Assembly of SPS/MgSi assisted by dopamine with excellent removal performance for ciprofloxacin

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ABSTRACT
In this work, magnesium silicate-based sulfonated polystyrene sphere composites (SPS/MgSi) were synthesized by one-step (SMD1) and two-step (SMD2) methods. For SMD1, MgSi particles were densely assembled on the surface of SPS, assisted by complexation between Fe"³⁺ and hydroxyl phenol. For SMD2, SPS/SiO₂ was firstly obtained by the same method as SMD1, and then SPS/SiO₂ was transformed directly to SPS/MgSi by hydrothermal conditions. Therefore, MgSi obtained by the two-step method had an interwoven structure. Compared to SPS, MgSi and SMD1, SMD2 presented a larger specific surface area and more negative surface charges. Therefore, SMD2 showed superior adsorption performance toward CIP with concentrations of 5, 10 and 50 mg/L, and for 50 mg/L, the equilibrium adsorption capacity could reach 329.7 mg/g. The adsorption process is fast and can be described by the pseudo-second-order kinetic model. The relationship between pH value and Zeta potential demonstrated that electrostatic interaction dominated the adsorption process. In addition, competitive adsorption showed that the effect of Na⁺ was negligible but the effect of Ca²⁺ was dependent on its concentration. Humid acid (HA) could slightly promote the absorption of CIP by SMD2. After five rounds of adsorption-desorption, the equilibrium adsorption capacity of SMD2 still remained at 288.6 mg/g for 50 mg/L CIP. Notably, SMD2 presented likewise superior adsorption capacity for CIP with concentrations of 10 and 50 mg/L in Minjiang source water. All the results indicated that this synthesis method is universal and that SMD2 has potential as an adsorbent for CIP removal from aquatic environments.

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Introduction
Antibiotics have been applied to kill or inactivate microbes since 1936 and more than 250 antibiotics have been applied in the fields of human health, livestock breeding and agriculture. Consequently, the massive consumption and discharge of antibiotics have caused their ubiquity in surface water, ground-water, drinking water, soil and other media (Kaeseberg et al., 2018; Luo et al., 2019b; Pan and Chu 2017). In addition, extended exposure to antibiotics can result in the development of drug resistant microbes. This drug resistance along with the potential threat of antibiotic pollution to human health and aquatic organisms has aroused wide public concern.

Many physical, chemical and biological methods have been adopted to remove antibiotics from water (Abazari et al., 2019; Chen et al., 2019; Ding et al., 2016; Ma et al., 2018; Paul et al., 2012). Among these methods, chemical oxidation methods are efficient for treating antibiotic-containing wastewater (ACW) with high concentrations (Cai et al., 2019; Chen et al., 2019; Martin et al., 2015). Nevertheless, these
methods are inefficient for low-concentration ACW. As to biological methods, it is difficult to cultivate appropriate microorganisms that can survive in ACW. Adsorption has been widely adopted to remove organic and inorganic pollutants because of its high efficiency, mild reaction conditions and simple operation (Ali et al., 2018; Ersan et al., 2017; Jiang et al., 2017; Xiao et al., 2017; Zuo et al., 2016). To date, a number of adsorptive materials have been applied to the treatment of ACW (Dong et al., 2019; Joshi et al., 2017; Kalhori et al., 2017; Liu et al., 2018; Li et al., 2014; Qin et al., 2014). For example, it was reported that two FAU-type zeolites could be used to remove three different antibiotics (de Sousa et al., 2013; Li et al., 2016) studied the influence of the alkyl chain length of templating molecules on the adsorption performance of mesoporous silica toward quinolone antibiotics. Tian et al. (2019) combined biochar powder and permanganate to remove sulfamethoxazole and dissolved organics. Kong et al. (2019) found that lignin xanthate resin (LXR)-intercalated bentonite clay composite achieved superior removal performance for organic doxycycline hydrochloride (DCH) antibiotics.

Sorbents have been widely applied in the fields of wastewater treatment (Christl et al., 2012; Fu et al., 2015; You et al., 2016), drug loading (Jin et al., 2015; Knezevic and Durand, 2015; Wicklein et al., 2011), substance refinement (ide et al., 2011; Kohay et al., 2015) and so on because of their environmental friendliness, superior chemical and thermal stability, exchangeable interlayer ions and abundant reserves. Nevertheless, natural silicates have low adsorption capacity because of their small specific surface areas resulting from high crystallinity. Hence, synthesizing nanoscale silicates (Wu et al., 2013; Xie et al., 2015; You et al., 2016) or tailoring the pore structure of silicates (Kohay et al., 2015; Vieira and Pastore, 2014) had been adopted to enhance their adsorption performance. However, nanoscale adsorbents are subject to agglomeration, which is detrimental to the adsorption performance of adsorbents. In addition, it is difficult to separate nanoscale adsorbents from liquid media. As a result, poor operability and high cost impede their actual application. It has been reported that loading silicates on some matrices with good mechanical properties can overcome the above disadvantages and improve their adsorption performance by synergistic effects (Cai et al., 2016; Kalhori et al., 2017; Kong et al., 2019; Zhao et al., 2014).

Graphene oxide (GO) (Sun et al., 2017; Wang et al., 2019), chitosan (Jiang et al., 2014; Song et al., 2018; Zhao et al., 2014), polymers (Huang et al., 2013; Misra et al., 2017) and active carbon (Sun et al., 2016; Wu et al., 2015) are typically used as the matrix for composites. Among these matrices, more attention has been paid to polymers on account of their excellent chemical modifiability and mechanical properties. Polymer-functionalized composites can be fabricated by direct compounding, in-situ synthesis, template synthesis, self-assembly, etc. (Lofrano et al., 2016; Zhao et al., 2011). However, forming larger aggregates of nanoparticles during blending is a problem with compounding. For other methods, the hard part is how to assure that the nanoparticles incorporate solidly with matrix. The self-assembly technique forms composites by strong chemical bonds, weak hydrogen bonds, van der Waals, and electric/magnetic dipole interactions. Hence, this method is preferable to obtain nanocomposites in which nanoparticles adhere tightly to the matrix.

Polystyrene is one of the most common host materials used to prepare composite materials by incorporating NPs into polymers, such as fire-proof materials (Zhou et al., 2018) or adsorbents (Moon et al., 2016; Zhang et al., 2013), because of its simple synthesis, controllable size, stable structure and easy functionalization. In addition, the spherical shape of the adsorbent is beneficial for the transmission of fluid during column or field experiments. In this work, sulfonated polystyrene spheres (SPS) and magnesium silicate were selected as components to form composite materials by the self-assembly method. The method is similar to assembly with “Legos building blocks” where both SPS and magnesium silicate (MgSi) are decorated by hydroxyl phenol. Then Fe$^{3+}$ is used as a link to assemble the decorated components by the complexation interaction between hydroxyl phenol and Fe$^{3+}$. To test the composite adsorbents, ciprofloxacin (CIP), a third-generation quinolone, was adopted as model antibiotic because of its broad-spectrum antibacterial activity and widespread usage. Finally, we evaluated the adsorption performance of the composites and analyzed the adsorption mechanism.

1. Experimental section

1.1. Materials

Hydrochloride Dapamime (C$_{6}$H$_{12}$NO$_{2}$·HCl, 98%), Ciprofloxacin (CIP, C$_{17}$H$_{20}$F$_{3}$O$_{7}$, 98%) and Tris(hydroxymethyl)aminomethane (Tris, C$_{6}$H$_{12}$N$_{3}$O$_{3}$, 99%) were purchased from Aladdin Chemical Reagent Co., Ltd. Styrene (CP), ammonium hydroxide (25%, AR) and polyvinylpyrrolidone (PVP, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetraethyloxysilicate (TEOS, AR), 2,2′-Azobis (2-methylpropionitrile) (AIBN, AR), magnesium chloride (MgCl$_{2}$·6H$_{2}$O, 98%) and ammonium chloride (NH$_{4}$Cl, 99.5%) were obtained from Tianjin Fuchen Chemical Reagent Plant. All reagents were used without further purification.

1.2. Synthesis of Sulfonated Polystyrene Spheres/Magnesium Silicate (SPS/MgSi)

1.2.1. Synthesis of SPS

40 mg AIBN was dissolved into 15 mL styrene at room temperature, and labeled as solution A. 0.7 g PVP, 50 mL ethanol and 10 mL deionized water were transferred into a 250-mL three-necked round bottom flask, allowing PVP to dissolve completely. Then solution A was poured into the flask after removing the air by purging with flowing N$_{2}$, followed by raising the temperature to 70 °C and maintaining for 24 hr. in the absence of air. Finally, the sediments were collected by centrifugation and rinsed with water and ethanol three times. The white powder product (polystyrene spheres, PS) was obtained after drying at 60 °C overnight. In order to acquire SPS, 2 g PS was added into 20 mL concentrated sulfuric acid and reacted at 40 °C for 12 hr. After reaction, deionized water was poured slowly into the above solution. The collection method was similar to that used for PS.

1.2.2. Synthesis of MgSi

5.54 g Na$_{2}$SiO$_{3}$·9H$_{2}$O and 5 g Mg(NO$_{3}$)$_{2}$·6H$_{2}$O were respectively dissolved into 400 mL deionized water and 500 mL ethanol, marked as solution B and solution C. Solution C was added slowly into solution B, followed by stirring for 3 hr. MgSi powders were obtained by centrifugation and dried at 60 °C overnight.

1.2.3. Synthesis of SiO$_{2}$

6 mL TEOS and 20 mL ethanol were mixed to form solution D. 10 mL NH$_{3}$·H$_{2}$O and 40 mL ethanol were mixed to form solution E. Then, solution D was added slowly into solution E and stirred for 3 hr. The process of collection and drying was similar to that used for MgSi.

1.2.4. One-step synthesis of SPS/MgSi (SMD1)

A given amount of MgSi (5, 15, 30, and 50 mg) was dispersed into 25 mL dopamine solution (2 mg/mL) and 3 mL Tris buffer
solution (10 mmol, pH=8.5) under stirring for 1 hr. 100 mg SPS dispersed in 10 mL ethanol was transferred into the above solution, then 3 mL MOPS (100 mmol) buffer solution and 3 mL FeCl₃·6H₂O (0.24 mmol) were added followed by stirring for 6 hr. Centrifugation was used to collect the sediment. SPS/MgSi powder was achieved after drying at 60 °C overnight.

1.2.5. Two-step synthesis of SPS/MgSi (SMD2)
Firstly, SPS/SiO₂ was synthesized according to the synthesis process of SMD1. 50 mg SPS/SiO₂ was dispersed into 20 mL deionized water to form solution F. 530.5 mg NH₄Cl and 50.8 mg MgCl₂·6H₂O were dissolved into 30 mL deionized water and 1 mL NH₃·H₂O to form solution G. Then solution F and solution G were mixed and transferred into a 100-mL autoclave and reacted at 140 °C for 6 hr. Finally, the SMD2 samples were obtained by centrifugation and dried at 60 °C overnight.

1.3. Adsorption experiments
Adsorption kinetics experiments were carried out on 50 mg/L CIP solution without adjusting the pH value. A given amount of SMD1 or SMD2 (100 mg/L) was dispersed into the above solution for 4 hr. to reach adsorption equilibrium. At regulated time intervals, samples of the suspension were removed and immediately filtered through 0.22 μm filters purchased from Sinopharm Chemical Reagent Co., Ltd. of China, followed by analysis for the concentration of CIP. The adsorption capacity was calculated according to the decrease of the concentration of CIP.

Adsorption isotherm experiments were performed by mixing different concentrations of CIP in the range 5–200 mg/L and a given amount of SMD1 or SMD2 (100 mg/L) for 4 hr. The solid-liquid separation process was similar to that used for the adsorption kinetics experiments. The pH value was adjusted by 0.1 mol/L NaOH or 0.1 mol/L HCl, in order to investigate the effect of pH on the adsorption of CIP.

The selectivity of adsorption was evaluated by adding different concentrations of Na⁺ (0.1–1 mol/L), Ca²⁺ (0.1–1 mol/L) or humic acid (20–200 mg/L) during the adsorption process, wherein the concentrations of CIP and adsorbent were respectively 50 mg/L and 100 mg/L. For recyclability experiments, 50 mL ethanol and ammonium hydroxide (V/V=7:3) mixed solution was used as the eluent to desorb CIP from the adsorbent by immersion in the solution for 3 hr. The adsorbent was rinsed with deionized water until the rinse pH≈7. The regenerated adsorbent was used for adsorption experiments in subsequent cycles.

1.4. Characterization
Powder X-ray diffraction (PXRD) (Rigaku Mini Flex 600, Rigaku, China) was used to determine the crystalline phase of the obtained adsorbent. The morphology and detailed structure were investigated by scanning electron microscopy (SEM) (JSM-6700F, JEOL Ltd., Japan) and transmission electron microscopy (TEM) (JEM-2010, JEOL Ltd., Japan). A Fourier transform infrared (FT-IR) spectrometer (Nicolet iS10, Thermo Fisher Scientific, USA) was adopted to analyze the chemical bonding in the materials. The Brunauer–Emmett–Teller (BET) surface area of the powders was measured using a Micrometrics ASAP 2020 system (ASAP2020 HD88, Micromeritics Instrument Corp., USA). The surface charges of the adsorbent were examined by a Zeta potentiometer (NanoBrook Omnisense, Brookhaven, USA) at fixed pH values from 2.0 to 12.0. The Mg²⁺ and Ca²⁺ concentrations in the supernatant after adsorption equilibrium were measured by Inductively Coupled Plasma spectroscopy (ICP) (Optima 7000 DV, Perkin Elmer, USA). The concentration of CIP was detected by a UV–Vis spectrophotometer (UV-2550, Shimadzu, Japan) at 276 nm.

2. Results and discussion

2.1. Synthesis and characterization
Fig. 1 shows a schematic of the synthesis of sulfonated polystyrene sphere/ magnesium silicate (SPS/MgSi) composites obtained by one-step and two-step methods; the samples were respectively denoted as SMD1 and SMD2. The detailed procedures are described in the supporting materials. Briefly, the adsorption of dopamine on MgSi (or SiO₂) and SPS occurred firstly, followed by complexion between Fe³⁺ and the phenolic hydroxyl group of dopamine, promoting the formation of SPS/MgSi (or SPS/SiO₂) composite materials. Additionally, gallotannic acid was also adopted to provide phenolic hydroxyl groups; SPS/MgSi with a similar morphology (Appendix
A Fig. S1) was also obtained, demonstrating that this method is universal.

The relevant characterization results are presented in Fig. 2. As shown in Fig. 2a, both SMD1 and SMD2-0.15 show a prominent diffraction peak at 20° ascribed to SPS and peaks at 35° and 60° belonging to 2MgO·3SiO2·2H2O (JCPDS, 02-0035). Plainly, the intensity of the diffraction pattern of SMD2-0.15 is stronger than that of SMD1. It is possible that the hydrothermal treatment improved the crystallinity of MgSi. In addition, the intensity of diffraction peaks is related to the morphology of MgSi distributed on the surface of SPS (Wang et al., 2018). As displayed in Fig. 3d—i, for SMD1 samples, MgSi nanoparticles totally coated SPS. However, MgSi nanoparticles usually exist in the amorphous state, giving weak diffraction intensity. As for SMD2-0.15, MgSi clusters composed of interwoven nanoplates deposited in a dispersed fashion on the smooth surface of SPS, and this interwoven structure is beneficial for the exposure of crystal planes (220) and (−332). In addition, TEM images (Fig. 2h and i) also manifest the interwoven structure, and the EDS spectrum (Appendix A Fig. S2) confirms the existence of MgSi.

Concentrated sulfuric acid was adopted for the treatment of sulfonate polystyrene spheres (PS) in order to improve their hydrophilicity. As indicated in Fig. 2b, the peaks at 2863 cm\(^{-1}\) and 2923 cm\(^{-1}\) belong to the stretching vibration peaks of methylene C–H, the peaks located at 500–1000 cm\(^{-1}\) and 3000–3100 cm\(^{-1}\) can be assigned to absorption peaks of C–H in benzene rings, and the peak located at 1400–1700 cm\(^{-1}\) can be ascribed to the stretching adsorption peak of benzene ring C=C. However, a new peak at 1224 cm\(^{-1}\) for SPS can be assigned to the -SO\(_3\)H group, indicating the successful sulfonation of PS. For SMD1 and SMD2-0.15 samples, besides the peaks resulting from SPS, the peaks at 533 cm\(^{-1}\) can be assigned to the bending vibration peak of Si–O–Mg, and the peaks at 1018 cm\(^{-1}\) can be ascribed to the stretching vibration peak of Si–O–Si, which indicate the formation of SPS/MgSi core-shell structures.

Fig. 2c shows N\(_2\) adsorption-desorption curves for SMD1 and SMD2-0.15. As can be seen, both materials exhibit IV-type adsorption isotherm curves with an H3 type hysteresis loop. It can be found that the specific surface areas of SMD1 and SMD2-0.15 are respectively 33.20 and 118.65 m\(^2\)/g. The large specific area of SMD2-0.15 originates mainly from the interwoven structure, allowing it achieve superior adsorption performance.

### 2.2. Kinetics and thermodynamics of adsorption

The mass ratio of MgSi and SPS is important for the adsorption performance of the composite materials. Therefore, four mass ratios (SMD2-0.05, SMD2-0.15, SMD2-0.3, and SMD2-0.5) were designed where the number, such as 0.05, 0.15, 0.3 and 0.5, represents the mass ratio of MgSi and SPS. It was found that SMD2-0.15 presented the optimum adsorption performance (Appendix A Fig. S3). In consequence, SMD2-0.15 was used in subsequent experiments.
The dependence of adsorption capacity on time for SMD2-0.15 and relevant adsorbents is shown in Fig. 3a. Clearly, the adsorption capacities of the composite materials SMD1 and SMD2-0.15 are higher than those of MgSi and SPS, and the former can reach adsorption equilibrium within 25 min. The equilibrium adsorption capacity \( Q_e \) is respectively 306.7 mg/g and 329.7 mg/g for SMD1 and SMD2-0.15. In contrast, MgSi and SPS could reach adsorption equilibrium within 120 min and their \( Q_e \) were only 121.0 mg/g and 144.8 mg/g, respectively, markedly lower than those of SMD1 and SMD2-0.15. Fig. 3b displays that the relationship between \( Q_e \) and time for different initial concentrations of CIP. It can be found that adsorption equilibrium is reached in 25 min for 50 mg/L and 10 mg/L CIP. However, 10 hr was required to reach adsorption equilibrium for 5 mg/L CIP. In the first 2 hr, the adsorption velocity was slow, and the adsorption capacity was below 10 mg/g. From 2 to 6 hr, the adsorption velocity accelerated greatly, and the adsorption capacity increased sharply to 35 mg/g. After 6 hr, the adsorption capacity increased slightly until equilibrium was attained.

Adsorption kinetics equations for different initial concentration CIP are shown in Fig. 3c, and the fitting parameters are listed in Table 1. The high correlation coefficient indicated that the adsorption behavior of SMD2-0.15 toward CIP is consistent with the quasi-second order kinetic model, and the fitted adsorption capacity is close to the experimental value (329.70 mg/g, 48.37 mg/g and 38.40 mg/g for 50 mg/L, 10 mg/L and 5 mg/L), manifesting that the adsorption of CIP by SMD2-0.15 is a kind of chemical process.

The dependence of the adsorption capacity of SMD2-0.15 for CIP on the equilibrium concentration at room temperature is presented at Fig. 2d, and the inset shows the Langmuir fitting curve. The adsorption behavior of SMD2-0.15 toward CIP is in line with the Langmuir isothermal model (Appendix A Table S1), and the fitted maximum adsorption capacity is 697.12 mg/g. The maximum adsorption capacity is an important index for evaluating the adsorption performance of an adsorbent. Table 2 lists the adsorption capacities of different adsorbents. Clearly, SMD2-0.15 exhibits superior adsorption performance compared to these absorbents.

### 2.3. Zeta potential and the effect of pH on the CIP removal

The pH value is also an important factor affecting the adsorption properties, since it is related to both the surface charge of the adsorbents and the protonation of adsorbates, in turn impacting the interaction between adsorbents and adsorbates. As shown in Fig. 4a, when the pH value is higher than 2, the surface of SMD2-0.15 has a negative charge and the amount of charge increases gradually to a stable level with the increase of pH value. In addition, the dissociation constants

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**Fig. 3** – (a) The dependence of adsorption capacity \( Q_t \) on time for MgSi, SPS, SMD1 and SMD2-0.15, (b) the dependence of adsorption capacity \( Q_t \) on time for different initial concentrations of CIP, (c) the fitted kinetic curves for CIP with concentration 5, 10 and 50 mg/L, (d) the variation of \( Q_e \) with the equilibrium concentration for SMD2-0.15.

**Table 1 – Kinetic parameters for the adsorption of CIP fitted by the pseudo-second-order kinetic model for SMD2-0.15.**

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Constant</th>
<th>5 mg/L</th>
<th>10 mg/L</th>
<th>50 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-second-order</td>
<td>( K_2 ) (g mg/min)</td>
<td>0.0247</td>
<td>0.0213</td>
<td>0.0025</td>
</tr>
<tr>
<td>R²</td>
<td></td>
<td>0.9985</td>
<td>0.9999</td>
<td>0.9998</td>
</tr>
<tr>
<td>kinetic model</td>
<td>( Q_e ) (mg/g)</td>
<td>39.11</td>
<td>49.16</td>
<td>329.70</td>
</tr>
</tbody>
</table>
of CIP are respectively $pK_a1=6$ and $pK_a2=8.7$. As such, CIP is mainly in the cationic form (CIP$^+$) when pH is less than 6. Therefore, SMD2-0.15 can absorb CIP by electrostatic interaction, and the adsorption capacity reaches the maximum value at pH=6. By contrast, CIP$^-$, when pH is higher than 8.7, is more prone to electrostatic repulsion from negatively charged SMD2-0.15, inducing a severe decrease of the adsorption capacity. The above results demonstrate that electrostatic interaction plays a dominant role during the adsorption process. Fig. 4b shows the dependence of surface charge on the pH value for SPS, SMD1 and SMD2-0.15. It can be found that SPS alone has a low adsorption capacity despite carrying high negative surface charge. After complexation with MgSi, both SMD1 and SMD2-0.15 exhibited high adsorption capacity, indicating that the synergistic effect of the two has a beneficial effect on CIP removal. Moreover, by comparison of the surface charges and adsorption capacities of SMD1 and SMD2-0.15, we found that the load state of magnesium silicate also affects the adsorption capacity of the composite materials. The interwoven structure of MgSi is beneficial for providing a larger specific surface area and greater surface charge, so SMD2-0.15 shows a higher adsorption capacity than that of SMD1.

2.4. The effect of ionic strength on CIP removal

Typically, there are large numbers of inorganic ions and some dissolved organic matter in actual water systems. Fig. 5a shows the influence of Na$^+$ and Ca$^{2+}$ with different concentrations on the adsorption of SMD2-0.15 toward CIP. Plainly, the influence of Na$^+$ was almost negligible, but the influence of Ca$^{2+}$ was dependent on the concentration. 0.1 mol/L Ca$^{2+}$ only caused the adsorption capacity to decrease to 323.01 mg/g. However, when the Ca$^{2+}$ concentration rose to 1 mol/L, the adsorption capacity decreased to 196.92 mg/g. In this case, more SMD2-0.15 was used to reduce the negative effect of Ca$^{2+}$. As shown in Appendix A Fig. 54, the use of more SMD2-0.15 can partially lessen the negative effect, but this compensation action leveled off when the additive amount of SMD2-0.15 was over 0.8 g/L, with adsorption capacity of 237.5 mg/g. Therefore, for a CIP solution containing a high Ca$^{2+}$ concentration, it is preferable to remove Ca$^{2+}$ firstly followed by removing CIP. Studies indicated that Ca$^{2+}$ and CIP can form a soluble complex (Cheng et al., 2019), thus changing the existence form of CIP in aqueous solution, and ultimately reducing the removal efficiency. As shown in Appendix A Table S2, no changes occurred for the concentration of Ca$^{2+}$ before or after adsorption in the presence of low- and high-concentration Ca$^{2+}$, indicating the possibility of a soluble complex, such as Ca-CIP.

Fig. 5b displays the influence of humic acid with different concentrations on the adsorption capacity of SMD2-0.15 toward CIP. Notably, the adsorption capacity increased from 330.2 to 349.8 mg/g when the concentration of humic acid increased from 0 to 100 mg/L, demonstrating that humic acid can slightly promote the adsorption of CIP. CIP is a strong $\pi$-acceptor on account of the nitrogen aromatic heterocyclic, therefore a slight amount of humic acid adsorbed by SMD2-0.15 can slightly promote the adsorption of CIP via $\pi-\pi$ interaction (Luo et al., 2019a).

2.5. Recycling experiment and CIP removal from Minjiang source water

As shown in Fig. 5c, the adsorption capacity of SMD2-0.15 was 288.6 mg/L after five rounds of adsorption-desorption cycles. Fig. 5d indicates the adsorption performance of SMD2-0.15 toward CIP in Minjiang source water. As shown in Appendix A Table S3, the pH value of Minjiang resource water is 6.88, which is suitable for the adsorption of CIP on SMD2-0.15. The total dissolved solids (TDS) indicates that the concentration of total soluble substances is relatively low. The adsorption capacity of SMD2-0.15 could reach 48.66 and 303.68 mg/L for CIP with initial concentration of 10 and 50 mg/L, prepared in Minjiang source water, indicating the potential of SMD2-0.15 in real water applications.

### Table 2 - Maximum adsorption capacity of CIP for other adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>White clay</td>
<td>3.26</td>
<td>(Li et al., 2011)</td>
</tr>
<tr>
<td>Chitosan/Biochar</td>
<td>76.0</td>
<td>(Afzal et al., 2018)</td>
</tr>
<tr>
<td>Carbon xerogel</td>
<td>112</td>
<td>(Carabiniero et al., 2012)</td>
</tr>
<tr>
<td>Carbon nanofiber</td>
<td>198.8</td>
<td>(Li et al., 2015)</td>
</tr>
<tr>
<td>KOH-activated graphene</td>
<td>194.6</td>
<td>(Yu et al., 2015)</td>
</tr>
<tr>
<td>Biocomposite fiber</td>
<td>16.0</td>
<td>(Carabiniero et al., 2011)</td>
</tr>
<tr>
<td>Sodium alginate/graphene oxide</td>
<td>235.6</td>
<td>(Fei et al., 2016)</td>
</tr>
<tr>
<td>nanoporous carbon</td>
<td>123.86</td>
<td>(Li et al., 2017)</td>
</tr>
<tr>
<td>SMD2-0.15</td>
<td>697.12</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 4 – (a) The effect of pH value on the Zeta potential and $Q_a$ for SMD2-0.15, (b) the effect of pH value on the Zeta potential for MgSi, SPS, SMD1 and SMD2-0.15.
3. Conclusion

In this work, SPS/MgSi composite materials were assembled by a method like building with Lego blocks, where Fe$^{3+}$ served as a link to connect SPS and MgSi decorated by hydroxyl phenols based on the complexation between the Fe$^{3+}$ and phenolic hydroxyl groups. MgSi has an interwoven structure and is distributed on the surface of SPS, allowing it exhibit a large specific area and high surface electro-negativity. As such, the composite materials appear to have superior adsorption capacity, 329.7 mg/g under the optimum conditions. In addition, SMD2-0.15 also presents high adsorption capacity toward CIP in Minjiang source water. Five-round recycling experiments along with investigation of competitive adsorption between CIP and inorganic ions or dissolved organic matter (humic acid for example) demonstrate that SPS/MgSi (SMD2-0.15) has potential as an adsorbent for CIP removal from aquatic environments.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.03.016.

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