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Removal of Congo Red from aqueous solution by cattail root

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ABSTRACT

In this study, cattail root was used to remove Congo Red (CR) from aqueous solution. The effects of operation variables, such as cattail root dosage, contact time, initial pH, ionic strength and temperature on the removal of CR were investigated using batch adsorption technique. Removal efficiency increased with increase of cattail root dosage and ionic strength, but decreased with increase of temperature. The equilibrium data fitted well to the Langmuir model ($R^2 > 0.98$) and the adsorption kinetic followed the pseudo-second-order equation ($R^2 > 0.99$). Thermodynamics parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were analyzed. The values of ΔG° were between -7.871 and $-4.702\,\mathrm{kJ\,mol^{-1}}$, of ΔH° was $-54.116\,\mathrm{kJ\,mol^{-1}}$, and of ΔS° was $-0.157\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$, revealing that the removal of CR from aqueous solution by cattail root was a spontaneous and exothermic adsorption process. The maximum adsorption capacities of CR on cattail root were 38.79, 34.59 and 30.61 mg g^{-1} at 20, 30 and 40 °C, respectively. These results suggest that cattail root is a potential low-cost adsorbent for the dye removal from industrial wastewater.

1. Introduction

More than 10,000 dyes have been widely used in textile, paper, rubber, plastics, leather, cosmetic, pharmaceutical, and food industries, which generated huge volume of wastewater every year [1]. The disposal of dye wastewater without proper treatment is a big challenge and has caused harms to the aquatic environment, such as reducing light penetration and photosynthesis [2]. Some of dyes contained in wastewater even decompose into carcinogenic aromatic amines under anaerobic conditions, which will cause serious health problems to human and animals [3]. Due to the complex molecular structure, dyes are usually very difficult to be biodegraded, making them hardly eliminated under natural aquatic environment [4].

Due to the low biodegradability, conventional biological wastewater treatment processes were not efficient in treating dyes wastewater [1]. Therefore, dyes wastewater was usually treated by physical and/or chemical methods, such as coagulation and flocculation [5], membrane separation [6], activated carbon adsorption [7], electrochemical removal [8], and photochemical degradation [9]. However, for the developing counties, these methods are still too expensive to be used widely. Developing economical adsorbents to treat dyes wastewater has attracted great interest in recent years [10]. Gupta and Suhas [11] recently reviewed the application of low-cost adsorbents for the dye removal. Many non-conventional, low-cost adsorbents such as coir pith [12], anaerobic granular sludge [13], hazelnut shells [14], bottom ash and de-oiled soya [15–21], carbon slurry [22,23], hen feathers [24], and other waste materials [25–29], have been attempted to remove dyes from wastewater. But the adsorption capacities of most of the above were still limited. New economical, locally available and highly effective adsorbents are still under development.

Cattail is an aquatic plant and has been widely used in artificially constructed wetlands for the removal and mineralization of phenol [30], the treatment of high-strength wastewater [31], and the removal of phosphorous and heavy metals [32]. However, the cattail biomass and its root produced in the phytoremediation probably become a potential pollution sources like water hyacinth if they are not properly managed. Previous studies have shown that cattail biomass could be subjected to anaerobic digestion for biogas production [33]. Cattail root has a porous structure and a large surface area, which might be utilized as adsorbent to treat dyes wastewater.

Congo Red (CR) is an anionic dye, which has been widely used in textiles, paper, rubber and plastic industries [34]. In this study, we investigated the feasibility using cattail root to remove CR from synthetic dye wastewater.

2. Materials and methods

2.1. Material

Cattail root used in this study was collected from a local pond in Hefei, China. The root was washed with tap water to remove soil and

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Nomenclature

C_0	initial dye concentration in aqueous solution ($mg\,L^{-1}$)
C_e	equilibrium concentration in solution ($mg\,L^{-1}$)
C_s	equilibrium concentration on adsorbent ($mg\,L^{-1}$)
h	initial adsorption rate at time approaching 0 ($mg\,g^{-1}\,min^{-1}$)
k_{ad}	rate constant of pseudo-first-order adsorption (min^{-1})
K_c	equilibrium constant
k_{id}	rate constant of intraparticle diffusion ($mg\,g^{-1}\,min^{-0.5}$)
k_2	rate constant of pseudo-second-order adsorption ($g\,mg^{-1}\,min^{-1}$)
q_e	amount of dye adsorbed on adsorbent at equilibrium time
q	amount of dye adsorbed on adsorbent at time t
Q^0	maximum adsorption capacity ($mg\,g^{-1}$)
t	time (min)
R	ideal gas constant, 8.314 $J\,mol^{-1}\,K^{-1}$
R^2	regression coefficient
T	temperature in Kelvin (K)
V	volume of aqueous solution to be treated (L)
ΔG°	standard free energy change ($kJ\,mol^{-1}$)
ΔH°	standard enthalpy change ($kJ\,mol^{-1}\,K^{-1}$)
ΔS°	standard entropy change ($kJ\,mol^{-1}$)

dust, sprayed with distilled water, and dried to a constant weight at 75 °C. The dry cattail root was ground and sieved to obtain particle sizes of 0.25–0.40 mm as adsorbent, and then stored in desiccators for use.

2.2. Preparation of dye solution

Congo Red used in this study was of commercial purity (C.I. 22120, FW = 696.7, λ_{max} = 500 nm; Shanghai Chemical Reagent Ltd.). The chemical structure is shown in Fig. 1. Stock solution of 500 $mg\,L^{-1}$ was prepared by dissolving accurately quantity of the dye in double-distilled water. The experimental solution was obtained by diluting the stock solution to the designed initial dye concentration.

2.3. Adsorption studies

The batch tests were carried out in 100 mL flasks with 50 mL of working volume. The ground cattail root was added into flasks with designed concentration of the dye solution. The initial pH of the solution was adjusted to 7.0 ± 0.3 using 0.01 M HCl or 0.01 M NaOH. The flasks were stirred at a rotary shaker at 140 rpm. Samples were collected from flasks at predetermined time intervals, and centrifuged at 10,000 × *g* for 10 min to remove adsorbent. The concentration of CR in the supernatant was measured immediately by a 722 Grating Spectrophotometer (Shanghai Instrument Ltd., China), at 498 nm of wavelength.

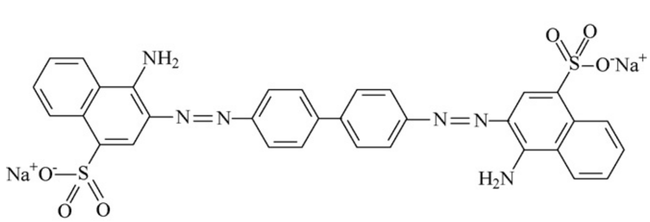

Fig. 1. Molecular structure of Congo Red.

In the test of contact time and adsorbent dosage, the initial pH of the dye solution was adjusted to 7.0 ± 0.3, the concentration of CR was 50 $mg\,L^{-1}$, and the temperature was controlled at 20 °C. The cattail root dosage used was 0.5, 1.0, 3.0, 5.0, 7.0 and 10.0 $g\,L^{-1}$, respectively.

In the investigation of pH, the pH of dye solutions was adjusted to the designed values using 0.01 M HCl or 0.01 M NaOH. The CR concentration was 50 $mg\,L^{-1}$ and the temperature was controlled at 20 °C. The adsorbent dosage used was 5.0 $g\,L^{-1}$.

In the investigation of ionic strength, NaCl was used to adjust the ionic strength and seven different concentrations of 0, 0.001, 0.01, 0.05, 0.1, 0.5, and 1.0 $mol\,L^{-1}$ were applied to adjust the ionic strength. The CR concentration used was 50 $mg\,L^{-1}$ and the temperature was 20 °C with adsorbent dosage 5.0 $g\,L^{-1}$.

Three different temperatures of 20, 30 and 40 °C were applied to investigate the influence of temperature. The CR concentration, temperature, pH, and adsorbent dosage were the same as the test of ionic strength.

2.4. Equations and calculations

In this study, Lagergren's pseudo-order equation was used to investigate the dynamics of the adsorption process from aqueous solution. The first-order Lagergren equation is given as

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303}t \qquad (1)$$

where k_{ad} is the rate constant of first-order adsorption (min^{-1}), q_e and q are the amounts of dye adsorbed on adsorbent at equilibrium and at time t (min), respectively.

The second-order Lagergren equation is expressed as

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

and

$$h = k_2 q_e^2 \qquad (3)$$

where k_2 is the pseudo-second-order rate constant ($g\,mg^{-1}\,min^{-1}$) and h is the initial adsorption rate at time approaching 0 ($mg\,g^{-1}\,min^{-1}$).

The effect of intraparticle diffusion resistance on adsorption can be evaluated by the following equation:

$$q = k_{id} t^{1/2} + I \qquad (4)$$

where k_{id} is the rate constant of intraparticle diffusion ($mg\,g^{-1}\,min^{-0.5}$). Values of I give the information regarding the thickness of boundary layer.

Thermodynamic parameters were calculated using the following equations:

$$\Delta G^0 = -RT \ln K_c \qquad (5)$$

$$K_c = \frac{C_s}{C_e} \qquad (6)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (7)$$

where ΔG°, ΔH° and ΔS° are respectively standard free energy change, standard enthalpy change, standard entropy change, K_c is the equilibrium constant, C_s is the equilibrium concentration of CR on adsorbent ($mg\,L^{-1}$), C_e is the equilibrium concentration of CR in solution ($mg\,L^{-1}$), R is the ideal gas constant (8.314 $J\,mol^{-1}\,K^{-1}$), and T is the adsorption temperature in Kelvin.