Study of adsorption properties of anionic dyes on graphene oxide/chitosan composite porous microspheres

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Abstract
Dyes wastewater produced during leather processing caused serious environmental pollution. Anionic dyes are always vital crisis in waste treatment. Removal of anionic dyes from tannery wastewater before their discharge into the environment is important for health and environment safety. The use of low-priced and biodegradable adsorbents could be a good method to minimize the environmental impact caused by dyes effluents. In this study, novel porous composite microspheres composed of graphene oxide and chitosan (GO/CS) were prepared. The morphology of the GO/CS porous composite microspheres were characterized using scanning electron microscopy. GO/CS porous microspheres were applied as adsorbent to remove the anionic dye in wastewater. The adsorption experiments were performed based on various parameters, such as initial anionic dye concentration, temperature, solution pH and contact time. The Langmuir and Freundlich isothermal models were employed to discuss the adsorption behavior. The results indicated that the anionic dyes adsorption by GO/CS porous microspheres could be described by Langmuir isothermal model. The maximum adsorption capacity reached 255 mg/g (at pH 3, 30°C). The kinetics data were analyzed using pseudo-first-order and pseudo-second-order, respectively. It was found that the pseudo-second-order model described the anionic dyes adsorption by GO/CS porous composite microspheres very well. Thermodynamic studies indicated that the adsorption of anionic dyes on GO/CS porous microspheres was an exothermic process. The present results show that the graphene oxide/chitosan composite porous microspheres can serve as a promising bio-adsorbent for the removal of anionic dyes from wastewater.

Keywords: adsorption, chitosan, graphene oxide, porous microspheres.

1 – Introduction

Water pollution due to the indiscriminate disposal of wastewater is a global environment concern. Wastewater from textiles, dyeing, rubber, printing, paper, plastic, and related industries contain various dyes. Most dyes have aromatic rings in their structures, which make them highly toxic, non-biodegradable, carcinogenic and mutagenic for human being and aquatic life (Hou 2012). Anionic dyes are always vital crisis in waste treatment. Removal of anionic dyes from tannery wastewater before their discharge into the environment is important for health and environment safety.

Various treatment process such as coagulation, flocculation, reverse osmosis, photo-degradation process and ion-exchange have been used to remove dyes from wastewater. However, these processes vary in their effectiveness, cost and environment impact (Chakraborty 2003). In this regard, adsorption appears to be an attractive method for treatment of dye effluents due to its low cost, simplicity of operation and wide-ranging available (Garg 2003).
Nowadays, one of the most promising adsorption methods for the removal of dyes is the application of chitosan. Chitosan can be produced commercially by chemical deacetylation of chitin. Chitin, a high molecular weight linear polymer of 2-acetamido-2-deoxy-D-glucopyranose units linked together by 1,4-glycosidic bonds (Wan Ngah 1998; Wan Ngah 2004), is the second abundant natural fiber, being similar to cellulose, the most abundant natural fiber, in many respects. The most abundant source of chitin is the shell of crab and shrimp (Juang 2002). Therefore chitosan contains a large number of -NH$_2$ and -OH groups and is able to remove dyes and metal ions from aqueous solutions. The performance of chitosan as adsorbent can be improved by: (i) the use of cross-linking reagents, which stabilize chitosan in acid solutions and enhance its mechanical properties and (ii) derivatization with grafting functional groups onto the chitosan backbone, which improve its adsorption capacity (Crini 2008).

Graphene oxide (GO), a novel 2D nanomaterial prepared from natural graphite, has recently attracted enormous attention owing to its unique structure and its superior chemical stability, excellent mechanical property, good biocompatibility and bactericidal potential (Hu 2010; Zhu 2010). The chemical groups of graphene oxide have been found to be a feasible and effective means of improving the dispersion of graphene. Additionally, functional side groups bound to the surface of graphene oxide may improve the interfacial interaction between graphene oxide and the matrix similarly to that observed for functionalized carbon nanotube-based nanocomposites (Colema 2004). These groups enable GO to be functionalized through covalent and noncovalent approaches, hence making it a building block for synthesizing versatile functional materials (Dreyer 2010). In addition, it has been reported that the epoxy groups in graphene oxide favor to react with primary amine group by addition, which has been widely used to modify graphene oxide. So it is possible to form a new mixture of chitosan and graphene oxide through the special interaction beside the H-bondings between them.

In this work, the aim was to explore and prepare GO/CS composite bioadsorbent with higher adsorption capacity. Acid red 18 was selected as model pollutant to evaluate the adsorption characteristics of GO/CS composite porous microspheres under laboratory conditions. The effect of various experimental parameters on acid red adsorption, such as the initial dye concentration, contact time, pH, and temperature were studied in detail.

2 – Material and Methods

2.1 Material

Chitosan was obtained from Jinhu Crust Co., Ltd in China (degree of deacetylation: 85%-90%) as a matrix material. Graphene oxide was purchased from Beijing. Acid red 18 (Chemical formula: C$_{20}$H$_{11}$N$_2$Na$_3$O$_{10}$, MW: 604.47 g/mol, AR) was purchased from Xiya Reagent (Chengdu, China). The other reagents (HAc, NaOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. in China and were used as received without further purification.

2.2 Preparation of GO/CS composite porous microspheres

A GO dispersion was prepared by sonicating GO for 30 min in ultrapure water. chitosan was prepared by dissolving 2.5 g chitosan in 100 mL (2.5% acetic acid) with different GO concentrations (the weight ratio of GO: chitosan was 0, 1:1000, 2:1000, 5:1000, respectively). The mixture was stirred vigorously stirred for 3 h, and then the mixture was ultrasound dispersed for 30 min to form a homogeneous solution. GO/CS composite microspheres were prepared by a drop-wise procedure into 3wt% sodium hydroxide solution. The beads so produced were allowed to harden by leaving them in the sodium hydroxide solution for 24 h and thereafter filtered and washed several times with distilled water to a neutral pH. Finally, the wet beads were dried in a freeze dryer.
2.3 Batch adsorption experiments

Batch adsorption experiments were conducted with GO/CS composite microspheres for the removal of acid red dye from aqueous solution. The desired concentration of dye was obtained by diluting a stock solution of acid red dye (1500 mg/L). The batch adsorption experiments were conducted in 100 mL conical flasks with 50 mL of solutions and 100 mg beads and performed for 12 h in a temperature-controlled water bath shaker. The concentration of acid red dye was measured using a UV-vis spectrophotometer at $\lambda_{\text{max}} = 517$ nm.

The adsorption capacity of acid red dye adsorbed by GO/CS microspheres at equilibrium, was evaluated using the following equation:

$$q = \frac{(c_0 - c_e)V}{m}$$

where $c_0$ and $c_e$ are initial and equilibrium concentrations acid red dye (mg/L), respectively, $m$ is the mass of adsorbent (g), $V$ is volume of the solution (L).

2.4 Characterization of GO/CS composite porous microspheres

Micro-structures of samples before and after adsorption were observed using a scanning electron microscope (SEM, JSM-6700F/INCA-ENERGY, Japan) and energy dispersive x-ray analysis (EDX).

3 – Results and Discussion

3.1 Characterization of GO/CS microspheres

Fig. 1 shows the cross-sectional images (left) and EDX (right) of pure CS beads (a: before adsorption, b: after adsorption) and GO/CS (2/1000) composite microspheres and (c: before adsorption, d: after adsorption). The microspheres were frozen in liquid nitrogen, and immediately snapped and then vacuum dried. With the incorporation of GO into chitosan, GO/CS composite microspheres show more porous structure, as shown in Figs. 1c (left). The porous structure is favorable for the dyes adsorption. The EDX spectrum in Fig. 1d (right) shows the presence of S peak in the cross-sectional area of GO/CS composite beads, suggesting the sorption of acid red dye.

Figure 1 SEM images (left) and EDX spectrum (right) of pure CS beads (a: before adsorption, b: after adsorption) and GO/CS (2/1000) composite microspheres and (c: before adsorption, d: after adsorption)
3.2 Effect of pH

The solution pH is the most important parameter to influence the adsorption as it can affect the chemical properties of both dye molecule and the adsorbent. The influence of pH from 2.0 to 7.0 on the removal of acid red was investigated and illustrated in Fig. 2.

![Figure 2 Effect of pH on the adsorption capacity of samples for Cr acid red 18](image)

To explain the effect mechanism of pH on adsorption, it is necessary to understand the surface charge on the adsorbent and adsorbate. The driving forces for anionic dyes adsorption could be given by the following equations:

\[ \begin{align*}
R-\text{NH}_2^+ + \text{H}^+ & \leftrightarrow R-\text{NH}_3^+ \\
\text{Dye-SO}_3\text{Na} \rightarrow \text{D-SO}_3^- + \text{Na}^+ \\
R-\text{NH}_3^+ + \text{Dye-SO}_3^- & \leftrightarrow R-\text{NH}_3^- \cdot \text{O}_3\text{S-Dye}
\end{align*} \]

Where R is the alkyl group originated from anionic dyes.

The optimum pH found for all adsorbents tested was acidic (pH=3). Increasing the pH of the solution, it is absolutely normal the weakening of forces and consequently the reduction of attraction/interaction between dye molecules and adsorbent.

3.3 Effect of initial concentration of acid red dye

![Figure 3 Effect of initial acid red concentration on the adsorption capacity of samples](image)

The effect of acid red concentration on the adsorption was evaluated in the range of 300-1800 mg/L at pH 3.0 (30 °C). Fig. 3 shows that the adsorption capacity of four adsorbents increased with increasing initial concentration of acid red dye. The maximum adsorption capacities are 232 mg/g, 255 mg/g, 214 mg/g, and 240 mg/g, respectively. The addition of GO can enhance the adsorption property of CS, which is possible due to its single atom-thick and two-dimensional sheet structure and the strong π-π interactions.
interactions between the benzene rings of acid red and the hexagonal arrays of carbon atoms in GO during adsorption.

3.4 Effect of contact time

The effect of contact time on adsorption is depicted in Fig. 4. The kinetic curves of adsorption obtained were qualitatively same as those in many papers. It is apparent that the adsorption is rapid in the initial 10 min and then it becomes slow till the equilibrium is reached. In the initial stage the high adsorption rate is probably due to rapid contact of acid red molecules with the active sites on the external surfaces of adsorbent. The following decreased rate is firstly attributed to the diminishing availability of the remaining active sites; secondly, long-range diffusion of dye molecules into the micro-pores of the adsorbent needs a long time to reach equilibrium.

Figure 4 Effect of time on the adsorption capacity of samples for acid red

3.5 Effect of temperature

The effect of temperature on acid red absorbed by chitosan and GO/CS composites is studied at various adsorption temperatures (303, 313, 323 and 333 K) with a constant initial acid red concentration of 1500 mg/L and show in Fig. 5. The equilibrium adsorption capacity of chitosan is found to decrease from 143 to 122 mg/g and the equilibrium adsorption capacity of GO/CS composite is found to decrease from 147 to 132 mg/g with increasing temperature from 303K to 333K, indicate that the adsorption acid red dyes onto chitosan and GO/CS composites is favored at lower temperatures and it is controlled by an exothermic process.

Figure 5 Effect of temperature on the adsorption capacity of samples for acid red
3.6 Adsorption isotherms

In order to describe the interactive behavior between the adsorbate and adsorbent and to predict the adsorption capacity of the adsorbent, Langmuir isotherm model and Freundlich isotherm model were used in the experiment (Fig. 6), respectively. The linear form of the Langmuir model could be expressed as follows:

\[ \frac{c_e}{q_e} = \frac{1}{q_{\text{max}}b} + \frac{c_e}{q_{\text{max}}} \]

The linear form of the Freundlich model could be expressed as follows:

\[ \ln q_e = \frac{1}{n} \ln c_e + \ln K_F \]

where \( c_e \) is the equilibrium concentration of acid red in aqueous solution (mg L\(^{-1}\)), \( q_e \) is the adsorption amount (mg/g) at equilibrium and \( q_m \) is the adsorption capacities of saturation, \( K_L \) represents enthalpy of sorption and should vary with temperature, and \( K_F \) and \( n \) are the Freundlich constants related to the sorption capacity and sorption intensity, respectively.

![Image](image.png)

Figure 6 Langmuir adsorption isotherms (right) and Freundlich adsorption isotherms (left) of pure CS and GO/CS composites

Table 1 reports the maximum adsorption capacities (\( q_{\text{max}} \)) and the other isothermal parameters resulted from the fitting. The correlation coefficients (\( R^2 > 0.996 \)) showed that the Langmuir model results in better fitting, suggesting that acid red dyes sorption on GO/CS is monolayer coverage.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir constant</th>
<th>Freundlich constant</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( q_{\text{max}} ) (mg/g)</td>
<td>( b ) (1/mg)</td>
</tr>
<tr>
<td>GO/CS(0/1000)</td>
<td>238.1</td>
<td>0.094</td>
</tr>
<tr>
<td>GO/CS(1/1000)</td>
<td>275.6</td>
<td>0.050</td>
</tr>
<tr>
<td>GO/CS(2/1000)</td>
<td>214.7</td>
<td>0.201</td>
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<tr>
<td>GO/CS(5/1000)</td>
<td>240.9</td>
<td>0.279</td>
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</tbody>
</table>

3.7 Kinetic studies

In order to investigate the controlling mechanism of adsorption process of chitosan and GO/CS composites for acid red, the pseudo-first order and the pseudo-second order kinetic models are cited to
evaluate the experimental data obtained from batch acid red dyes removal experiments (Fig. 7), all the corresponding parameters obtained from the linear plots are listed in Table 2.

The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k t$$

The pseudo-second order kinetics model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$$

Where $q_e$ and $q_t$ (mg/g) are the adsorption capacities at equilibrium and at time $t$, respectively. $k_1$ (min$^{-1}$) is the rate constant of the pseudo-first order adsorption. $k_2$ (g mg$^{-1}$ min$^{-1}$) is the rate constant of the pseudo-second order adsorption.

Table 2 presents the kinetic parameters resulted by fitting the models to the experimental data. According to the correlation coefficients ($R^2$) exported, the best fitting was for the pseudo-second order kinetic model ($R^2 \approx 0.999$).

<table>
<thead>
<tr>
<th>GO/CS (0/1000)</th>
<th>GO/CS (2/1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$ (mg/L)</td>
<td>1500</td>
</tr>
<tr>
<td>$q_{e, exp}$ (mg/g)</td>
<td>252.9</td>
</tr>
<tr>
<td>$q_{e, cal}$ (mg/g)</td>
<td>267.4</td>
</tr>
<tr>
<td>$K_1$ (min$^{-1}$)</td>
<td>$6.890 \times 10^4$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9994</td>
</tr>
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</table>

4 – Conclusion

A GO/CS composite was prepared in order to remove anionic dyes (acid red) from aqueous solutions. SEM image showed that the fracture surface of GO/CS composite microspheres were porous. The experimental factors such as initial acid red concentration, pH, and contact time to affect the adsorption were measured in detail. The results showed that acidic condition benefited for acid red dye
adsorption and the adsorption capacity reached 255 mg/g at pH 3.0. Thermodynamic studies indicated that the adsorption of acid red dyes on GO/CS porous microspheres was an exothermic process. The kinetic parameters obtained indicated that the adsorption of acid red dyes followed the pseudo-second order kinetics. The equilibrium data fitted well with the Langmuir isotherm and the maximum adsorption capacity of acid red onto GO/CS composite microspheres was 255 mg/g, which was higher than CS (232 mg/g). It suggests that GO/CS composite porous microspheres exhibit a bright future for their application in anionic dyes removal from the wastewater.

5 – Acknowledgements

Support from Zhengzhou University for Graduate Students Creative Project 2014 is greatly acknowledged.

6 – References