjian Shi, Yan Zhou, Yuanzhang Zhang, Liang Li and Qinlin Yang

ABSTRACT

The synthesization and characterization of a new environmental functional material—sulfonic cellulose—were studied in this paper. The preparation conditions were optimized through an orthogonal experiment. The modified cellulose was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The adsorption rules of cationic organic pollutants and heavy metal ions by this new material were discussed. Regeneration and recycling performances of the sulfonic cellulose were also investigated. At the temperature of 323 K, sulfonic cellulose was prepared by grafting 2-acrylamido-2-methylpropane sulfonic acid (AMPS) onto alkali-treated cellulose for 4 h with the employing of ceric ammonium nitrate as initiator. The mass ratio of AMPS to cellulose was 3:1 and the concentration of ceric ammonium nitrate was 63.8 mmol/L. The sulfur content of sulfonic cellulose was 7.32 wt%. The peaks of 1,303 and 1,159 cm\(^{-1}\) in IR suggested the existence of the sulfonic group in sulfonic cellulose. The XRD and SEM results showed that the crystallinity decreased while the specific surface area increased after modification. Batch adsorption results showed that sulfonic cellulose had a favorable adsorption capacity for model contaminants at pH 6.0–7.0. The adsorption process was endothermic and reached equilibrium in 180 min. The adsorption rules of cationic organic pollutants and heavy metal ions indicated that sulfonic cellulose had high adsorption capacity for the cationic dyes with a coplanar macromolecule structure and organic compounds carrying the amino group. Under room temperature, 1.0 mol/L HCl can be used as a desorption solution and the equilibrium adsorption capacity had little decrease (less than 7%) after six adsorption–desorption cycles.

Key words | adsorption, cationic organic pollutants, characterization, heavy metal ions, sulfonic cellulose

INTRODUCTION

Soluble persistent pollutants in the water include heavy metals and aromatic organics, which are present in the waste streams of many industries, and have attracted wide attention in the environment science and technology field in recent years. Dye molecules or their metabolites (e.g. aromatic amines) and aromatic organic pollutants may be highly toxic, potentially carcinogenic, mutagenic and allergenic (Shakir et al. 2010). They contaminate not only the environment but also traverse through the entire food chain, leading to biomagnifications (Gupta & Suhas 2009). There are about 3,000 types of dyes in the world market. Among them, cationic dyes are more toxic than anionic dyes, and their tinctorial values are very high (less than 1.0 mg/L) (Bayramoglu et al. 2009). The discharge of metallic ions in industrial effluent is of great concern because their presence and accumulation have a toxic effect on living species (Vinodh et al. 2011). Industrial wastewater containing metal ions such as nickel, lead, copper, cadmium and chromium are common because their metals are used in a large number of industries such as electroplating, batteries manufacture, mining and pharmaceuticals (Pu & Wang 2011). Heavy metals are toxic to aquatic organisms even at very low concentrations (Ozay et al. 2009). Conventional methods for removing dyes and heavy metals from industrial effluents include chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation and adsorption (Azarudeen et al. 2011; Soto et al. 2011). Among them, adsorption has been...
found to be superior to other techniques for the treatment of water soluble persistent pollutants for its low cost, simplicity of design, ease of operation, insensitivity to toxic substances and good regeneration-recycling performance (Fletcher et al. 2006). Many solid materials as adsorbent have been investigated, including activated carbon, ion exchange resin, chitosan and cellulose (Monier et al. 2010; Zhang et al. 2011). Among them, activated carbons are usually used in the adsorption treatment of nonpolar organic pollutants (Figueiredo et al. 2011). Ion exchange resin is mainly applied to the removal of inorganic ions (NH$_4^+$, Ca$^{2+}$, NO$_3^-$, Cl$^-$ etc.) (Milmile et al. 2011). As a natural polymer material, cellulose and modified cellulose have been employed as a new and good adsorbent for the adsorption of dyes and heavy metals recently (Siroký et al. 2011).

Cellulose, one of the most chemically uniform biopolymers synthesized, is also one of the most abundant and important renewable biopolymers in nature. Due to the presence of ordered hydrogen bonds it forms various supramolecular crystalline structures, which are essential for many of its native and commercial fibrous application. So functionalization of cellulose has been a research focus in recent years. Using cellulose derivatives as the adsorbent of water-soluble persistent pollutants has been focused on in recent years due to their characteristics of being cheap, non-toxic, renewable and easily degradable (Alila & Boufi 2009). As a new functional cellulose material, sulfonic cellulose was synthesized by derivatization of hydroxyl on the molecular chain of cellulose to introduce a sulfonic acid group on the molecular structure of cellulose. Many investigators have done much on the modification of cellulose (Heinze & Liebert 2001; Rajalaxmi et al. 2010).

This study investigated the preparation and application of a modified cellulose adsorbent, namely sulfonic cellulose containing the sulfonic acid group, for separation of heavy metals and cationic organic pollutants from water. The sulfonic cellulose with high sulfur content was synthesized with optimized preparation conditions and characterized with Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Batch adsorption and column adsorption were conducted to evaluate the adsorption capacity of made sulfonic cellulose for three typical soluble persistent pollutants mentioned above including cationic red X-GRL, Pb$^{2+}$ and aniline, which would provide basic research for the synthesisation, characterization and adsorption performance of sulfonic cellulose on cationic organic pollutants and heavy metals.

**MATERIALS AND METHODS**

**Materials**

Commercial medical adsorbent cotton, strong acid styrene anion exchange resins (Resin Company Co. Ltd, Shanghai, China) and lignin granular active carbon (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) was used in this study. The ceric ammonium nitrate, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acetone, ether, sodium hydroxide, hydrochloric acid (36%wt), silver nitrate, lead chloride, copper chloride, cadmium sulfate, nickel sulfate, cobaltous sulfate, chromic chloride, N-(1-naphthyl) ethylenediamine, aniline, cetylpyridinium chloride (CPC) and other medicinals were of analytical reagent grade and were purchased from Sinopharm Chemical Reagent Co. Ltd. The dyes methylene blue (C.I. 52015), cationic red X-GRL (C.I. 11465) and basic brilliant blue BO (C.I. 42595) were purified and dried. Stock solution of these dyes was 1,000 mg/L and was used by diluting.

**Instruments**

The apparatus used for the characterization of sulfonic cellulose included a NEXUS 670 FTIR spectrometer (Nicolet Co.), a D/max-γB X-ray diffractometer (Rigaku Industrial Co.) and a SEM515 SEM (Philip Co.). Dyes and heavy metals were measured by the UV757CRT UV/Vis spectrophotometer (Shanghai Precision & Scientific Instrument Co.) and the TAS-990 atomic absorption spectrophotometer (Beijing Purkinje General Instrument Co.) respectively. The acidity of the aqueous solution was measured by a PHS-3C precise acidimeter (Shanghai Precision & Scientific Instrument Co.). Batch adsorption experiments were conducted by a SHS-BA water bath oscillator (Shanghai Precision & Scientific Instrument Co.).

**Preparation of sulfonic cellulose**

Sulfonic cellulose was synthesized by grafting AMPS on the molecular structure of cellulose with ceric ammonium nitrate as initiator (Yang et al. 2009). First, alkali cellulose was made by immersing absorbent cotton in 17.5% sodium hydroxide solution for 24 h at room temperature, then washing with deionized water to neutral, squeezing by filter and drying to constant weight at 318 K. Secondly, 1.6 g alkali cellulose was mixed with 100 mL deionized water in a neck flask and sparged with nitrogen stream to
remove oxygen. After stirring for 10 min at ambient temperature, 3.5 g ceric ammonium nitrate and 4.8 g AMPS were added to the mixture over 1.0 h. The mixture was stirred for 3.0 h at 323 K. Finally, the obtained product was cooled and filtered. After washing with water, acetone and ether and drying to constant weight at 318 K, the sulfonic cellulose was obtained. The modified effect of absorbent cotton could be evaluated by measuring sulfur content using the oxygen flask combustion method (Hordijk et al. 1989).

Characterization of sulfonic cellulose

The FTIR spectrum of dried sulfonic cellulose was measured with KBr pellet by NEXUS 670 FTIR spectroscopy with precision of 0.01 cm⁻¹ in the range of 400–4,000 cm⁻¹.

X-ray diffractogram of sulfonic cellulose was obtained from a D/max-2B diffractometer with a scanning speed of 4° min⁻¹ and scanning angle 2θ range of 5–80° at 40 kV and 70 mA.

The surface morphology of cellulose and sulfonic cellulose was detected by using SEM515 SEM with amplification 5,000.

Batch adsorption studies

Batch adsorption experiments were carried out by allowing an accurately weighed amount of sulfonic cellulose to reach equilibrium with pollutant solutions of known concentrations in conical flasks (250 mL). The flasks with mixture solutions were shaken in a temperature-controlled water bath oscillator for a certain time at constant temperature and frequency (120 rpm). The adsorption capacity of sulfonic cellulose for pollutant solutions was calculated using the following equation (Aloulou et al. 2006):

\[ Q = \frac{(C_0 - C_t)V}{m} \]  

(1)

where \( C_0 \) and \( C_t \) are initial and remaining concentrations of pollutant in the solution (mg/L) at initial time and time \( t \) (minutes), respectively. \( Q \) is the amount of pollutant adsorbed onto a unit dry mass of sulfonic cellulose in mg/g. \( V \) is the volume of the pollutant solution in L and \( m \) is the weight of dry sulfonic cellulose in g. The dyes and CPC were detected by a UV/Vis spectrophotometer. The metal ions were detected by an atomic absorption spectrophotometer. Aniline was determined by an N-(1-naphthyl) ethylenediamine spectrophotometer.

Column adsorption

Dynamic flow adsorption was carried out in a glass column (length 25 cm, internal diameter 1 cm). The column was filled with 1 g sulfonic cellulose and tapped to ensure the column was filled without gaps. The top of the column was connected to a 500 mL separating funnel. The pollutant solution with known concentration and pH value was allowed to flow gradually from the separating funnel to the column at a constant flow rate. The effluent was collected and measured at a specified time interval. The sulfonic cellulose reached adsorption equilibrium when the concentration of the effluent was close to its initial concentration. The dynamic adsorption curve was modeled and the saturated adsorption amount was calculated.

Regeneration of sulfonic cellulose

The desorption of solutes from loaded sulfonic cellulose was performed by a solvent elution method, which used 1.0 mol/L HCl as an eluent maintained at a fixed flow rate (5 mL/min). Then the adsorbent column was washed with 100 mL distilled water at a fixed flow rate (25 mL/min); 25 mL 0.1 mol/L NaOH was used to elute the column. After regeneration, the adsorbent column was washed with deionized water to neutral before the influent adsorbate solution was reintroduced for the subsequent adsorption-desorption cycles.

RESULTS AND DISCUSSION

Optimal synthesis conditions for sulfonic cellulose

During the preparation of sulfonic cellulose, the influencing factors for the sulfur content of cellulose include the concentration of ceric ammonium nitrate, mass ratio of AMPS to cellulose, reaction temperature and time. To investigate different factors for the influence on the sulfur content of cellulose, an orthogonal experiment of four factors at three levels was designed. The results showed that the impact extent of the four factors on the sulfur content of cellulose, from high to low, was the reaction temperature, time, mass ratio of AMPS to cellulose and the concentration of ceric ammonium nitrate. Then every single factor was studied respectively as shown in Table 1. The optimal conditions of the preparation of sulfonic cellulose were determined, and were listed as follows: reaction temperature 323 K,
reaction time 4 h, the mass ratio of AMPS to cellulose 3:1, the concentration of ceric ammonium nitrate 63.8 mmol/L. Under these conditions, the sulfur content of cellulose was 7.32 wt%, which was equal to 2.28 mmol sulfonic group per gram sulfonic cellulose.

**Characterization of sulfonic cellulose**

**FTIR spectroscopy**

The infrared spectrograms of cellulose and sulfonic cellulose are shown in Figure 1. The peaks at 3,345 and 2,899 cm\(^{-1}\) in cellulose were characteristic peaks resulting from OH and >CHOH stretching vibrations, respectively. The peaks at 1,058 and 1,030 cm\(^{-1}\) were characteristic vibration peaks of carbon–carbon and carbon–oxygen bonds of glucose ring. After copolymerization, the graft copolymer not only reserved some characteristic peaks of cellulose but also had a characteristic peak at 1,303 and 1,159 cm\(^{-1}\) resulting from the asymmetric and symmetric stretching vibration adsorption peak of sulfur–oxygen bond of sulfonic group. Also, a bending vibration peak of carbon–oxygen bond and carbon–nitrogen bond of amide group at 1,650 and 1,548 cm\(^{-1}\) was observed, which confirmed that AMPS had successfully been grafted to the molecular structure of cellulose.

**XRD analysis**

The cellulose molecule is a long chain which contains a crystallization region and non-crystalline region. Differences of crystal structures can be detected from the XRD pattern. The XRD patterns of cellulose and sulfonic cellulose are depicted in Figure 2. The cellulose with diffraction peaks at 2\(\theta\) = 22.66\(^\circ\) showed the characteristic crystalline form.

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**Table 1 | Influence of different factors on sulfur contents**

<table>
<thead>
<tr>
<th>Ratio of materials</th>
<th>S (wt%) at different conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt (AMPS):wt (cellulose) = 4:1, time = 3 h, initiator concentration = 63.8 mmol/L</td>
<td>Temperature (K) 303 313 323 333</td>
</tr>
<tr>
<td></td>
<td>S (wt%)</td>
</tr>
<tr>
<td>wt (AMPS):wt (cellulose) = 4:1, temperature = 323 K, initiator concentration = 63.8 mmol/L</td>
<td>Time (h) 3 4 5 6</td>
</tr>
<tr>
<td></td>
<td>S (wt%)</td>
</tr>
<tr>
<td>Time = 3 h, temperature = 323 K, initiator concentration = 63.8 mmol/L</td>
<td>wt (AMPS):wt (cellulose) = 4:1</td>
</tr>
<tr>
<td></td>
<td>S (wt%)</td>
</tr>
<tr>
<td>wt (AMPS):wt (cellulose) = 3:1, temperature = 323 K, time = 3 h</td>
<td>Initiator concentration (mmol/L) 45.6 63.8 82.1 100</td>
</tr>
<tr>
<td></td>
<td>S (wt%)</td>
</tr>
</tbody>
</table>
After the etherification reaction, diffraction peaks at 2θ of 20.20° and 21.36° were observed, which could be assigned to the typical diffraction peaks of modified cellulose. This indicated that the crystalline transformation of cellulose occurred during etherification. Moreover, in comparison with the cellulose fiber, the peak intensity of sulfonic cellulose obviously decreased, indicating a decrease of crystallinity, which would result in the increase of reaction ability of the sulfonic cellulose.

SEM analysis

The morphology of cellulose and sulfonic cellulose was studied with SEM as presented in Figure 3. After the etherification reaction, the shape of cellulose changed from cylindrical to flat, and the surface varied from smooth to rough and contained cracks, which increased the specific surface area of sulfonic cellulose. This could be explained by the fact that etherification hindered the forming of hydrogen bonds between cellulose chains and destroyed the crystal structure of cellulose. The result was consistent with XRD analyses.

Batch adsorption of sulfonic cellulose

Effect of pH

Solution pH is an important controlling parameter in the adsorption process and may influence the uptake of adsorbate. The adsorption of model contaminants from aqueous solution onto sulfonic cellulose is primarily influenced by the surface charge of the adsorbent and the degree of ionization of the adsorptive sites. The effect of pH on adsorption capacity of the sulfonic cellulose was investigated with cationic red X-GRL, Pb²⁺ and aniline in the pH range of 2.0–11.0. As seen in Figure 4, the equilibrium adsorption capacity of sulfonic cellulose increased with an increasing of solution pH under the acid aqueous condition (from 116.9 to 320.5 mg/g, 43.0 to 89.0 mg/g and 38.8 to 91.7 mg/g for cationic red X-GRL, Pb²⁺ and aniline respectively, calculated according to Equation (1)). The sulfonic cellulose had the highest equilibrium adsorption capacity in the pH ranging from 6.0 to 7.0. Under the alkaline aqueous solution, the equilibrium adsorption capacity decreased as pH increased. It performed a similar adsorption process to that of the sulfonated poly-grafted cellulose studied by Anirudhan & Senan (2011). In the aqueous solution, the main reactions between sulfonic cellulose (R₁SO₃H) and cationic pollutant (R₂-A⁺) were listed as follows (Wan Ngah et al. 2011):

(a) Dissociation of sulfonic cellulose

\[
R₁SO₃H + H₂O ⇌ OH⁻ + R₁SO₃⁻ + H₃O⁺
\]

(b) Dissociation of cationic pollutant

\[
R₂ - A⁺ + H₂O ⇌ R₂ - AOH + H⁺
\]
(c) Associated matter of sulfonic cellulose adsorption of cationic pollutant:

\[ R_1\text{SO}_3^- + R_2 - A^+ \rightleftharpoons R_1\text{SO}_3^- + A^- + R_2 \]

The solution acidity had a great impact on equilibrium of the dissociation of sulfonic cellulose and cationic pollutants. In acidic solution, cationic pollutants mainly existed in ionic form, while sulfonic cellulose was in molecular form, which was not good for adsorption because of the masking of most of the sulfonic acid group (Anirudhan & Senan 2011a). In alkaline solution, the situation was contrary to that in acidic solution, which was also adverse to the adsorption due to the tendency of heavy metal ions to sediment (Reddad et al. 2002). It was confirmed by the experiment that the equilibrium adsorption capacity decreased as pH increased in alkaline aqueous solution. Generally speaking, the optimal condition for adsorption occurs when the adsorbent and adsorbate were both in the form of ion. And the experiment results were in accordance with the theory, showing that the sulfonic cellulose had the highest adsorption capacity for cationic red X-GRL, Pb\(^{2+}\) and aniline when the initial pH values were 6.0–7.0.

**Effect of contact time and temperature on adsorption capacity**

The adsorption capacities for the uptake of cationic red X-GRL, Pb\(^{2+}\) and aniline versus contact time at different temperature are shown in Figure 5. It was obvious that a rapid adsorption happened at the initial stage, while the equilibrium time required for the adsorption process was almost 180 min. At 318 K, the saturated adsorption capacities of sulfonic cellulose for cationic red X-GRL, Pb\(^{2+}\) and aniline were 783 mg/g (1.58 mmol/g), 159 mg/g (0.768 mmol/g) and 180 mg/g (1.95 mmol/g), respectively. Furthermore, the adsorption capacity increased with the increase of temperature, indicating the process was endothermic. The increase of the adsorption capacity for the three model contaminants with temperature might be due to the enhanced rate of intraparticle diffusion of adsorbate and changes in the size of the pores.

**Adsorption rules of sulfonic cellulose with other contaminants**

The adsorption rules of sulfonic cellulose with selected contaminants including dyes, organic compounds and metal ions are shown in Table 2. The data showed that the adsorption capacity of sulfonic cellulose on cationic red X-GRL, basic brilliant blue BO, methylene blue, aniline and CPC was high, indicating that sulfonic cellulose had a favorable removal of coplanar macromolecule and nitrogenous organic compounds. Furthermore, the adsorption capacity of sulfonic cellulose for the metal ions was as follows: \( \text{Ag}^+ > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} \). The adsorption of sulfonic cellulose on metal ions is mainly chemisorption including electrostatic force and coordinating chelation. The adsorption of sulfonic cellulose on cationic dyes is mainly chemisorption with partial physisorption.
Comparison with other adsorption materials

The adsorption capacities of another two adsorption materials, strong acidic styrene cationic exchange resin (001 × 7(732)) and wooden particle activated carbon (20–30 meshes) were tested under the same experiment condition as sulfonic cellulose. The results are also listed in Table 2. It can be concluded that the adsorption capacity of sulfonic cellulose was as high as commercialized strong acidic styrene cationic exchange resin and apparently higher than activated carbon, indicating that the sulfonic cellulose was a fairly good adsorbent for these kinds of contaminants.

Dynamic adsorption curve

To be useful in separation and removal processes, adsorbed species should be easily desorbed under mild conditions and adsorbents should be reused many times in order to reduce cost. The results of dynamic flow experiments were used to obtain the breakthrough curves for adsorption of cationic red X-GRL, Pb²⁺ and aniline from aqueous solutions by plotting the time versus Ct/C₀. It was found that when contaminant solution passed through the column packed with sulfonic cellulose at a flow rate of 10 mL/min for Pb²⁺ and aniline, and 5 mL/min for red X-GRL upstream, no leakage of solute was observed up to the time of 100 min in all cases in the first cycle. The slopes of the breakthrough curves were comparatively steep at the point of leaking, indicating that the rate of dynamic adsorption was very fast. Also, the dynamic equilibrium adsorption capacity of cationic red X-GRL was calculated to be 473 mg/g, which was slightly less than the saturated adsorption amount. As for Pb²⁺ and aniline, the dynamic equilibrium adsorption capacities were 95.6 and 100 mg/g, respectively, which was analogous to the static adsorption result.

Desorption and regeneration

The economic feasibility of using an adsorbent to remove contaminants from wastewater relies on its regeneration

### Table 2 | Adsorption capacity of sulfonic cellulose for different contaminants compared with two other adsorption materials. Adsorption conditions – initial concentration of solution: 500 mg/L for dyes and organic compounds, 200 mg/L for metal ions; solution volume: 50 mL; amount of adsorbents: 0.03 g; pH: 6.0–7.0; temperature: 298 K; adsorption time: 2 h

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Sulfonic cellulose (mg/g)</th>
<th>Cationic exchange resin (mg/g)</th>
<th>Activated carbon (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mmol/g)</td>
<td>(mmol/g)</td>
<td>(mmol/g)</td>
</tr>
<tr>
<td>Cationic red X-GRL</td>
<td>794</td>
<td>1.60</td>
<td>770</td>
</tr>
<tr>
<td>Basic brilliant BO</td>
<td>825</td>
<td>1.61</td>
<td>802</td>
</tr>
<tr>
<td>Aniline</td>
<td>179</td>
<td>1.92</td>
<td>156</td>
</tr>
<tr>
<td>CPC</td>
<td>317</td>
<td>0.885</td>
<td>383</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>236</td>
<td>0.631</td>
<td>253</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>101</td>
<td>0.935</td>
<td>132</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>158</td>
<td>0.760</td>
<td>208</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>39.6</td>
<td>0.619</td>
<td>45.6</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>63.1</td>
<td>0.561</td>
<td>70.1</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>31.4</td>
<td>0.534</td>
<td>35.6</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>29.3</td>
<td>0.498</td>
<td>36.1</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>21.2</td>
<td>0.408</td>
<td>23.5</td>
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</table>

### Table 3 | Adsorption-desorption cycles of model contaminants on sulfonic cellulose

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Equilibrium adsorption capacity</th>
<th>Cycle time 1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic red X-GRL</td>
<td>Qₑ (mg/g)</td>
<td>589</td>
<td>575</td>
<td>568</td>
<td>562</td>
<td>565</td>
<td>569</td>
</tr>
<tr>
<td></td>
<td>Qₑ/Q₀, %</td>
<td>100</td>
<td>97.6</td>
<td>96.4</td>
<td>95.4</td>
<td>95.9</td>
<td>96.6</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Qₑ (mg/g)</td>
<td>106</td>
<td>101</td>
<td>99.7</td>
<td>99.5</td>
<td>98.3</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>Qₑ/Q₀, %</td>
<td>100</td>
<td>95.3</td>
<td>94.1</td>
<td>93.9</td>
<td>92.7</td>
<td>94.0</td>
</tr>
<tr>
<td>Aniline</td>
<td>Qₑ (mg/g)</td>
<td>116</td>
<td>111</td>
<td>110</td>
<td>112</td>
<td>109</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>Qₑ/Q₀, %</td>
<td>100</td>
<td>95.7</td>
<td>94.8</td>
<td>96.6</td>
<td>94.0</td>
<td>93.1</td>
</tr>
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</table>
ability during multiple adsorption–desorption cycles. In this study, 1.0 mol/L HCl was found to be suitable for desorption and regeneration of sulfonic cellulose. Six adsorption–desorption cycles of the three model contaminants on the sulfonic cellulose were performed and the result are listed in Table 3. The results indicated that the adsorption capacity had little decrease (less than 7%) and tended to be steady. Therefore, the sulfonic cellulose had good regeneration ability and could be recycled.

CONCLUSION

As new functional environment material, sulfonic cellulose was modified by a natural and renewable high polymer material – cellulose, which has the advantages of low-cost, wide availability, biodegradable and no harmful effect on the environment. The characterizations of sulfonic cellulose showed that AMPS was successfully grafted onto cellulose by ceric ammonium nitrate as initiator. The optimal conditions for the grafting were established, and the sulfur content of cellulose was 7.32 wt%. Sulfonic cellulose had high adsorption capacity and fast adsorption rate for cationic dyes, metal ions and nitrogenous organic compounds under the pH ranging from 6 to 7. At 318 K, the saturated adsorption capacities of sulfonic cellulose for cationic red X-GRL, Pb$^{2+}$ and aniline were 783, 159 and 180 mg/g, respectively. The adsorption capacity of sulfonic cellulose for metal ions was as follows: Ag$^{+}$ > Pb$^{2+}$ > Cu$^{2+}$ > Cd$^{2+}$ > Ni$^{2+}$ > Co$^{2+}$ > Cr$^{3+}$. The saturated sulfonic cellulose could be eluted by hydrochloric acid and had favorable recycling ability. The synthesisization and application performance of sulfonic cellulose provided a new material and also a new method for the treatment of heavy metals and cationic organic pollutants in water.

ACKNOWLEDGEMENTS

This study was supported by the National Natural Science Foundation of China (10872133).

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First received 27 April 2012; accepted in revised form 9 July 2012