Microporous spongy chitosan monoliths doped with graphene oxide as highly effective adsorbent for methyl orange and copper nitrate (Cu(NO₃)₂) ions

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ABSTRACT

In the current study, microporous spongy chitosan monoliths doped with small amount of graphene oxide (CSGO monoliths) with high porosity (96–98%), extraordinary high water absorption (more than 2000%) and low density (0.0436–0.0607 g cm⁻³) were prepared by the freeze-drying method and used as adsorbents for anionic dyes methyl orange (MO) and Cu²⁺ ions. The adsorption behavior of the CSGO monoliths and influencing factors such as pH value, graphene oxide (GO) content, concentration of pollutants as well as adsorption kinetics were studied. Specifically, the saturated adsorption capacity for MO is 567.07 mg g⁻¹, the highest comparing with other publication results, and it is 53.69 mg g⁻¹ for Cu²⁺ ions. Since they are biodegradable, non-toxic, efficient, low-cost and easy to prepare, we believe that these microporous spongy CSGO monoliths will be the promising candidates for water purification.

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1. Introduction

Nowadays water contamination has become a great problem and a global environmental concern. Wastewater often contains many kinds of toxic dyes or heavy metal ions, arising from many industries, such as metallurgical, mining, chemical manufacturing, and battery manufacturing industries [1]. To achieve efficient removal of these ions and dyes, several concurrent technologies are being developed, for example, adsorption, ion exchange, osmosis, sedimentation and membrane processes [2–6]. Among these technologies, adsorption has attracted considerable attention due to its high efficiency, economic feasibility and simply operating [5]. Adsorption is the surface phenomenon where pollutants are adsorbed on the surface of an adsorbent via physical or chemical forces. In this regard, porous materials are good candidates for adsorbents because of its high surface areas and connected pores. Porous materials are primarily fabricated by two methods: porogen and non-porogen methods, in which foam forming, particle leaching, and freeze-drying are typical porogen methods [5,7]. Among these porogen methods, freeze-drying or lyophilization is the simplest way and widely applied to prepare porous materials [9–13].

Natural biomasses as adsorbents are drawing more and more attentions because of their biodegradability, biocompatibility and renewability [14,15]. As one of the most representative biopolymers, chitosan (CS) is a multifunctional polysaccharide comprising of copious chelating groups including primary and secondary hydroxyl groups, as well as highly reactive amino groups [16,17]. Meanwhile, it is low-cost, non-toxic and biodegradable, so it has been considered as a green adsorbent for the removal of metal ions and dyes [14,18,19]. However, the applications of chitosan are limited because of its solubility in acid solution. Hence, it is necessary to crosslink chitosan in order to make it stable in acid solution [20]. Additionally, the enhancement of the adsorption capacity of chitosan-based adsorbents is highly expected. For this aim, there have been many investigations on the chemical activation of chitosan to increase its adsorption capacity, such as thiourea-modified CS [21], EDTA- and/or DTPA-modified CS [22], reactive blue 2 dye-modified CS [23] and N-Succinyl modified CS [24]. These chemical modifications can improve adsorption properties to some degree, but usually complicated processes are involved. Therefore, a simple strategy for an effective absorbent is highly desired.

Graphene is a one-atom-thick two-dimensional (2D) layer of sp²-bonded carbon materials with lots of outstanding features, such as superior chemical stability, large surface-to-volume ratio, mechanical flexibility, high thermal conductivity and thermal stability [25–27]. Being one of the graphene derivatives, GO has gained considerable attention as a significant adsorbent as plenty of oxygen atoms on the graphitic backbone of GO in the forms of
epoxy, hydroxyl, and carboxyl groups, protruding from its layers [20,28]. These groups result in interesting binding capacity to metal ions [20] and organic dyes [29]. In addition, the huge surface area of GO (2630 m² g⁻¹) will endow it a large adsorption capacity [1]. What is more, as a significant carbonaceous layered material, the GO incorporation can enhance the strength of polymer composites [5]. Therefore, it will be interesting to prepare porous CS materials with incorporation of GO.

In this work, highly microporous spongy chitosan doped with small amount of graphene oxide (CSGO monoliths) were prepared by freeze-drying, i.e., lyophilization, and their adsorbing behavior for anionic dyes methyl orange (MO) and Cu²⁺ ions was systematically studied. Its saturated adsorption capacity for MO is 567.07 mg g⁻¹ in the current condition, which is the highest when compared to those existing literature, and the saturated adsorption capacity for Cu²⁺ ions is 53.69 mg g⁻¹. Meanwhile, the effects of pH value, concentration of pollutants, content of graphene oxide on the adsorption for MO and Cu²⁺ as well as adsorption kinetics were studied.

2. Experiment

2.1. Materials

CS (Mn = 700 K, DD (degree of deacetylation) = 95%) was purchased from Zhejiang Yuhuan Marine Bio-chemical Co., Ltd. GO was prepared by Hummer’s method, and the detail about its synthesis could be found elsewhere [30]. Methyl orange (MO), copper nitrate (Cu(NO₃)₂), nitric acid, sodium hydroxide and methyl aldehyde were purchased from commercial suppliers (Sinopharm, Beijing) and used without further purification.

2.2. Preparation of microporous CS and CSGO monoliths

Firstly, 0.5 g CS was dissolved in 12 mL aqueous acetic acid 1% (V/V) to form CS solution. Various amounts of GO aqueous solution (1.6 mg mL⁻¹) were added to the prepared CS solution and then treated by a Vibra-Cell sonicator with a steel horn of 13 mm in diameter (JY-92IIN, 650 W, China) for 15 min (working time 2 s and interval time 3 s, 20% of the full output power) in an ice bath to yield homogeneous CSGO solution, followed by stirring for 3 h. Subsequently, 50 mL 2% (V/V) methyl aldehyde aqueous solution was added to the CSGO mixture dropwise with stirring and then kept stirring for 30 min. After that the mixture was stand under static conditions for 3 h. Finally, the mixture was poured into 50 mL centrifuge tube and was frozen below −18 °C. The solidified mixture was then transferred to a lyophilizer (FD-1CE, Boyikang Co., Ltd., Beijing) with a condenser temperature of −55 °C and inside pressure 20–30 Pa. After 2-day lyophilization process the microporous CSGO monoliths were obtained. In order to remove excess acetic acid, the obtained porous CSGO monoliths were dipped in anhydrous ethanol containing a small amount of sodium hydroxide for 1 h then taken out and rinsed with anhydrous ethanol. The treated microporous CSGO monoliths were dried under vacuum (vacuum degree: 0.1 MPa) at 27 °C for 72 h.

In this case, CSGO monoliths with different GO contents, which are 0.16 wt%, 0.32 wt%, 0.64 wt%, 0.96 wt% were prepared, respectively. Similarly, CS monoliths were prepared in the absence of GO.

2.3. Calculation of the water absorption of microporous CSGO monoliths

The CSGO monoliths were put into deionized water for 1 h, and their water adsorption was calculated according to the following equation:

Water absorption (%) = \( \frac{m_t - m_0}{m_0} \times 100\% \)

where \( m_0 \) (g) and \( m_t \) (g) are the weight of the CSGO monoliths before and after immersing into deionized water respectively.

2.4. Porosity and density of microporous CSGO monoliths

The porosity and apparent density of the porous CSGO monoliths were calculated according to the following equation:

\[
\text{Porosity} (\%) = \left( \frac{V_t - V_a}{V_t} \right) \times 100\% = \left( \frac{V_t - m_a/\rho}{V_t} \right) \times 100\%
\]

\[
\text{Density} = \frac{V_t}{m_a}
\]

where \( V_t \) (cm³) is the total volume of CSGO monoliths, \( V_a \) (cm³) is the actual volume of the material, \( m_a \) (g) is the mass of the monoliths, and \( \rho \) (g cm⁻³) is the actual density of the material. Each sample was measured in triplicate and the average value was adopted.

2.5. Batch adsorption experiments

The stored MO and copper nitrate solution were prepared by directly dissolving these compounds with known weight in deionized water. Batch adsorption experiments were carried out in 25 ml flasks, where \( m = 0.013–0.015 \) g of the adsorbents were put into \( V = 13–15 \) mL of MO or Cu²⁺ ions aqueous solutions (the \( V/m \) was kept at 1 L/g) and allowed to adsorb at room temperature (26 ± 1 °C) without stirring or shaking. At given time intervals, the concentrations of pollutant solutions were measured and adsorbents were collected. The MO concentration was determined by the absorbance at 464 nm in the ultraviolet–visible (UV–vis) spectrum (UV-2550, Shimadzu, Japan) while the concentrations of Cu²⁺ ions were determined by using an atomic absorption spectrometer (PinAAcle 900T, PerkinElmer, US).

The adsorption capacity (Q) and adsorption efficiency (Ade) were calculated according to the following equation:

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

\[
\text{Ade} (\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%
\]

where \( C_0 \) (mg L⁻¹) and \( C_t \) (mg L⁻¹) are the concentrations of pollutants in solution at the beginning and \( t \) h, \( V \) (L) is the volume of solution and \( m \) (g) is the mass of the adsorbent. \( Q_t \) (mg g⁻¹) is the apparent adsorption capacity of the porous monoliths after \( t \) h, which if given a long enough adsorption period (the time required to achieve the equilibrium adsorption state), is equal to the equilibrium adsorption capacity \( Q_e \) (mg g⁻¹).

The time required to achieve the equilibrium adsorption state \( (t_e) \) was determined by the adsorption kinetic curve. The adsorption time in the adsorption experiments measuring \( Q_t \) was set longer than \( t_e \). The isotherm measurement was conducted by changing the initial concentration of the pollutant solutions.

2.6. Characterization

X-ray powder diffraction data were collected on MSAL-XD2 with Cu Kα radiation (\( \lambda = 0.1542 \) nm) at 36 kV and 20 mA. Scanning electron microscopy testing was carried out on a field emission SEM (Hitachi S-4800) at an accelerating voltage of 10 kV. Thermogravimetric analyzer curves were determined by SDT-Q600 analyzer (TA Corp., US) at a heating rate of 10 °C min⁻¹ in N₂.
atmosphere. UV–visible spectra were recorded on a UV-2550 (Shimadzu Corporation, Japan) at room temperature.

Fourier transform infrared spectroscopy was carried out on a Nicolet VERTEX 70 (Bruker) spectrometer using the attenuated total reflectance (ATR) method from 4000 to 400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). The spectrum was generated and collected 16 times and corrected for the background noise. The experiments were performed on the samples directly, without KBr addition.

X-ray photoelectron spectrometer (XPS) measurements were taken via an ESCALAB250Xi (Thermo Scientific, USA) using a unmonochromatic Al K\(_\alpha\) line at 1486.6 eV in an ultra-high-vacuum system with a base pressure 3 \(\times\) 10\(^{-9}\) mbar and an analyzer pass energy of 150 eV, giving a full width at half-maximum of 1.7 eV for the Au 4f\(_{7/2}\) peak. The binding-energy scale was calibrated by assigning the main C1s peak at 284.8 eV. The XPS core-level spectra were analyzed by decomposing each spectrum into individual mixed Gaussian–Lorentzian peaks.

3. Results and discussion

3.1. Characterization of the CSGO monoliths

Fig. 1 shows the optical (a and b) and SEM images (c–f) of the CSGO monoliths (GO: 0.32 wt%), indicating the microporous structure of the prepared CSGO. Table 1 reveals water absorption, porosity and density of the prepared CSGO monoliths with different GO contents. All the obtained monoliths have high porosity (ca. 96–98%), extraordinary high water absorption ability (ca. 2100–2300%) and low density (ca. 0.0436–0.0644 g cm\(^{-3}\)). The high porosity and water absorption ability should contribute to the diffusion of dyes and metal ions to the surface and interior regions of the microporous CSGO monoliths, leading to high adsorption abilities and rates for dyes and metal ions.

Fig. 2 displays intuitively the water absorption ability and shape recovery ability after being compressed in the water adsorbed state. A slight volume increase in the CSGO monolith (GO: 0.32 wt%) after being immersed in water is revealed (Fig. 2a and b). And the shape can be quickly recovered after being pressed in the impregnated state (Fig. 2c–e). When the spongy CSGO monoliths (GO: 0.32 wt%) contact MO solution, it can rapidly adsorb the MO solution (Fig. 2f–h).

![Fig. 1. Optical images (a and b), SEM images of cross-sections (c and d) and vertical-sections (e and f) of the CSGO monoliths (GO: 0.32 wt%).](image-url)
Fig. 3 shows the XRD spectra of CS, GO and CSGO monoliths with different GO contents. Both the pure CS and CSGO monoliths show a characteristic peak at about 2θ = 15° and 20° attributed to chitosan [31], and no changes are observed with the increase in GO content, indicating that the GO has no obvious influence on the crystalline properties of CS [5]. Meanwhile, the characteristic diffraction peak of GO at 2θ = 12.36° is not clearly demonstrated in the CSGO monoliths because of its low content and there is just a small peak at 2θ = 9.86° which can be attributed to the shift of characteristic diffraction peak of GO, indicating the interlayer distance between the carbon layers of GO changes [32,33]. We calculated the change in the interlayer distance according to Bragg’s law and found that the interlayer distance of GO in the CSGO monolith (GO: 0.32 wt%) increases from 0.7162 nm to 0.8971 nm, implying that a significant fraction of the amines of the chitosan were inserted between the GO layers [32–34].

To further study the change in GO in the CSGO monoliths, UV–vis absorption spectra of GO in aqueous solution and chitosan acetic acid solution (GO: CS = 0.32 wt%) were obtained with the background of solution deducted (Fig. S1). The UV–vis spectrum of GO in water shows an absorption peak at 230 nm and this peak is not changed in chitosan acetic acid solution, suggesting that the electronic conjugation within the graphene sheets is not varied during the ultrasound and dissolution process in chitosan acetic acid solution [35,36].

Fig. 4 shows the FTIR spectra of CS, GO and CSGO monoliths with different GO contents. Spectra of GO show characteristic absorption bands of vibration of C=O at 1042 cm⁻¹ and the stretching vibration of carboxyl groups on the edges of the layer planes or conjugated carbonyl groups at about 1716 cm⁻¹, respectively [37–39]. Further, the band at 1620 cm⁻¹ can be attributed to the C=C stretching mode of the sp² carbon skeletal network [32]. In comparison, all the GO-related peaks are not detected in the CSGO spectra because of GO’s low content. It is noteworthy that the broad band at 3200–3400 cm⁻¹ is attributed to the stretching vibration mode of —OH and —NH₂ (N—H) group [32,40], and it decreases in intensity and becomes smoother in CSGO monoliths, suggesting that hydrogen bonding is formed or strengthened [41,42]. So we can conclude the —OH and —NH₂ groups of chitosan react with oxygen-containing functional groups of GO (carboxyl and epoxy groups) to form hydrogen bonding. In addition, the intensity of the amino absorption band at 1401 cm⁻¹ [32] enhanced gradually with the increasing loading of GO compared with the intensity of the amino group of —NHCO— (amide I) at 1646 cm⁻¹ [32,40], suggesting that the amino groups from the CS component can react with epoxy functional groups of GO, as recently revealed by Deliyanni in the graphite oxide and magnetic chitosan system [32].

To further confirm the above issue, X-ray photoelectron spectra of GO, CS monolith and CSGO monolith (GO: 0.96 wt%) were
analyzed (Fig. 5). The peak at the position of 284.8 eV is assigned to non-oxygenated carbon (C–C/C–C), whereas the peak at 286.5 eV is assigned to carbons bound to oxygen, as either epoxy or hydroxyl. The peak at 288.0 eV is attributed to C=O [31,32,43] while the peak at 285.7 eV is attributed to C–N [44]. The degree of oxidation of GO is 40.5% derived from the C1s spectra of GO. Also, the XPS spectra of CSGO monolith display no obvious changes in the C1s spectrum in comparison with CS monolith because of the low content of GO. However, there is still a weak decrease in the content C–C/C–C when doped with 0.96 wt% GO from 17.1% to 14.6% (Table 2), very likely due to the contribution of GO. The result reveals that GO still exist as its pristine state without being reduced in the CSGO monoliths, which is consistent with the result of UV–vis absorption spectra. The O1s spectra were curve-fitted by two peaks: the first peak at 532.2 eV is due to O–H groups, and the second at 533 ± 0.2 eV is relevant to O–C moieties (epoxy, carboxyl groups) [32]. The peak attributed to O–H groups increased in the CSGO monolith from 44.4% to 63.0% (Table 2), indicating the hydroxyl formation by the reaction of the chitosan amino groups with the oxygen-containing functional group of GO, which is consistent with the above FTIR result.

Thermogravimetric (TG) analysis was carried out to investigate thermal decomposition behavior of the CSGO monoliths, as shown in Fig. 6. The differential thermogravimetry (DTG) curve of CSGO presents two peaks with maxima at 150 and 250 °C, corresponding to the two weight loss stage of the thermogravimetry curve. The first peak is related to the decomposition of surface functional groups of GO and the second peak related to the degradation of chitosan according to the previous reports [32,45] and the curves of pure GO and CS in the current condition. The CSGO monoliths show slightly lower thermal decomposition temperatures than neat CS, while they are almost identical regardless of the different GO contents, indicating that GO has almost no effect on the thermal stability of the CSGO material at low content.

3.2. Adsorption of MO by CSGO monolith

3.2.1. Effect of pH, GO content and initial MO concentration

Fig. 7a shows the adsorption efficiency for MO of the microporous CSGO monoliths, with 0.32 wt% GO, in 400 mg L\(^{-1}\) MO aqueous solution with different pH values, which were adjust at first and allowed to be free during adsorption. The adsorption ability of the microporous CSGO monoliths for MO is weakly influenced by the pH values at pH 5.32–9.43, with adsorption efficiency decrease very weakly. The adsorption efficiency reaches the maximum at pH 4.19. At lower pH, the amino groups of the CS macromolecules become protonated, and electrostatic attraction between the MO and the protonated amino groups may contribute to the adsorption of the MO onto the CSGO monoliths.

Fig. 7b shows the adsorption efficiency for MO adsorption of the microporous CSGO monoliths in 400 mg L\(^{-1}\) MO aqueous solution at pH 6.78 with different GO contents. When the GO content is 0.16 wt%, the adsorption ability of the CSGO monolith improves weakly compared to CS monolith, but a marked enhancement followed with more GO content (0.32 wt%), and no further increase for more GO addition. This observation indicates that the incorporation of GO can indeed increase the adsorption capacity of CS.

Fig. 4. FTIR spectra of CS (a), neat GO (f) and CSGO monoliths with different of GO loading (b–e).

Fig. 5. C1s XPS spectra of GO (a), CS monolith (b), and CSGO (GO: 0.96 wt%) monolith (c); O1s XPS spectra of CS monolith (d) and CSGO (GO: 0.96 wt%) monolith (e).
However, the existence of carboxyl groups might reduce the adsorption capacity of the amine groups due to the electrostatic forces between the carboxyl and amine groups, which may decrease the adsorption capacity of the microporous CSGO monoliths, and cause the limited growth of the adsorption capacity with more GO incorporation [5]. Based on this result, we chose CSGO monolith with 0.32 wt% GO for the following studies.

Table 2  
XPS date of GO, CS monolith and CSGO (GO: 0.96 wt%) monolith.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s C–C/C=O (%)</th>
<th>C=O– and C–O– (%)</th>
<th>O1s O– (%)</th>
<th>O–H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>59.5</td>
<td>40.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CS</td>
<td>17.1</td>
<td>65.5</td>
<td>55.6</td>
<td>44.4</td>
</tr>
<tr>
<td>CSGO (GO: 0.96%)</td>
<td>14.6</td>
<td>67.8</td>
<td>37</td>
<td>63.0</td>
</tr>
</tbody>
</table>

Fig. 6. Thermogravimetry (TG) and differential thermogravimetry (DTG) curves of GO, CSGO and CS. (a) TG curves, (b) DTG curves.

Fig. 7c shows the $Q_e$ and $Ade$ for MO adsorption of the microporous CSGO monoliths (GO: 0.32 wt%, pH = 6.3 ± 0.3) with different initial MO concentrations.

However, the existence of carboxyl groups might reduce the adsorption capacity of the amine groups due to the electrostatic forces between the carboxyl and amine groups, which may decrease the adsorption capacity of the microporous CSGO monoliths, and cause the limited growth of the adsorption capacity with more GO incorporation [5]. Based on this result, we chose CSGO monolith with 0.32 wt% GO for the following studies.

Fig. 7c shows the $Q_e$ and $Ade$ for MO adsorption of the microporous CSGO monoliths with different initial MO concentrations. As the MO concentration increases, $Q_e$ gradually increases until it reaches a maximum value of 567.07 mg g$^{-1}$, which is the saturated adsorption capacity. In contrast, the $Ade$ shows a tendency of decrease as the MO concentration increases. This phenomenon can be easily understood. At high MO concentration, more MO molecules are adsorbed onto the microporous CSGO monoliths because of the adsorption–desorption equilibrium, which results in an increase in $Q_e$. Meanwhile, at higher MO concentration, more MO molecules are left in the solution because the total amount of more MO molecules is exceeds the adsorbing capacity of the microporous CSGO monoliths, leading to a reduction in $Ade$.

3.2.2. Effect of contact time (adsorption kinetics)

Fig. 8 shows the effect of contact time on adsorption in 400 mg L$^{-1}$ MO solution. For the CSGO monolith, very fast dye removal occurs at the initial stage (0–1 h). Then, the dye adsorption is milder and more gradual during the second time period (1–24 h). And at the last stage (24–72 h) the dye adsorption is characterized by the equilibrium state. The fast adsorption in the initial stage might be due to the fact that a large number of surface sites are available for adsorption. After a period of adsorption, the remaining surface sites are more resistive for the dye molecules to occupy because of the repulsion between the solute molecules of the solid and bulk phases, which makes it milder and takes a long time to reach equilibrium [32].
To investigate the controlling mechanism of the adsorption processes, pseudo-first-order and pseudo-second-order kinetic models were used to study the experimental data obtained.

The pseudo-first-order kinetic model is given as follows [19,46]

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t$$

The pseudo-second-order kinetic model can be expressed as follows [19,46]

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

where $Q_t$ and $Q_e$ are the amounts of MO adsorbed (mg g\(^{-1}\)) per unit of adsorbent at equilibrium and at time $t$, respectively. $k_1$ is the pseudo-first-order rate constant (h\(^{-1}\)). The rate constant ($k_1$) and correlation coefficients ($R^2$) are determined from the linear plots of $\log(Q_e - Q_t)$ versus $t$. $k_2$ is the pseudo-second-order rate constant of adsorption (g mg\(^{-1}\) h\(^{-1}\)). The linear plots of $\frac{t}{Q_t}$ versus $t$ are used to determine the rate constant ($k_2$) and correlation coefficients ($R^2$).

The linear fitting of pseudo-first-order and pseudo-second-order kinetic models is shown in Fig. S2 and the kinetic parameters resulting from the fitting equations are presented in Table 3. According to the correlation coefficients ($R^2$), the best fitting was obtained with the pseudo-second-order equation ($R^2 = 0.9997$), which is further confirmed by the fact that the calculative $Q_e$ ($Q_{\text{cal}}$), according to the linear equation of pseudo-second-order model is more close to the $Q_e$ obtained from the experiment ($Q_{\text{exp}}$).

### 3.2.3. Adsorption isotherm

The adsorption isotherm of MO on the CSGO monoliths is shown in Fig. 9. The isotherm can be classified as H-type (high affinity type), because the initial slope is very high, suggesting that there exists high affinity between MO and CSGO monoliths. Further studies reveal that the adsorption isotherm of MO on CSGO deviates seriously from the Langmuir isothermal equation ($R^2 = 0.8373$) and Freundlich isothermal equation ($R^2 = 0.7260$) (Fig. S3). This can be attributed to the limitations of the two equations. For example, the Langmuir isotherm is established based on the assumption that the surface of the absorber is homogenous, and every adsorption site has equal adsorbate affinity while the Freundlich equation is put forward as an empirical equation, which may be not suitable for the adsorption of MO by CSGO monoliths.

A comparison of the maximum adsorption capacity for MO on the prepared CSGO monolith with other publication adsorbents is shown in Table 4. The adsorption capacity of the prepared microporous spongy CSGO monolith is much higher than other reported adsorbents. So the prepared microporous spongy CSGO monoliths can be a kind of promising adsorbent for the removal of MO from aqueous solutions because it has much higher adsorption capacity than other adsorbents and it is low-cost, environmentally friendly and easy to prepare.

### 3.3. Adsorption of Cu\(^{2+}\) ions by CSGO monolith

Heavy metal ions are another type of water pollutant. We examined the Cu\(^{2+}\) ions adsorption ability of the CSGO monolith. According to our studies, the GO content has almost no effect on the adsorption (Fig. 10a). GO, in principle can enhance adsorption ability for metal ions when introduced into the porous material owing to the carboxyl groups located at the edges of the GO sheets. But the existence of carboxyl groups might reduce the chelating ability for metal ions when introduced into the porous material. According to our studies, the GO content has almost no effect on the adsorption ability of the prepared CSGO monolith for Cu\(^{2+}\) ions.

Fig. 10b shows the $Q_e$ for Cu\(^{2+}\) ions of the microporous CSGO monoliths in 150 mg L\(^{-1}\) Cu\(^{2+}\) aqueous solution with different pH values, indicating that the optimal pH for Cu\(^{2+}\) ions adsorption is 5, although the effect of pH is weak. At low pH, the amino groups of the CS macromolecules become protonated, and electrostatic repulsions between the Cu\(^{2+}\) ions and the protonated amino groups

**Table 3**

<table>
<thead>
<tr>
<th>Kinetic constants for the adsorption of MO onto CSGO monolith.</th>
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<tbody>
<tr>
<td><strong>Pseudo-first-order</strong></td>
</tr>
<tr>
<td>$Q_{\text{exp}}$ (mg g(^{-1}))</td>
</tr>
<tr>
<td>369.64</td>
</tr>
</tbody>
</table>
may prevent the adsorption of the Cu$^{2+}$ ions onto the CSGO monoliths [5,18]. At higher pH, precipitation phenomenon occurs for part of the Cu$^{2+}$ ions, depending on the total concentration of Cu$^{2+}$ ions [18], which also leads to a decrease in $Q_e$. On this account, pH 5 was chosen in our further studies.

Further studies show that the effect of initial Cu$^{2+}$ ions concentration on adsorption is similar to that of MO (Fig. S4a). Kinetic study exhibits a fast Cu$^{2+}$ ions removal stage (0–1 h), a milder and more gradual Cu$^{2+}$ ions removal stage (1–8 h) and an equilibrium stage (8–14 h) (Fig. S4b). The adsorption process is more aligned with pseudo-second-order kinetic model ($R^2 = 0.9966$) (Fig. S5) and the kinetic constants were calculated (Table S1). The saturated adsorption capacity is 53.69 mg g$^{-1}$, which is obtained by varying initial Cu$^{2+}$ ions concentration (Fig. 3c). The adsorption is fit to Langmuir isotherm ($R^2 = 0.9942$) (Fig. S6). Comparison with other adsorbents shows that the adsorption capacity for Cu$^{2+}$ ions of the prepared CSGO is not the highest (Table S2), but it is still acceptable while considering the low-cost and simple strategy.

4. Conclusions

In this paper we have prepared microporous spongy chitosan monoliths doped with small amount of GO by lyophilization as highly effective adsorbent for MO and Cu$^{2+}$ ions. The high porosity (ca. 96–98%) and water absorption (ca. 2100–2300%) make the microporous CSGO monoliths effective adsorbents for MO and Cu$^{2+}$ ions. The saturated adsorption capacity for MO is 567.07 mg g$^{-1}$, which is the highest when compared with other adsorbents, and it is 53.69 mg g$^{-1}$ for Cu$^{2+}$ ions. The adsorption capacity is a function of pH value, adsorbing time, the amount of doped GO and the initial concentration of pollutants. Specifically, the adsorption capacity for MO reaches a maximum when 0.32 wt% GO is incorporated into the monolith, while the adsorption capacity for Cu$^{2+}$ ions is weakly influenced by the GO loading. Since these monoliths are biodegradable, non-toxic, efficient, low-cost and easy to prepare, we believe that the microporous spongy CSGO monoliths will become the promising candidates for water purification, and the current investigations may pave the way to the easy fabrication of efficient CS-based microporous materials for water purification and environment remediation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2013.11.012.

References


Table 4

Comparison of the adsorption capacity of CSGO monolith for the removal of MO with other adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$Q_{\text{max}}$ (mg g$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Fe$_2$O$_3$/chitosan composite films</td>
<td>29.41</td>
<td>[46]</td>
</tr>
<tr>
<td>γ-Fe$_2$O$_3$/MWCNTs/chitosan</td>
<td>60.5–66.1</td>
<td>[47]</td>
</tr>
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<td>Hypercrosslinked chloromethylated PS adsorbent functionalized with formaldehyde carbonyl groups (HJ-1)</td>
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<td>Mesoporous magnetic Co-NPs/carbon nanocomposites</td>
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<td>Acid modified carbon coated monolith</td>
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<td>Calcined layered double hydroxides</td>
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<td>Alkali-activated multiwalled carbon nanotubes</td>
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<td>Pinecone derived activated carbon</td>
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<td>carbon nanotubes</td>
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<td>Chitin/alginate magnetic nano-gel beads (MCAs)</td>
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<td>Porous spongy CSGO monolith</td>
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