Kinetic Sorption of 2,4-Dichlorophenol and Rhodamine-B from Aqueous Solutions onto Modified Phragmites Australis
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ABSTRACT

This study investigates the potential use of activated carbon prepared from Phragmites Australis for the removal of 2,4-dichlorophenol (DCP) and Rhodamine-B (RB) from aqueous solutions. P. Australis activated carbon (PAAC), a new adsorbent, was prepared from P. Australis by H3PO4 activation. The sorption behavior and the rate-controlling sorption step has been discussed from the pseudo-first-order, pseudo-second-order, Elovich equation and intraparticle diffusion models. It was found that the adsorption of 2,4-DCP and RB onto PAAC both followed pseudo-second-order model. Adsorption mechanism studies revealed that the process followed both surface adsorption and particle diffusion. Accordingly, the activated carbon developed in this study is effective and practical for utilization in wastewater treatment for 2,4-DCP and RB removal.

INTRODUCTION

Chlorophenols are very important water pollutants generally present in the effluents, generated from petroleum refineries, plastics, pharmaceuticals, disinfectants, wood-preserving and steel industries[1,2]. They have been considered as priority water pollutants by the United States Environmental Protection Agency (EPA) and Environmental Monitoring of China, because of...
their high toxicity to organisms at low concentrations[3,4]. Since most of the
dyes are biologically non-degradable, it is difficult to remove them from
wastewater. Rhodamine-B (RB) is widely used as a colorant in food and textiles
stuffs, and is also a well-known water tracer fluorescent compound. RB is toxic,
neurotoxic and carcinogenic if ingested by human beings and animals.

Several chemical and physical treatment techniques have been used for
removing organics from wastewater, such as coagulation, ion exchange,
oxidization, and sorption. Among these, sorption has been noted to be superior
compared to other techniques for wastewater treatment in terms of its capability
for efficiently adsorbing a wide variety of adsorbates, simplicity of design[3]
and its economic feasibility. Activated carbon is the most widely used adsorbent
due to its vast surface area, microporous character, adequate porous and
chemical features[5], but its high cost limits its commercial application on a
large scale. Therefore, in recent years, many studies have examined the
preparation of activated carbon from low-cost and readily available materials,
mainly industrial and agricultural byproducts. Coconut husks[6], papermill
sludges[7], fly ash[8] and rice husks[9] have been reported as raw materials for
the adsorption of organic pollutants and dyes.

In this study, we used Phragmites Australis as an alternative low-cost
precursor to prepare activated carbon for the removal of 2,4-DCP and RB dye
from aqueous solutions. P. Australis, a perennial aquatic plant, is widely
distributed in freshwater wetlands in China. Recycling of this solid waste for
wastewater treatment would not only be economical but would also help to
reduce the adverse impact on the environment and can provide a potentially
inexpensive raw material for commercial activated carbon. In view of the low
cost of such adsorbents prepared in this study and the high cost regeneration, it
would not be necessary to regenerate the spent activated carbon. The objective
of the present work was to investigate the potential feasibility of P. Australis
activated carbon (PAAC) for the adsorption of 2,4-DCP and RB. The kinetic
data of the sorption process were then evaluated to investigate the adsorption
mechanism of 2,4-DCP and RB molecules onto PAAC.

MATERIALS AND METHODS

Preparation

P. Australis used in this work was obtained from a wetland of the Nansi
Lake area in Shandong province. The precursor was first washed with water to
remove impurities, and then dried at 105 °C until it reached a constant weight.

The dried P. Australis was crushed in a laboratory mill. Phosphoric acid
activation was adopted to produce PAAC. Forty grams of dried precursor was
treated with 85 wt.% concentration phosphoric acid at a H₃PO₄ : dried precursor
ratio of 2:1 (w:w), then stirred thoroughly until well mixed, and kept in a
desiccator overnight to achieve good soaking. After 24 h, the mass was then
transferred to a muffle furnace and heated slowly to a final temperature of 450
°C where it stayed for 1 h, then was allowed to cool to room temperature. The
produced carbonized sample was repeatedly washed with hot distilled water and
deionized water until a constant near neutral pH of the solution was reached.
Finally, the resulting product was dried in a vacuum oven at 120 °C to a constant weight. The dried sample of PAAC was ground and sieved to 140-160 mesh particle sizes by standard sieves (Model Φ200) before storage and further testing. The PAAC was then stored in a desiccator for later use.

**Regents**

2,4-DCP was purchased from Shanghai Chemical Co., China, and RB was purchased from Shanghai Third Reagent Co., China. Both of the chemicals used were of analytical reagent grade and were used without further purification.

**Sorption Experiments**

The adsorption kinetics experiments were carried out at room temperature. Then 2.00 g PAAC was added to 2000 mL adsorbate solutions with different initial concentrations. The mixture was agitated on an electromagnetic stirrer (Model 78-1) at 21±1 °C and 300 rpm. At predetermined time intervals (0-300 min), 10 mL samples were drawn out and filtered. Then the filtrate samples were analyzed to determine the residual adsorbate concentration using the same methods as above. The adsorption amount at time \( t \), \( q_t \) (mg/g), was also calculated using Eq. 1 in which \( C_t \), the concentrations of adsorbate solutions at time \( t \) (mg/L) is substituted for \( C_e \).

**RESULTS AND DISCUSSION**

In order to investigate the controlling mechanism of the adsorption processes and potential rate such as chemical reaction, mass transfer and diffusion control, three kinetic models were applied to the experimental data.

**Pseudo-first-order Kinetic Model**

The pseudo-first-order model can be represented by the following Lagergren rate equation[10]:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

where \( q_e \) and \( q_t \) are the amounts of 2,4-DCP and RB adsorbed (mg/g) at equilibrium and at time \( t \) (min), respectively and \( k_1 \) is the rate constant of pseudo-first-order adsorption (min\(^{-1}\)). The values of \( q_e \) and \( k_1 \) for the pseudo-first-order kinetic model were determined from the intercepts and the slopes of the plots of \( \log(q_e - q_t) \) versus \( t \), respectively (not shown). The correlation coefficients were greater than 0.98 and 0.92 for all 2,4-DCP and RB concentrations, respectively (Table 1). But the experimental \( q_e \) values \( (q_{e,exp}) \) did not agree with the calculated \( q_e \) values \( (q_{e,cal}) \) obtained from the linear plots, as shown in Table 1. This indicates that the adsorption of 2,4-DCP and RB onto PAAC does not follow the pseudo-first-order equation.

**Pseudo-second-order Kinetic Model**

The pseudo-second-order model can be represented in the following form[2]:
\[
\frac{t}{q_e} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t
\]

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

The \(q_e\) values and the pseudo-second-order rate constant \(k_2\) were determined experimentally from the slopes and intercepts of plots of \(t/q_t\) versus \(t\) as seen in Fig. 1. The correlation coefficients for the pseudo-second-order kinetic model were extremely close to 1 for all 2,4-DCP concentrations and varied from 0.9980 to 1 for RB (Table 1). Furthermore, the \(q_{e,\text{cal}}\) values agreed very well with the \(q_{e,\text{exp}}\) values as shown in Table 1. These both demonstrate that the adsorption process of 2,4-DCP and RB onto the prepared activated carbon could be described well by the pseudo-second-order kinetic model. Similar adsorption kinetic results for 2,4-DCP and RB have been reported in the literature[2].

Concerning the pseudo-second-order rate constant \((k_2)\), it was found that \(k_2\) significantly decreased with the increase in initial concentration. It is also observed in Table 2 that as the 2,4-DCP initial concentration varies from 30 to 70 mg/L, \(k_2\) decreases from \(5.75\times10^{-2}\) to \(1.20\times10^{-2}\) mg/g min and the RB initial concentration varies from 160 to 200 mg/L, \(k_2\) decreases from \(5.25\times10^{-4}\) to \(1.98\times10^{-4}\) mg/g min. This trend of the pseudo-second-order rate constant and the fact that the plots of \(t/q_t\) versus \(t\) over the whole contact time are straight lines for all the initial concentrations studied suggests that the overall rate of the adsorption process is controlled by chemisorption[20].

**Figure 1.** Pseudo-second-order kinetics plots for (a) 2,4-DCP and (b) RB onto PAAC at different initial concentrations (conditions: pH = natural, temperature = 21±1°C).

### Elovich Equation

Elovich equation is one of the most useful models for describing chemisorption, which is expressed by the following equation[12]:

\[
q_t = \frac{1}{\beta} \ln(a\beta) + \frac{1}{\beta} \ln(t)
\]

where \(\alpha\) is the initial sorption rate (mg/(g min)) and \(\beta\) is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The parameters \((1/\beta)\) and \((1/\beta)\ln(a\beta)\) can be calculated from the slope and intercept of the plot of \(q_t\) versus \(\ln t\) (not shown). The values of \(\alpha\) and \(\beta\) are summarized in Table 1 along with correlation coefficient \((R^2)\) for different initial dye concentrations. The values of \(R^2\) obtained from this model was in the range of 0.6934-0.8536 for 2,4-DCP initial
concentration of 30-70 mg/L and of 0.9738-0.9917 for RB initial concentration of 160-240 mg/L (Table 1).

**TABLE 1. KINETIC PARAMETERS FOR THE ADSORPTION OF 2,4-DCP AND RB ONTO PAAC AT DIFFERENT INITIAL CONCENTRATIONS.**

| Adsorbates | $C_0$ (mg/L) | $q_{e,ex}$ (mg/L) | $Pseudo$-first-order | $Pseudo$-second-order | Elovich equation |
|------------|--------------|-------------------|----------------------|-----------------------|------------------|
|            | $k_1$ (min$^{-1}$) | $q_{e,ca}$ (mg/g) | $k^2$ (g/mg min) | $q_{e,ca}$ (mg/g) | $R^2$ | $\alpha$ (mg/($g \text{ min}$)) | $\beta$ (g/mg) | $R^2$ |
| 2,4-DCP    | 30           | 55.0              | 1.69×10$^{-2}$      | 12.43                 | 0.9791           | 5.75×10$^{-2}$    | 55.25               | 1.0000       | 1.13×10$^{12}$ | 0.58          | 0.68034        |
|            | 50           | 88.3              | 1.56×10$^{-2}$      | 25.95                 | 0.9789           | 2.46×10$^{-2}$    | 88.50               | 1.0000       | 7.95×10$^{9}$  | 0.30          | 0.7505         |
|            | 70           | 118.05            | 8.75×10$^{-2}$      | 25.36                 | 0.9790           | 1.20×10$^{-2}$    | 119.05              | 1.0000       | 1.99×10$^{10}$ | 0.23          | 0.8536         |
| RB         | 160          | 313.76            | 2.19×10$^{-2}$      | 142.7                 | 0.9795           | 5.25×10$^{-4}$    | 322.58              | 0.9998       | 8.50×10$^{2}$  | 2.67×10$^{-2}$ | 0.9738         |
|            | 200          | 367.32            | 1.98×10$^{-2}$      | 226.78                | 0.9789           | 2.79×10$^{-4}$    | 370.37              | 0.9988       | 3.16×10$^{2}$  | 1.99×10$^{-2}$ | 0.9762         |
|            | 240          | 397.65            | 2.00×10$^{-2}$      | 277.08                | 0.9789           | 1.98×10$^{-4}$    | 416.67              | 0.9980       | 2.90×10$^{2}$  | 1.85×10$^{-2}$ | 0.9717         |
Sorption Mechanism

Since the 2,4-DCP and RB species are most probably transported from the bulk of the solution to the PAAC through an intraparticle diffusion/transport process which is often the rate-limiting step in many adsorption processes, intraparticle diffusion is another kinetic model which should be used to study the rate of 2,4-DCP and RB adsorption onto PAAC. The possibility of intraparticular diffusion was explored by using the following equation, proposed by Weber and Morris[13]:

\[ q_t = k_{id} t^{1/2} + C \]  

where \( C \) is the intercept (mg/L) and \( k_{id} \) is the intraparticle diffusion rate constant (mg/g min\(^{1/2}\)).

Fig. 2 shows the uptake of 2,4-DCP and RB versus \( t^{1/2} \) for intraparticle transport at different initial concentrations. If the Weber–Morris plot of \( q_t \) versus \( t^{1/2} \) gives a straight line, then the sorption process is controlled only by intraparticle diffusion. The data exhibit multi-linear plots, indicating more than one step influences the sorption process. From the figure it is observed that there are three linear regions. The initial curve portion is attributed to the instantaneous adsorption or external surface adsorption. Followed a linear region represents pore diffusion where intraparticle diffusion is the rate limiting. In certain situations, the third portion exists, which is a horizontal linear region where intraparticle diffusion initiate to slow down as a result of the highly low adsorbate concentrations remained in the solutions[14]. The intraparticle diffusion parameter, \( k_{id} \), is determined from the slope of the second linear region while the intercept \( C \) gives an idea about the thickness (or resistance) of the boundary layer, i.e., the larger the intercept the greater is the boundary layer effect. The values of \( k_{id} \) and \( C \) which were calculated from the second linear portion are shown in Table 2. It is observed that the value of the intercept increased from 47.28 to 93.38 as the 2,4-DCP concentration increased from 30 to 70 mg/L, which indicates growth of the boundary layer and a decreased chance for external mass transfer (and hence increased likelihood of internal mass transfer) in this range[15]. However, the intercept decreased as the RB concentration increased from 160 to 240 mg/L, which reflects a decrease of the thickness of the boundary layer and hence increased chance of external mass transfer. The values of \( R^2 \) given in Table 2 are close to unity, indicating the applicability of this model. This may confirm that the rate-limiting step is the intraparticle diffusion process. As can be seen from Fig. 2, the lines do not pass through the origin, suggesting that intraparticle diffusion is not the only rate-controlling step, but that some other mechanisms may also be involved in the sorption of 2,4-DCP and RB by PAAC.
Figure 2. Intraparticle diffusion plots for (a) 2,4-DCP and (b) RB onto PAAC at different initial concentrations (conditions: pH = natural, temperature = 21 ± 1 °C).

Table 2. Parameters of the Intraparticle Diffusion Model for the Adsorption of 2,4-DCP and RB onto PAAC at Different Initial Concentrations.

| Adsorbates | C₀ (mg/L) | kₚ (mg/g min⁻¹/²) | C   | R²    |
|------------|-----------|-------------------|-----|-------|
| 2,4-DCP    | 30        | 1.6799            | 47.28 | 0.9580 |
|            | 50        | 4.6004            | 67.41 | 0.9303 |
|            | 70        | 4.5174            | 93.38 | 0.9911 |
| RB         | 160       | 11.3490           | 192.96 | 0.9729 |
|            | 200       | 15.7720           | 179.76 | 0.9704 |
|            | 240       | 19.4230           | 162.02 | 0.9913 |

Conclusion

P. Australis was chemically activated under the conditions of 85 wt.% H₃PO₄ at 450 °C. The adsorption characteristics of 2,4-DCP and RB on the prepared activated carbon were measured to determine the potential for practical applications of the activated carbon. The following conclusions were obtained:

(a) PAAC can be successfully utilized as a low-cost alternative adsorbent for the removal of 2,4-DCP and RB from aqueous solutions.

(b) Kinetics studies of the adsorption of 2,4-DCP and RB on PAAC indicate that the adsorption kinetics follows the pseudo-second-order model with intraparticle diffusion as one of the rate determining steps.

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