Mechanism and kinetics of dye desorption from dye-loaded carbon (XC-72) with alcohol-water system as desorbent
Xiang Xing, Hongxia Qu, Ri Shao, Quuyang Wang and Huifang Xie

ABSTRACT
In this paper, alcohol (methanol, ethanol, n-propanol)-water system was used as solution for the desorption of Acid Orange 7 (AO7), Ponceau 2R and Rhodamine B (Rhb) from dye-loaded carbon (XC-72). Excellent degradation efficiency was obtained (desorption efficiency reaches 77.35%, 85.60%, 96.86% for Ponceau 2R, AO7 and Rhodamine B, respectively) and it was significantly influenced by alcohol content and the length of carbon chain in alcohol (hydrophobicity). In addition, desorption kinetics was fitted by a second-order desorption model, and the desorbed quantity at equilibrium (q_e) and rate constant (k_d) were calculated, respectively.

INTRODUCTION
Physical adsorption has been widely applied for the removal of organic pollutants over the past few decades because it is a cheaper and more efficient technique for the elimination of contaminants from wastewater (Zhang et al. 2011; Zhou et al. 2014). But for a complete adsorption/desorption process, desorption is considered as an inevitable step for regenerating the adsorption material. If an adsorbent does not exhibit high desorption efficiency, it can hardly be used in industrial designed applications (Kyzas et al. 2014; Malekbala et al. 2015). Furthermore, the cheap purchased adsorbent may be abandoned to soil directly after first run in some factories. A desorption process can not only ensure the regeneration of adsorbent but also avoid the secondary pollution which abandoned organic pollutant-loaded adsorbent leads to. Therefore, simple and efficient desorption process has tremendous potential in industrial application.

Recently, the study of the regeneration of adsorbent has received extensive attention, and the desorbents which previous researchers had developed may generally be divided into two categories: inorganic dominated desorbent and organic dominated desorbent. Gupta (Gupta et al. 2005; Mittal et al. 2009) revealed that both quinoline yellow and Congo red were easily desorbed by NaOH solution from dye-loaded adsorbent because these two dyes were acidic in nature and they exhibited good attraction toward basic medium. Therefore, NaOH solution was likely to be used as an eluent for the desorption of acidic dyes. For the development of organic dominated desorbent, Robinson (Robinson et al. 2002) reported that solvent A (methanol, chloroform, water in the ratio of 1:1:1) and solvent B (50% methanol) exhibited excellent desorption effect to different dyes. He (He et al. 2015) demonstrated that only 50% methylene blue was desorbed from carbon monolith by ethanol while desorption efficiency reached 95% when acetonitrile was employed as desorbent. Hang (Hang & He 2014) revealed that ethanol-water system was an excellent solution for dye desorption, and the optimal volume ratio of ethanol and water for the desorption of hydrolysed reactive dyes was 4:6. In our previous work, it was demonstrated that the desorption of three dyes (Acid Orange 7 (AO7), Ponceau 2R and Rhb) from dye-adsorbed carbon (XC-72) by ethanol-water solution had a close correlation with hydrophilic and hydrophobic groups of organics (Xing et al. 2016). However, it is interesting to observe that all organics (CH3OH, CH3CH2OH, CH3CN) in above desorbent contain hydrophilic (–OH, –CN) and hydrophobic (–CH3, –CH2CH3) groups; hydrophobic group is closely adsorbed on the hydrophobic part of adsorbent while hydrophilic group is more likely to interact with surface hydrophilic functional group of adsorbent, which might be the driving force for the desorption of dye molecules.
Based on above illustrations, it is reasonably assumed that not only methanol and ethanol but also n-propanol has a certain effect on dye desorption. It is speculated that the length of carbon chain in alcohol may influence the desorption effect, because longer carbon chain has stronger hydrophobic property while shorter carbon chain has weaker hydrophobic property. Besides, compared with inorganics dominated desorbent, organic dominated desorbents can be recycled, for they have lower boiling point, which ensures the easy separation between desorbent and dye molecules by simple distillation. Meanwhile, ethanol-water system used for dye desorption has higher desorption efficiency, and it is convenient to be operate.

In this paper, carbon (XC-72) was selected as an adsorbent to remove AO7, Ponceau 2R and RhB because it had high surface area (Celorio et al. 2012) and exhibited excellent adsorption capacity for the removal of organic pollutants from aqueous solution (Shao et al. 2010). After adsorption, the mixture solution (difference in the mass content of methanol, ethanol and propanol) was employed as desorbent to extract above three dyes from dye-loaded carbon, and the best condition was optimized. Besides, desorption kinetics was fitted by a second-order desorption model, and the desorbed quantity at equilibrium ($q_e$) and rate constant ($k_d$) were calculated as well.

**MATERIALS AND METHODS**

**Materials**

Three dyes (AO7, Ponceau 2R, RhB) and alcohols (methanol, ethanol, n-propanol, n-butanol) 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.

**Characterizations**

Fourier transform infrared (FTIR) spectra (Nicolet IZ10FTIR) were recorded in the range of 4,000–400 cm$^{-1}$ to identify functional group of carbon (XC-72). X-ray photoelectron spectroscopy (XPS) (PerkinElmer, PHI Quantera II) was performed with Al K$_\alpha$, X-rays ($h\nu = 1,486.6$) radiation operated at 150 W to identify oxygen-containing functional groups in the sample. Ultraviolet visible spectrophotometer (T6, Beijing Purkinje General Instrument Co. Ltd) was employed to measure the concentration of dye solution.

**Adsorption/desorption experiment**

0.30 g carbon (XC-72) was dispersed in 2,250 mL Ponceau 2R (24 mg/L) for 360 min under vigorous stirring to reach adsorption equilibrium. Then, the solution was separated by centrifugation and the concentration of obtained solution was calculated according to the standard curve by the identification of absorbance at maximum absorption wavelength ($\lambda_{\text{max}}$). The obtained Ponceau 2R-loaded carbon was washed twice by deionized water and dried at 50°C for 24 h (used for desorption experiment). Similarly, the adsorption of AO7 (3,000 mL, 24 mg/L) and RhB (3,750 mL, 24 mg/L) by carbon (0.300 g) was conducted as mentioned above as well.

The adsorption quantity of dye on carbon was calculated according to the equation as below.

$$q_t = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

where $C_0$ (mg/L) is the initial concentration of adsorbate, $C_t$ (mg/L) is the concentration of adsorbate at 360 min, $V$ (L) is the solution volume, $m$ (g) is the carbon mass and $q_t$ (mg/g) is the adsorption quantity at time 360 min.

Alcohol-water system is an excellent solution for dye desorption. The difference in the volume ratio of methanol-water ($V_{\text{M/W}}$), ethanol-water ($V_{\text{E/W}}$), n-propanol-water ($V_{\text{P/W}}$) and the length of carbon chain in alcohol have diverse effects on dye desorption. In our work, 10 mL deionized water, alcohol-water solution ($V_{\text{M/W}} = V_{\text{E/W}} = V_{\text{P/W}} = 9:1$, $8:2$, $7:3$, $6:4$, $5:5$, $4:6$, $3:7$, $2:8$, $1:9$) and alcohols (methanol, ethanol and n-propanol) were respectively employed as desorbent to extract three dyes from 0.002 g dye-loaded carbon. And the best desorption condition was optimized.

The desorption quantity was calculated using the following equation.

$$D_t = \frac{C_t \times V}{m_2} \tag{2}$$

where $C_t$ (mg/L) is the concentration of dye in desorbent at time $t$ (min), $V$ (L) is the volume of desorption solution, $m_2$ (g) is the carbon mass (the mass of dye is not included) and $D_t$ (mg/g) is the desorption quantity at time $t$ (min).

For the study of desorption kinetics, the experiments were conducted as follows: 0.060 g Ponceau 2R-loaded carbon was mixed with 300 mL desorbent (optimal $V_{\text{M/W}}$, $V_{\text{E/W}}$, $V_{\text{P/W}}$ for the desorption of Ponceau 2R) under vigorous magnetic stirring. Then, 4 mL solution was respectively separated at time 2, 4, 7, 10, 15, 30, 60, 180, 360 min from
above mixture by syringe membrane filter to measure absorbance at $\lambda_{\text{max}}$. The dye concentration at different times was calculated according to the standard curves by the identification of absorbance at $\lambda_{\text{max}}$, then the desorption quantity was calculated by above equation (Equation (2)). Similarly, the desorption of AO7 and RhB by alcohol-water system was conducted as well.

RESULTS AND DISCUSSION

XPS and FTIR analysis

Carbon (XC-72) is analyzed by XPS to indicate the surface functional groups. Figure 1(a) shows that two major elements (C, O) are detected and the content of surface O in carbon (XC-72) is 4.8%, which shows that abundant hydrophobic conjugated sp² C = C bonds (in the form of aromatic structure) still appear on the surface of carbon (XC-72). Figure 1(b) shows that the XPS spectrum of high resolution O 1 s can be split into three individual peaks. The peak at 530.8 eV corresponds to carboxyl functional groups (–CO-O), and the peaks at 532.0 eV and 533.4 eV correspond to carbonyl functional group (C = O) and hydroxyl functional group (–OH), respectively (Zuo et al. 2013). As is shown in Figure 1(c), a typical band at 1,628 cm⁻¹ is assigned to conjugated sp² C = C stretching. The bands at 1,735 cm⁻¹ and 1,080 cm⁻¹ are attributed to C = O and C-O stretching vibrations from carboxylic groups (–COOH). 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. The broad band emerging in the range of 3,000–3,700 cm⁻¹ is assigned to the O-H stretching vibration of adsorbed water and O-H group of carbon surface (Ren et al. 2011; Vinoth et al. 2015). The FTIR result is in good agreement with XPS analysis, which further illustrates the existence of hydrophilic groups (–OH, –COOH) and hydrophobic groups (aromatic structure) on carbon surface. Hydrophilic groups (–OH, –COOH) are more likely

Figure 1 | XPS spectra of carbon (XC-72): (a) survey; (b) O 1 s; (c) FTIR spectrum of fresh carbon (XC-72).
to interact with –OH in alcohol, while alkyl groups (–CH₃, –CH₂CH₃, –CH₂CH₂CH₃) in alcohol can be firmly connected with hydrophobic groups (aromatic structure), which is the driving force for the desorption of dye molecules from dye-loaded carbon. In addition, the carbon (XC-72) material after dye desorption is measured by FTIR in Figure 2, and the result shows that no functional groups change when the material goes through adsorption/desorption processes. Hence, the removal of dyes is a physical process.

**Effect of different V<sub>alcohol/water</sub> and hydrophobic groups on the desorption of dyes**

The difference in alcohol content had various effects on dye desorption. Figure 3(a) shows that deionized water has no effect on dye desorption, while methanol exhibits different levels of desorption effect on three dyes. But interestingly, the desorption effect is dramatically improved when methanol-water system is used as desorvent; desorption efficiency reaches 84.19%, 47.35% and 43.94% for RhB, AO7 and Ponceau 2R, respectively, when the content of methanol reaches 87.68%, 75.98% and 64.86% (corresponding to V<sub>M/W</sub> = 9:1, 8:2, 7:3) for the desorption of RhB, AO7 and Ponceau 2R, respectively. According to our experiments, the solubility value of dye in water is much higher than that in alcohols (Table 1). Hence, for alcohol-water system, the role of water may increase the solubility of dye, while the role of methanol may be to compete with dye molecules on the surface of carbon. However, solubility is not the main reason for the desorption of dyes, because the three dyes exhibit great solubility in deionized water, and they can hardly be extracted from dye-loaded carbon by using deionized water. Simultaneously, dye molecules can be desorbed from dye-loaded carbon by using methanol, which reveals that methanol exhibits desorption effects on the three dyes to some degree. For further illustration, methanol has both hydrophobic (–CH₃) and hydrophilic (–OH) functional groups; hydrophobic group can be strongly adsorbed on aromatic structure of carbon (Gerard & Örjan 2005) while the

![Figure 2](https://iwaponline.com/wst/article-pdf/76/5/1243/450327/wst076051243.pdf)
hydrophilic group interacts with surface functional groups (–OH, –COOH) of carbon, which keeps methanol molecules firmly adsorbed on carbon surface and blocks the interaction between carbon and dye molecules to some extent. Hence, the desorption of dye molecules conducted by methanol-water system actually includes two processes; dye molecules are first replaced by methanol molecules and then dissolve in methanol-water solution. Meanwhile, Table 1 shows that solubility value of three dyes in methanol follows a descending order: RhB > AO7 > Ponceau 2R, and it is much lower than that in water. RhB exhibits great solubility in methanol, so small amount of water (mass content: 12.32%) is required when it reaches the best desorption condition. But for AO7 and Ponceau 2R, they both exhibit low solubility in ethanol, so it is reasonable that much more water (mass content: 24.02%, 35.14% for AO7 and Ponceau 2R, respectively) is required to reach the best desorption condition. Hence, we may possibly explain why methanol content requires the most for the desorption of RhB and requires the least for the desorption of Ponceau 2R when it reaches the best desorption condition. Simultaneously, it is shown in Figure 3(b) and 3(c) that the contents of ethanol and n-propanol require the most for the desorption of RhB and require the least for the desorption of Ponceau 2R.

Table 1 | Solubility of three dyes in different solvents at room temperature

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility (g/L)</th>
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<tbody>
<tr>
<td></td>
<td>Ponceau 2R</td>
</tr>
<tr>
<td>Deionized water</td>
<td>10.22</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.55</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.63</td>
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<tr>
<td>Propanol</td>
<td>0.12</td>
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Figure 3 | Effect of different alcohol contents (mass content) on the desorption of three dyes: (a) methanol-water system, (b) ethanol-water system, (c) n-propanol-water system. Desorption time is 20 min at room temperature.

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under the best desorption condition, and the experimental data are in good agreement with our assumption. Besides, Figure 3(a)–3(c) show that n-propanol-water system as desorbent always exhibits the best desorption effect for same dye when the volume ratio of alcohol (methanol, ethanol and propanol) and water reaches 1:9. Reasonable explanation is that propanol possesses longer carbon chain (–CH₂CH₂CH₃), so it presents stronger hydrophobic property, and the dye molecules on the surface of carbon are more likely to be replaced by n-propanol molecules and then dissolve in mixed solution. Similarly, it can be reasonably explained why methanol-water system exhibits the worst desorption effect under the same desorption condition. Meanwhile, we predict that n-butanol-water system is likely to exhibit better desorption effect. So, saturated n-butanol solution (volume ratio of n-butanol and water is 0.93:9.07) is employed to extract dye from dye-loaded carbon and the desorption effect is better than with the propanol-water system (VP/W = 1:9), which further illustrates the validity of our theory. However, it cannot obtain the best desorption effect when pure methanol, ethanol or propanol is employed as desorbent, which is mainly limited by lower solubility of three dyes in alcohol. Based on above illustrations, the conclusion may be drawn that the difference in V_{alcohol/water} and hydrophobic groups has a significant effect on dye desorption.

Desorption kinetics

As can be seen from Figure 4(a)–4(c), the desorption rate of three dyes is rather fast in the first 60 min and it changes very little in the last 180 min. Therefore, desorption quantity at time 360 min can be regarded as equilibrium desorption quantity. The desorption efficiency of Ponceau 2R conducted by VM/W = 7:3, VE/W = 5:5, VP/W = 2:8 is 49.76%, 70.62% and 77.35%, respectively; desorption efficiency of

![Figure 4](https://iwaponline.com/wst/article-pdf/76/5/1243/450327/wst076051243.pdf)

Desorption kinetics of (a) Ponceau 2R, (b) AO7, (c) RhB conducted by alcohol-water system under best desorption condition. (d) Adsorption quantity conducted by fresh carbon (XC-72) and the carbon after regeneration, [Ponceau 2R] = [AO7] = [RhB] = 24 mg/L. Room temperature.
AO7 conducted by $V_{M/W} = 8:2$, $V_{E/W} = 7:3$, $V_{P/W} = 4:6$ is 57.88%, 69.31% and 85.60%, respectively; and desorption efficiency of RhB conducted by $V_{M/W} = 9:1$, $V_{E/W} = 8:2$, $V_{P/W} = 5:5$ is 92.83%, 94.23% and 96.86%, respectively. As is shown by the above data, for the same dye, n-propanol-water system always obtains the best desorption effect even though a lower amount of n-propanol is required, which means that hydrophobic group plays a major role in the desorption of dye. Meanwhile, Figure 4(d) shows that the regenerated carbon still exhibits great adsorption ability to three dyes, indicating alcohol-water system is a promising method for the regeneration of adsorbent.

In order to determine the desorption kinetics, the experimental data are fitted by a second-order desorption model (Gerbase-Delima et al. 2009). The equation is expressed as follows:

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

where $q_t$ (mg/g) is the desorbed quantity at time $t$, $k_d$ (g/(mg min)) is the rate constant, and $q_e$ (mg/g) is the desorbed quantity at equilibrium. The above equation can be integrated with the initial condition of $q_t = 0$ at $t = 0$.

The values of $q_{e,cal}$ and $k_d$ were calculated from the linear plot of $t/q_t$ with time (Figure 5, based on Equation (3)). The kinetic parameters ($q_{e,exp}$, $q_{e,cal}$, $k_d$ and $R^2$) are listed in Table 2. As can be seen from this table, the experimental values $q_{e,exp}$ are quite close to calculated values $q_{e,cal}$, and all the $R^2 > 0.99$. Therefore, the desorption kinetics of three dyes from dye-loaded carbon are well-presented by a second-order desorption model.

**CONCLUSIONS**

Three dyes (Ponceau 2R, AO7 and RhB) were first adsorbed by carbon (XC-72). Then, dye-loaded carbon was used for desorption experiment. The best desorption condition for Ponceau 2R was $V_{M/W} = 7:3$, $V_{E/W} = 5:5$, $V_{P/W} = 2:8$; the best desorption condition for AO7 was $V_{M/W} = 8:2$, $V_{E/W} = 7:3$, $V_{P/W} = 4:6$, and the best desorption condition for RhB was $V_{M/W} = 9:1$, $V_{E/W} = 8:2$, $V_{P/W} = 5:5$. The
determination of optimal desorption condition was firmly related to the solubility of dye in alcohols. Meanwhile, n-propanol-water system (with less propanol content) could reach better desorption effect for every single dye under optimal desorption condition compared with the ethanol-water system and methanol-water system, which meant that the alcohol with longer carbon chain could dramatically improve desorption efficiency. Besides, the desorption kinetics of three dyes were modeled by a second-order desorption model under best desorption condition; the experimental values $q_{e,exp}$ were quite close to calculated values $q_{e,cal}$, and all the $R^2 > 0.99$. This work is meaningful because it has guiding effect on the development of new economical and environmental desorber.

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**REFERENCES**


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**Table 2** Kinetic parameters of pseudo-second-order kinetic models for the desorption of three dyes from dye-loaded carbon

<table>
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<tr>
<th>Dyes</th>
<th>Desorvent</th>
<th>$q_{e,exp}$ (mg/g)</th>
<th>$q_{e,cal}$ (mg/g)</th>
<th>$k_d$ (g/(mg min))</th>
<th>$R^2$</th>
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<tbody>
<tr>
<td>Ponceau 2R</td>
<td>$V_{P/W}$ = 2:8</td>
<td>35.431</td>
<td>35.689</td>
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<td>$V_{M/W}$ = 7:3</td>
<td>22.795</td>
<td>22.957</td>
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<td>AO7</td>
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<td>79.554</td>
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