



# Removal of the Dye Congo Red in Aqueous Solution by the Modified Camphor Sawdust Adsorbent

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Nat. Env. & Poll. Tech.  
Website: [www.neptjournal.com](http://www.neptjournal.com)

Received: 17-06-2015

Accepted: 15-08-2015

## Key Words:

Dye Congo red  
Wastewater  
Adsorption  
Modified camphor sawdust

## ABSTRACT

In recent years, there has been growing interest in finding inexpensive and effective adsorbents such as tea waste, wood, sawdust, kaolin, bentonite and peat. Sawdust is one of the promising adsorbents for removing dye pollutants from wastewaters. In this paper, the modified camphor sawdust is obtained from camphor sawdust with 5% cetyltrimethyl ammonium bromide solution activation. Then, the pore structure characteristics and adsorption dye wastewater in the aqueous solution capacity of the camphor sawdust were investigated. The kinetic and isotherm adsorption of dye wastewater by the camphor sawdust modified with surfactant are discussed in detail. The dye Congo red was chosen as the dye wastewater. The equilibrium data were better represented by Langmuir isotherm model than done by the Freundlich isotherm model. The adsorption process of the modified camphor sawdust for dye Congo red is homogenous. The maximum adsorption capacity obtained from the Langmuir isotherm is 125.39 mg/g.

## INTRODUCTION

The textile industry plays an important role in the economies of numerous countries around the world. But the dye wastewater from the textile industry has become one of the most serious environmental problems today, for its harm especially in the aquatic environment. Dyes are aromatic organic colorants and have potential applications in textile, plastic, rubber, paper and food industries. Therefore, the treatment of the dye wastewater is of interest. Various treatment techniques, such as coagulation, oxidation, filtration, adsorption, etc., have been developed for treating water and wastewaters embedded with dyes (Hawari & Mulligan 2006, Hashemian & Salimi 2012). Among these techniques of treatment, adsorption method can be used both effectively and economically for dye removal. Activated carbon has been successfully used as an adsorbent for removal of dyes from wastewater. Although activated carbon is the most used adsorbent, it is expensive. Furthermore, a regeneration step is needed after either exhausting the adsorbent capacity or the adsorption efficiency decrease below the process requirements. The selected adsorbent should be environment friendly, economical and demonstrates high removal efficiency (Ates & Un 2013).

In recent years, there has been growing interest in finding inexpensive and effective adsorbents such as tea waste, wood, sawdust, kaolin, bentonite and peat (Ho & McKay

1998, Garg et al. 2003, Amarasinghe & Williams 2007, Ferrero 2007, Hashemian 2007, Hashemian 2011).

Among these, sawdust is one of the promising adsorbents for removing dye pollutants from wastewaters. Processing of the sawdust generates lignocellulosic biomass, which can amount to 20% of the total input mass. These residues are disposed off by onsite abundantly available biomass, and microwave irradiation for preparation of activated carbon from sawdust through  $K_2CO_3$  activation was explored. Some reports have shown that sawdust and the modified sawdust have a sorption capacity for the removal of most kind of dyes from aqueous solution (Argun et al. 2007, Piyawan et al. 2009).

In this work, the modified camphor sawdust is obtained from camphor sawdust with 5% cetyltrimethyl ammonium bromide solution activation. Then, the pore structure characteristics and adsorption of dye Congo red in the aqueous solution capacity of the camphor sawdust were investigated. The equilibrium adsorption of dye Congo red in the aqueous solution by the modified camphor sawdust has been investigated and discussed.

## MATERIALS AND METHODS

**Preparation of the modified camphor sawdust and dye Congo red:** The molecular formula of the dye Congo red is  $C_{32}H_{22}N_6Na_2O_6S_2$ . The structural figure of the dye Congo red

is shown in Fig. 1. The camphor sawdust was obtained from wood plant of Shaoxing in Zhejiang province of P.R. China. The camphor sawdust was dried at 378 K for 12 h in order to achieve constant weight. Then they were grounded and sieved into a uniform size of 200 meshes. The 50 g of the camphor sawdust was soaked stillly with 500mL 5% cetyltrimethyl ammonium bromide solution in 100 mL Erlenmeyer flasks for 24 h at room temperature. Then, it was dried again at 105°C for 12 h to constant weight. The product of 200 mesh modified camphor sawdust was thus obtained and then stored for later adsorption experiments.

**Adsorption experiments:** Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.1 g of modified camphor sawdust and 100 mL of dye Congo red with various initial concentrations (100, 200, 300, 400 and 500 mg/L) and pH 6.0 in aqueous solution. The flasks were placed in a shaker at a constant temperature (308 K) and 200 rpm.

**Analytical methods:** The surface physical morphology of the modified camphor sawdust was observed by a scanning electron microscope. The value of pH was measured with a pH probe, according to APHA Standard Methods. The concentration of dye Congo red was measured with a UV-1600 spectrophotometer at 450 nm. The amount of adsorbed dye Congo red  $q_t$  (mg/g) at different time, was calculated as follows:

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

Where,  $C_0$  and  $C_t$  (mg/L) are the initial and equilibrium liquid-phase concentrations of dye Congo red respectively.  $V$  (L) is the solution volume and  $m$  (g) is the mass of adsorbent used.

**Statistical analyses of data:** All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All error estimates given in the text and error bars in figures are the standard deviation of the mean (mean±SD). All statistical significance were noted at  $\alpha=0.05$  unless otherwise noted.

## RESULTS AND DISCUSSION

**Characterization of the modified camphor sawdust:** The surface physical morphology of the modified camphor sawdust was observed by a scanning electron microscope. The surface morphology of the modified camphor sawdust was shown in Fig. 2.

It can be seen from the micrograph that the modified camphor sawdust contains irregular and porous structures, indicating that the modified camphor sawdust presents adequate

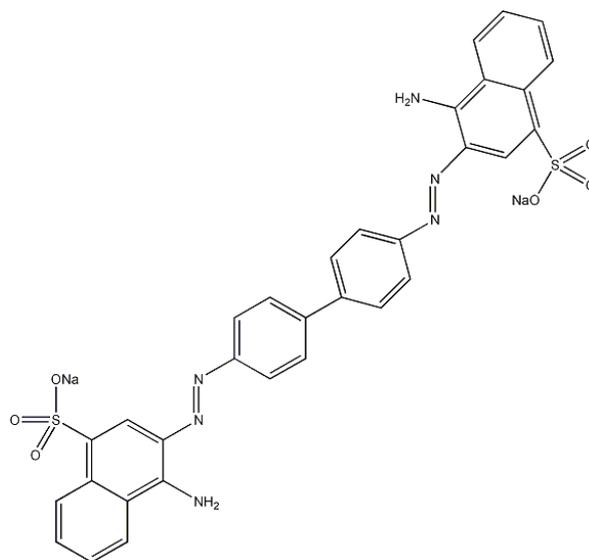


Fig. 1: The structural figure of the dye Congo red.

morphology for the dye Congo red adsorption.

**Effect of contact time:** Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.1 g of the modified camphor sawdust and 100 mL of dye Congo red with various initial concentrations of 200 mg/L and pH 6.0 in aqueous solution. The flasks were placed in a shaker at a constant temperature (308 K) and 200 rpm.

The influence of contact time on the removal of dye Congo red in aqueous solution by the modified camphor sawdust is shown in Fig. 3.

It can be concluded that the adsorption process is very rapid at first 20 minutes. The adsorption rate of dye Congo red increases sharply at a short contact time and slowed down gradually as equilibrium was approached. It may be due to the availability of an initial large number of vacant surface active sites for adsorption and the adsorption rate is very fast. As equilibrium was approached, the filling of vacant sites becomes difficult due to repulsive forces between dye Congo red adsorbed on solid surface and dye Congo red from solution (Shi et al. 2013).

**Effect of dye Congo red concentration:** To investigate the effect of dye Congo red concentration on adsorption of the dye, the tests were conducted with different dye concentration. The experiment results obtained are shown in Fig.4. It can be observed that the removal rate of dye Congo red increased with increasing dye concentration.

**Adsorption isotherm:** The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches

an equilibrium state. The Langmuir adsorption model and the Freundlich adsorption isotherm model are applied in this study (Freundlich 1906, Langmuir 1916).

The Langmuir adsorption model is given as:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad \dots(2)$$

The linearized form of Langmuir can be written as follows:

$$\frac{1}{q_e} = \frac{1}{C_e Q_m K_L} + \frac{1}{Q_m} \quad \dots(3)$$

Where,  $q_e$  is the solid phase equilibrium concentration (ng/g);  $C_e$  is the liquid equilibrium concentration of dye in solution (mg/L);  $K_L$  is the equilibrium adsorption constant related to the affinity of binding sites (L/mg);  $Q_m$  is the maximum amount of dye per unit weight of adsorbent for complete monolayer (mg/g).

The Freundlich adsorption isotherm model, which is an empirical equation used to describe heterogeneous adsorption systems, can be represented as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \quad \dots(4)$$

Where,  $q_e$  and  $C_e$  are defined as above,  $K_F$  is the Freundlich constant representing the adsorption capacity (mg/g), and  $n$  is the heterogeneity factor depicting the adsorption intensity. In most references, Freundlich adsorption Eq. (4) may also be expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots(5)$$

According to Fig. 4 and Eq. (3) and Eq. (5), the adsorption isotherm parameters of Langmuir and Freundlich for the modified camphor sawdust are given in Table 1.

It is evident from Table 1 that the equilibrium data were better represented by Langmuir isotherm model than done by the Freundlich isotherm model. It is known that the Langmuir isotherm is used on the supposition that the surface of the adsorbent is a homogenous surface, whereas the Freundlich isotherm applies to the adsorption process on a heterogeneous surface. So, the adsorption process of the modified camphor sawdust for dye Congo red is homogenous.

## CONCLUSIONS

In this work, the modified camphor sawdust is obtained from camphor sawdust with 5% cetyltrimethyl ammonium bromide solution activation. Then, the pore structure characteristics and adsorption dye Congo red in the aqueous solution

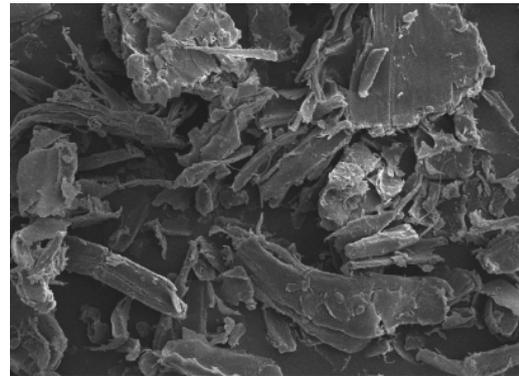


Fig. 2: SEM micrograph of the modified camphor sawdust.

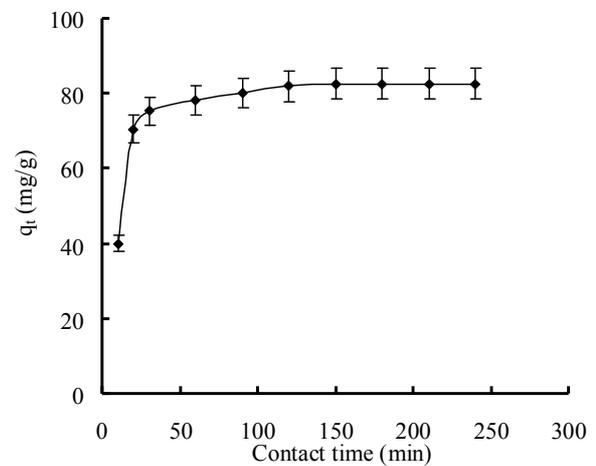


Fig. 3: Effect of contact time on the adsorption by the modified camphor sawdust.

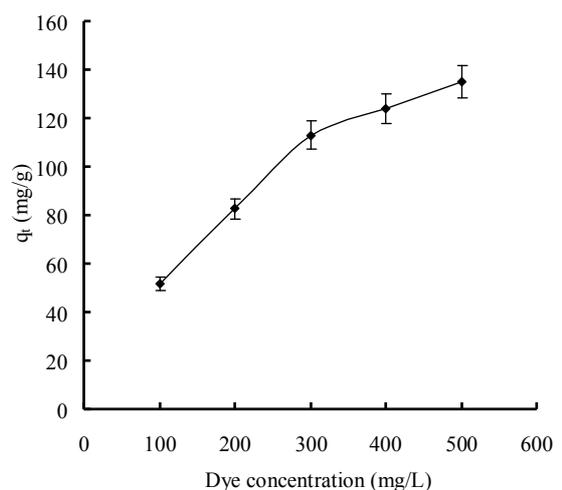


Fig. 4: Effect of dye Congo red concentration on the adsorption by the modified camphor sawdust.

Table 1: The adsorption isotherm parameters of Langmuir and Freundlich for the adsorption of dye Congo red on the camphor sawdust.

Langmuir			Freundlich		
$Q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	$K_F$ [(mg/g) <sup>1/n</sup> ]	$n$	$R^2$
125.39	0.086	0.9817	43.29	6.32	0.8317

capacity of the camphor sawdust were investigated. The surface physical morphology of the modified camphor sawdust was observed by a scanning electron microscope. It can be seen from the micrograph that the modified camphor sawdust contains irregular and porous structures, indicating that the modified camphor sawdust presents adequate morphology for dye Congo red adsorption. The equilibrium data were better represented by Langmuir isotherm model than done by the Freundlich isotherm model. The adsorption process of the modified camphor sawdust for dye Congo red is homogenous. The maximum adsorption capacity obtained from the Langmuir isotherm is 125.39 mg/g.

#### ACKNOWLEDGEMENTS

This study was financially supported by the project of science and technology plan in Shaoxing City (2014B70050 and 2013B70058).

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