Studies on competitive adsorption of dyes onto carbon (XC-72) and regeneration of adsorbent
Xiang Xing, Hongxia Qu, Peng Chen, Bin Chi and Huifang Xie

ABSTRACT

Carbon as an adsorbent has been widely studied for wastewater treatment, but the regeneration of adsorbent has been scarcely reported. In this paper, an economical and environmental method was applied to regenerate carbon (XC-72). Results showed that both anhydrous ethanol and deionized water did not obtain optimal effect for the desorption of Acid Orange 7, Ponceau 2R and Rhodamine B, but the desorption effect was dramatically improved when anhydrous ethanol and deionized water were mixed in a certain volume ratio. In addition, the adsorption kinetics of the three dyes were investigated, which showed that the process of adsorption could be well represented by the pseudo-second-order model. For the study of competitive adsorption, this indicated that the interaction between adsorbent and adsorbate had something to do with electrostatic attraction.

INTRODUCTION

Wastewater produced by organic dyes has become a serious environmental issue, for not only can it be hard to degrade completely (Srivastava & Mukhopadhyay 2014), it also has toxic, mutagenic, carcinogenic and teratogenic effects (Wong et al. 2009). Therefore, the removal of organic pollutants has attracted extensive attention both in fundamental research and practical application. Generally speaking, wastewater treatment can be divided into physical, chemical and biological processes (Barat et al. 2013; Liu et al. 2013). Although these methods have all been attempted to get rid of contaminants, physical adsorption is a comparatively cheaper and more efficient technique for the elimination of organic pollutants from wastewater (Zhang et al. 2011; Xiangyu et al. 2014). However, for a complete adsorption/desorption process, desorption is considered as an inevitable step for regenerating the adsorption material, though the regeneration of adsorbent has been scarcely reported. He et al. (2013) reported that acetonitrile was a perfect desorbent to extract methylene blue (MB) from carbon monolith. Malekbala et al. (2015) revealed that MB was extracted from the adsorbent by 0.1 N HCl as eluents and desorption efficiency was up to 82.1%. Robinson et al. (2002) demonstrated that solvent A (methanol, chloroform, water in the ratio of 1:1:1) and solvent B (methanol) exhibited excellent desorption effects to different dyes. All desorbents mentioned above contain toxic chemicals (CH3CN, HCl, CHCl3, CH3OH) which are harmful to human beings and the environment. However, it is interestingly observed that organics (CH3OH, CH3CN) contain hydrophilic (-OH, -CN) and hydrophobic (-CH3) groups. The methyl group is closely adsorbed on the hydrophobic part of the adsorbent, while -OH and -CN groups are more likely to interact with the surface hydrophilic functional groups of the adsorbent, which might be the driving force for the desorption of dye molecules. CH3CH2OH, as an amphiphilic molecule, still possesses hydrophilic (-OH) and hydrophobic (CH3CH3) groups, and it is more environmental and economical.

In this paper, we aim to explore a new mechanism to illustrate the desorption process. Carbon (XC-72) was first used to remove Acid Orange 7 (AO7), Ponceau 2R and Rhodamine B (RhB), due to its low cost (Ma et al. 2014), high surface area (Pozio et al. 2002) and high adsorption capacity (Shao et al. 2010). Apart from the inherent attributes mentioned above, the functional groups (-COOH and -OH) on the surface of carbon may contribute to the formation of the hydrogen bond as well as electrostatic attraction between the adsorbent and adsorbate (Wu et al. 2009).
which remarkably affects adsorptivity. After adsorption, the dye molecules were extracted from the dye-adsorbed carbon by an ethanol–water system, and it exhibited great desorption effect. Compared with conventional thermal regeneration, an ethanol–water system requires less energy, the desorption process is convenient to operate and the desorbent can be more easily separated by simple distillation. Also, the adsorption material and desorbents are both recyclable. Finally, the experimental result shows that hydrophilic and hydrophobic groups, as well as the dye solubility in ethanol, can dramatically influence the desorption effect, which is meaningful for the discovery of new desorbents.

**MATERIALS AND METHODS**

**Materials**

The dyes (AO7, Ponceau 2R, RhB) and anhydrous ethanol were purchased from Aladdin Co. Ltd. The chemicals were of analytical grade without further purification. Carbon (XC-72) was obtained from Cabot Chemical Co. Ltd.

**Characterization**

A morphology image of carbon (XC-72) was taken on a transmission electron microscope (TEM) (Philips Tecnai 12). Fourier transform infrared spectroscopy (FTIR) (Nicolet IZ10FTIR) spectra were recorded in the range of 4,000–400 cm⁻¹ to identify the functional group change of dyes before and after adsorption by carbon (XC-72). Brunauer-Emmett-Teller (BET) surface area and pore size distribution (calculated by the Barrett-Joyner-Halenda method) of carbon (XC-72) were determined by N₂ adsorption–desorption isotherms at 196 °C using a Gold App V-sorb 2008 Analyzer. Prior to N₂ measurements, the sample was outgassed at 200 °C for 12 h in a vacuum. An ultraviolet visible spectrophotometer (T6, Beijing Purkinje General Instrument Co. Ltd) was employed to identify the concentration of the dye solution.

**Adsorption kinetics**

The adsorption experiment was conducted as follows: 0.060 g carbon was dispersed in 250 mL deionized water under vigorous magnetic stirring for 30 min and then 250 mL AO7 solution (17.5 mg/L) was stirred with the above mixture. Next, 3 mL solution was separated from the above mixture by syringe membrane filter at times of 1, 2, 4, 7, 10, 15, 30, 50, and 60 min, respectively. The dye concentration at different times was calculated according to the standard curves by identifying the absorbance at the maximum absorption wavelength. The same method was applied to study the adsorption of Ponceau 2R and RhB. The maximum absorption wavelength of AO7, Ponceau 2R and RhB in deionized water was 485 nm, 508 nm and 554 nm, respectively.

The adsorption quantity of dye onto carbon was calculated according to the equation below:

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

where \(C_0\) (mg/L) is the initial adsorbate concentration, \(C_t\) (mg/L) is the concentration of adsorbate at time \(t\) (min), \(V\) (L) is the solution volume, \(m\) (g) is the mass of carbon and \(q_t\) is the adsorption quantity (mg/g) at time \(t\) (min).

**Competitive adsorption**

The mechanism of competitive adsorption in this paper was studied: 25 mL Ponceau 2R solution (24.0 mg/L) was stirred with 0.012 g carbon for 1 h. After centrifugation, the concentration of dye in solution was monitored by ultraviolet visible spectrophotometer; the solid was washed twice with deionized water and dried at 40 °C for 6 h to obtain Ponceau 2R-adsorbed carbon. This Ponceau 2R-adsorbed carbon was then added into 25 mL AO7 solution (17.5 mg/L) and stirred for 1 h. After centrifugation, the concentration of the obtained solution was identified by ultraviolet visible spectrophotometer. The same operation was applied to illustrate the competitive adsorption of Ponceau 2R and RhB, AO7 and RhB.

**Desorption experiments**

The difference in ethanol–water volume ratio \(V_{e/w}\) had a significant effect on dye desorption. In our work, 10 mL anhydrous ethanol, mixture solution \((V_{e/w} = 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9)\) and deionized water were respectively employed as desorbent to extract three dyes for 5 min from 0.002 g dye-loaded carbon, and the best condition was optimized.

A desorption experiment was carried out: 0.030 g AO7-adsorbed carbon was dissolved in 300 mL desorption solution (optimal \(V_{e/w}\) for AO7, Ponceau 2R and RhB) under vigorous magnetic stirring. Then, 3 mL solution was separated from the above mixture by syringe membrane filter.
filter at times of 1, 2, 4, 7, 10, 15, 30, 60, and 180 min, respectively. The dye concentration in the desorption solution at different times was calculated according to the standard curves by the identification of absorbance at the maximum absorption wavelength. The same method was applied to study the desorption of Ponceau 2R and RhB. The maximum absorption wavelength of AO7, Ponceau 2R and RhB in the desorption solution was 486 nm, 507 nm and 545 nm, respectively.

The desorption efficiency was calculated as the following equation:

$$D_t = \frac{C_t \times V}{q \times m_1} \times 100\%$$

where $C_t$ (mg/L) is the concentration of dye in desorption solution at time $t$ (min), $V$ (L) is the volume of desorption solution, $q$ is the adsorbed quantity (mg/g) of dye, $m_1$ is the required mass of dye-adsorbed carbon and $D_t$ (%) is the desorption efficiency at time $t$ (min).

In order to illustrate the role of ethanol, the following experiments were carried out: 0.006 g carbon was dispersed in 50 mL AO7 (10 mg/L, anhydrous ethanol as solvent) under vigorous magnetic stirring for 60 min. The concentration of dye in solution was monitored by ultraviolet visible spectrophotometer after centrifugation. Then, the adsorption quantity of AO7 in ethanol solution was calculated. The same method was applied to calculate the adsorption quantity of Ponceau 2R and RhB onto carbon.

**RESULTS AND DISCUSSION**

**TEM image and FTIR analysis**

As is shown in Figure 1(a), the carbon (XC-72) particle is a nanosphere with a diameter of 40 nm. Table 1 shows that the surface area of the carbon (XC-72) is 186 m$^2$/g, and the pore size and pore volume of the carbon (XC-72) are 1.949 nm and 0.459 cc/g, respectively. For the FTIR spectra of the carbon, Figure 1(b) shows that two broad bands emerge in the range of 3,000-3,600 cm$^{-1}$, and are assigned to the O-H stretching vibration of adsorbed water and O-H group of the carbon surface. The band at 1,727 cm$^{-1}$ is attributed to C=O stretching vibrations from carbonyl and carboxylic groups. The band in the 1,100–1,300 cm$^{-1}$ region is ascribed to the overlapping of the C-OH and C-O stretching vibrations (Garigliulo et al. 2016). For the FTIR spectra of AO7, Figure 1(c) shows that the band at 1,620 cm$^{-1}$ is assigned to a combination of phenyl ring vibrations with stretching of the C=N group. The band at 1,510 cm$^{-1}$ corresponds to the bending vibration $\delta$ (N-H) whereas the band at 1,450 cm$^{-1}$ belongs to the Azo-N=N- vibration. The peaks observed at 1,320 cm$^{-1}$ and 1,400 cm$^{-1}$ are the O-H bending vibration. The bands located at 1,450, 1,570, 1,600 and 1,620 cm$^{-1}$ are attributed to C=C aromatic skeletal vibrations. The bands at 1,030 cm$^{-1}$ and 1,120 cm$^{-1}$ are attributed to the coupling between benzene ring mode 1 and $\nu_s$ (SO$_3$), while the bands at 1,180 cm$^{-1}$ and 1,210 cm$^{-1}$ are ascribed to the $\nu_{as}$ (SO$_3$) stretching mode (Bauer et al. 1999; Zhang et al. 2005; Yue et al. 2014). All the bands described above are correspondingly found in the FTIR of AO7-adsorbed carbon. Figure 1(d) shows that the band at 1,650 cm$^{-1}$ is assigned to the bending vibration of the C=N+ group of RhB. The bands at 1,590, 1,530, 1,470 cm$^{-1}$ are attributed to the aromatic ring. The bands at 1,410, 1,340, and 1,250 cm$^{-1}$ are ascribed to the bending vibration of CH$_2$ in -N((CH$_3$)$_2$, the stretching vibration of the C-N-linked benzene ring and the stretching vibration of C-N in a -N(C$_2$H$_5$)$_3$ group, respectively. The band at 1,180 cm$^{-1}$ corresponds to asymmetrical stretching vibration of C-O-C (Li et al. 2007; Zhang et al. 2014). All the peaks could be observed in the FTIR of RhB-adsorbed carbon. Similarly, all the characteristic bands of Ponceau 2R could be observed in Ponceau 2R-adsorbed carbon (Figure 1(e)). However, the bands at 1,727 cm$^{-1}$ and 1,100–1,300 cm$^{-1}$ are very weak when in dye-adsorbed carbon, which may result from the decrease of functional group (COOH, COH) content with the increase in adsorbed dye molecules on the surface of the carbon. Therefore, the FTIR result illustrates that there is no functional group change for dye removal. Furthermore, Figure 2 shows that the UV-vis spectra of the three dyes always keep the same trend within the wavelength range from 190 nm to 600 nm as time moves forward, which indicates no chemical reaction occurs in this course. Thus, the removal of dyes by carbon is a physical process.

**Adsorption kinetics**

A series of experiments were conducted to investigate the adsorption of AO7, Ponceau 2R and RhB onto carbon (XC-72). Figure 3 shows that the adsorption rate of the three dyes is rather fast in the first 10 min and it changes very little in the last 10 min. Therefore, the adsorption quantity at time 60 min can be regarded as the equilibrium adsorption quantity and it is up to 66.586, 62.021, 90.424 mg/g for AO7, Ponceau 2R and RhB, respectively.

In order to better understand the mechanism and rate-controlling step in this process, pseudo-first-order and
pseudo-second-order models were conducted to fit the experimental data. The pseudo-first-order kinetic model is expressed as:

\[
\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{q_e}
\]
where $k_1$ (min$^{-1}$) is the rate constant of pseudo-first-order adsorption, $q_e$ (mg/g) and $q_t$ (mg/g) are the equilibrium adsorption quantity of dyes and adsorption quantity at time $t$ (min), respectively.

The pseudo-second-order kinetic model has the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t$$

where $k_2$ (g/(mg min)) is the rate constant of pseudo-second-order adsorption.

The kinetic parameters and nonlinear regression correlation coefficients are listed in Table 2. As can be seen from this table, the pseudo-second-order model of the three dyes ($R^2 > 0.99$) are more fitted than the pseudo-first-order model ($R^2 < 0.84$), and the experimental values $q_{e,exp}$ are quite close to the calculated values $q_{e,cal}$ via the pseudo-second-order model. Therefore, the adsorption kinetics of the three dyes onto carbon (XC-72) are well represented by the pseudo-second-order model.

**Competitive adsorption**

The characteristic absorption peaks of AO7, Ponceau 2R and RhB are 485 nm, 508 nm and 554 nm, respectively.
Table 2 | Kinetic parameters of the pseudo-first-order and pseudo-second-order kinetic models for adsorption of dyes onto carbon (XC-72)

<table>
<thead>
<tr>
<th>Dyes</th>
<th>(q_{e,exp}) (mg/g)</th>
<th>(q_{e,cal}) (mg/g)</th>
<th>(k_1)</th>
<th>(R^2)</th>
<th>(q_{e,cal}) (mg/g)</th>
<th>(k_2)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ponceau 2R</td>
<td>62.021</td>
<td>30.762</td>
<td>0.08475</td>
<td>0.8366</td>
<td>63.291</td>
<td>0.009</td>
<td>0.9995</td>
</tr>
<tr>
<td>AO7</td>
<td>66.586</td>
<td>27.450</td>
<td>0.08337</td>
<td>0.8050</td>
<td>67.573</td>
<td>0.011</td>
<td>0.9994</td>
</tr>
<tr>
<td>RhB</td>
<td>90.424</td>
<td>36.745</td>
<td>0.07922</td>
<td>0.7715</td>
<td>91.743</td>
<td>0.008</td>
<td>0.9993</td>
</tr>
</tbody>
</table>

Figure 4 | UV-vis spectra of solution (deionized water as solvent) in competitive adsorption: (a) AO7 and Ponceau 2R, (b) Ponceau 2R and RhB, (c) AO7 and RhB. The concentrations of AO7, Ponceau 2R and RhB are 17.5 mg/L, 24.0 mg/L, 24.0 mg/L, respectively, the solution volume is 25 mL if there is no particular statement to the contrary. Adsorption time is 1 h at 25°C. (d) Molecular structures of AO7, RhB and Ponceau 2R.
Figure 4(a) shows that 0.012 g carbon is stirred with Ponceau 2R solution for 1 h and Ponceau 2R-adsorbed carbon is obtained after centrifugation, washing and drying. Interestingly, no peak is found at the position of 485 nm, whereas the peak is observed at the position of 508 nm when the AO7 solution is added into the Ponceau 2R-adsorbed carbon. It is convincing that AO7 takes the place of Ponceau 2R completely, which may mainly be caused by competitive adsorption of various dyes. Carbon (XC-72) exhibits favourable adsorptivity, which is nonselective to dye molecules, but the strength of the adsorptivity is determined by the interaction (hydrophobic interaction, hydrogen bond and electrostatic attraction) between adsorbent and adsorbate (Özcan & Özcan 2004; Hu et al. 2015). It can be seen from the structure of the dyes (Figure 4(d)) that both AO7 and Ponceau 2R are negatively charged, and carbon is negatively charged (−COO−) as well. However, the difference is that the AO7 molecule possesses one negative charge while Ponceau 2R possesses two, which results in a stronger repulsive force between the surface of the carbon and the Ponceau 2R molecules. Thus, the conclusion may be drawn that competitive adsorption exists between AO7 and Ponceau 2R; AO7 molecules with less negative charge may be more easily adsorbed on carbon, which leads to the desorption of Ponceau 2R molecules. For further illustration, the competitive adsorption of Ponceau 2R and RhB, AO7 and RhB onto carbon were conducted as well. Figure 4(b) shows that Ponceau 2R-adsorbed carbon was obtained as mentioned above. Unsurprisingly, the peak is found in the 508 nm position rather than 554 nm when the RhB solution is added to the Ponceau 2R-adsorbed carbon. What leads to this phenomenon is that RhB is a positively charged dye, which is more likely to be attracted by the negatively charged carbon and completely replaces the adsorptive site that Ponceau 2R originally possessed. The same analytical method can be applied to explain competitive adsorption between RhB and AO7 as well (Figure 4(c)). Hence, the electrostatic attraction between the adsorbent and adsorbate has a dominant impact on the order of dye adsorption.

Regeneration of carbon (XC-72)

Based on a large number of experiments (Figure 5(a)–5(c)), it could be noted that the carbon regeneration typically has something to do with the content of ethanol in the desorbent. Deionized water has no obvious effect on dye desorption, while anhydrous ethanol exhibits different degrees of desorption effect on the three dyes. However, interestingly, the desorption effect is dramatically improved when ethanol and water are mixed in a certain volume ratio of 7:3, 5:5, 9:1 for AO7, Ponceau 2R and RhB, respectively. Also, the desorption efficiency is up to 73.05%, 63.45%, and 78.42% for AO7, Ponceau 2R and RhB, respectively, when carbon is regenerated for 3 h. It is worthwhile noting that both anhydrous ethanol and deionized water are cost-effective and environmentally friendly. Meanwhile, the regenerated carbon (regenerated by desorbent under the best desorption condition three times) can be recycled and the readsorption quantities of the three dyes (65.483, 52.292, 88.462 mg/g for AO7, Ponceau 2R and RhB, respectively, under the same operational conditions as the kinetic study) are still large. Hence, a mixture solution as a desorbent to regenerate adsorbent is a promising method. For the study of the desorption mechanism, a possible explanation may be that the role of water is to increase the solubility of the dyes, while the role of the ethanol is to compete with the dye molecules on the surface of the carbon. What can be deduced from Figure 5(a)–5(c) and Table 3 is that solubility is not the main reason for the desorption of dyes, because the dye molecules can hardly be desorbed from carbon by using deionized water as a desorbent. However, dye molecules can be desorbed from carbon by using anhydrous ethanol, which reveals that the role of ethanol is even stronger than water for dye desorption. For greater illustration, we may know that ethanol has both hydrophobic (−CH₂CH₃) and hydrophilic (−OH) functional groups; the hydrophobic group is strongly adsorbed to the aromatic structure of carbon (Gerard & Örjan 2005) while the hydrophilic group interacts with the surface functional group of carbon, which makes ethanol molecules firmly adsorbed on the carbon surface. Figure 6 shows that a small minority of dyes were adsorbed on carbon in ethanol (11.4, 10.726, 2.548 mg/g for AO7, Ponceau 2R and RhB, respectively). It is possible that the existence of ethanol blocks the interaction between the carbon and the dye molecules to some extent. Thus, the desorption of dye molecules from carbon by mixed solution (anhydrous ethanol and deionized water) is actually a type of competitive adsorption; the dye molecules are replaced by ethanol and dissolve in liquid with the addition of water, which results in an excellent desorption effect on different dyes from carbon. Meanwhile, Table 5 shows that the solubility value of the three dyes in anhydrous ethanol is much smaller than that in water, and follows a descending order: RhB > AO7 > Ponceau 2R. RhB exhibits great solubility in ethanol, so a small amount of water is required for its desorption;
however, AO7 and Ponceau 2R both exhibit low solubility in ethanol, so it is reasonable that much more water is required for their desorption. Thus, we may possibly explain why the optimal Ve/w for the desorption of RhB, AO7 and Ponceau 2R is 9:1, 7:3 and 5:5, respectively. Based on the above illustrations, the conclusion may be drawn that ethanol, as the main active substance, exhibits an excellent desorption effect on different dyes with the addition of deionized water.

<table>
<thead>
<tr>
<th>Solubility (g/L)</th>
<th>Solvent</th>
<th>Ponceau 2R</th>
<th>AO7</th>
<th>RhB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>10.215</td>
<td>31.726</td>
<td>307.531</td>
<td></td>
</tr>
<tr>
<td>Anhydrous ethanol</td>
<td>0.632</td>
<td>1.751</td>
<td>78.924</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 | Effect of different volume ratio of ethanol and water for the dye desorption from carbon: (a) AO7, (b) Ponceau 2R, (c) RhB; (d) time course for the desorption efficiency of three dyes. Desorption time is 3 h at 25 °C.

Table 3 | Solubility of three dyes in different solution at room temperature

CONCLUSIONS

To sum up, carbon (XC-72) was employed as an adsorbent to remove three dyes from wastewater, and the equilibrium adsorption quantity was up to 66.586, 62.021, and 90.424 mg/g for AO7, Ponceau 2R and RhB, respectively. The adsorption kinetics of the three dyes were also studied, which revealed that the pseudo-second-order kinetic model was consistent with the adsorption process of the three dyes. The competitive adsorption of dyes onto carbon (X-72) indicated that electrostatic attraction between the adsorbent and adsorbate had a massive influence on the order of dye adsorption. We explored an economical and environmental method to regenerate the adsorbent. The result showed that the best performance for dye desorption was exhibited when anhydrous ethanol and water were mixed in a certain volume ratio of 7:3, 5:5, 9:1 for AO7, Ponceau 2R and
RhB, respectively; the desorption efficiency reached 73.05%, 63.45%, and 78.42% for AO7, Ponceau 2R and RhB, respectively, when it was regenerated for 3 h. Finally, we observed that two aspects should be considered for the choice of desorbent: the main active substance and the substance that increases the solubility of the adsorbate. Water is cheap and widely available, it is also a great substance to increase the solubility of the adsorbate. Thus, our next work will concentrate on the development of an active substance that could compete more than the dye molecules on the adsorbent.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51106076, 21276127).

REFERENCES


He, X., Male, K. B., Nesterenko, P. N., Brabazon, D., Paull, B. & Luong, J. H. T. 2013 Adsorption and desorption of methylene
blue on porous carbon monoliths and nanocrystalline cellulose. ACS Applied Materials & Interfaces 5 (17), 8796–8804.


First received 5 May 2016; accepted in revised form 18 August 2016. Available online 14 September 2016.