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Original Research Paper

Adsorption Isotherm and Equilibrium Process of Dye Wastewater onto Camphor Sawdust

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ABSTRACT

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 aquatic environments. Dyes are aromatic organic colorants and have potential applications in textile, plastic, rubber, paper and food industries. Therefore, the treatment of dye wastewater is of interest. The potential and effectiveness of the camphor sawdust was studied as an alternative adsorbent for the removal of dye wastewater. The dye Congo red was used as the pollutant. The effects of camphor sawdust dosage, pH in aqueous solution, the contact time and dye Congo red concentration on dye Congo red adsorption by the camphor sawdust were investigated. The results showed that the reaction factors had an important influence on adsorption process. The adsorption isotherm fitted better with the Langmuir model and the adsorption process was an endothermic process. The maximum adsorption capacity obtained from the Langmuir isotherm is 29.51 mg/g.

INTRODUCTION

Dyes are an important class of pollutants that are of environmental concern because of their known toxicity and tendency to accumulate in the natural environment (Husain 2006, Bae & Freeman 2007, Hai et al. 2007). They are used in large quantities in many industries for colouring the products, such as textile, tannery, food, paper and pulp, printing, cosmetics, plastic, pharmaceuticals and dye houses (Sun et al. 2008, Zhang et al. 2011). Wastewaters containing the residual colour are visible to the human eye and are therefore obnoxious on aesthetic grounds. They may significantly affect photosynthetic activity in aquatic life because of reduced light penetration, and they may also be toxic to some aquatic life due to the presence of aromatics, metals, chlorides etc. (Altlnlslk et al. 2010). Therefore, the treatment of dye wastewater is of interest.

A great deal of literature has reported some waste treatment methods, such as chemical coagulation, reverse osmosis, ion exchange, adsorption, ozonation, membrane, electrochemical, etc. (Chulhwan et al. 2004, Muthukumar & Selvakumar 2004, Guibal & Roussy 2007). Among these methods, adsorption treatment is still the cheapest, most profitable and efficient method for removing the dye from the wastewater (Hashemian & Salimi 2012). Biosorbents have received increasing interest owing to their low cost, good performance and environmental benignity. They are generally derived from renewable resources and may also be originated from wastes or by products of industrial and agricultural processes (Foo & Hameed 2012, Xia et al. 2014). Sawdust is one of the most attractive materials used for removing pollutants from the wastewater. The lignocellulosic material is a by-product of the timber industry, which is available in large quantities in lumber mills and this waste often represents a disposal problem. The material consists of cellulose, lignin and hemicellulose. Cellulose is composed of a long chain of glucose molecules, linked to one another primarily with glycosidic bonds. Lignin is a complex polymer composed of phenylpropane units, which are cross linked to each other by a variety of different chemical bonds. Hemicelluloses are branched polymers composed of xylose, arabinose, galactose, mannose and glucose. Hemicellulose bind the bundles of cellulose fibrils to form microfibrils, which enhance the stability of the cell wall. They also crosslink with lignin, creating a complex web of bonds, which were provided structural strength, and also were challenged microbial degradation (Raji & Anirudhan 1998, Pekkuz et al. 2008). In addition to its complex chemical structure, the lignocellulosic matrix of sawdust, embodies a wide variety of functional groups that play a major role for binding dyes through different mechanisms. The adsorption generally takes place by complication, ion exchange and hydrogen bonding. Consequently, the use of lignocellulosic wastes in their raw state will ultimately lead to fair adsorption capacities of contaminants due to the antagonism of different mechanisms evolving throughout the removal process (Kirk & Farrell 1987, Batzias & Sidiras 2007).

In this paper, the potential and effectiveness of the camphor sawdust was studied as an alternative adsorbent for the removal of dye Congo red in the aqueous solution. Then, the effects of camphor sawdust dosage, pH in aqueous solution, the contact time and dye Congo red concentration on dye Congo red adsorption by the camphor sawdust were investigated. Then, the equilibrium sorption isotherms are discussed to understand the mechanism of dye Congo red onto the camphor sawdust.

MATERIALS AND METHODS

Preparation of the adsorbents and dye Congo red: 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 a constant weight. Then they were grounded and sieved into a uniform size of 200 meshes and then stored for later adsorption experiments.

All chemicals used were of analytical reagent grade. The dye Congo red was used as a pollutant. 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.

Adsorption experiments: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing camphor sawdust (0.02, 0.04, 0.06, 0.08 and 0.10 g) and 100 mL of dye Congo red with various initial concentrations (10, 20, 50, 100, 150 and 200 mg/L) and pH (2.0, 4.0, 6.0, 8.0 and 10.0) 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 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:

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

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.

The removal rate of dye Congo red was calculated as follows:

$$\text{Removal rate}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad ...(2)$$

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 means (mean±SD). All statistical significance was noted at $\alpha = 0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

Characterization of camphor sawdust: The surface physical morphology of camphor sawdust was observed by a scanning electron microscope. The surface morphology of camphor sawdust is shown in Fig. 2. The camphor sawdust has a smooth and compact surface. It was featured by an irregular structure with cracks and crevices on the surface.

Influence of the initial pH of solution: The adsorption of dye Congo red onto the camphor sawdust as a function of pH value in aqueous solution was verified in the range from 2.0 to 10.0. The initial concentration of dye Congo red was 100 mg/L and the contact time for adsorption was kept at 3 h to ensure the complete equilibrium. The camphor sawdust dosage was 0.06 g and the react temperature was kept at 308 K. The experiment results obtained are shown in Fig. 3.

From Fig. 3, the initial pH value has a significant influence on the camphor sawdust adsorption capacity. At pH ≤

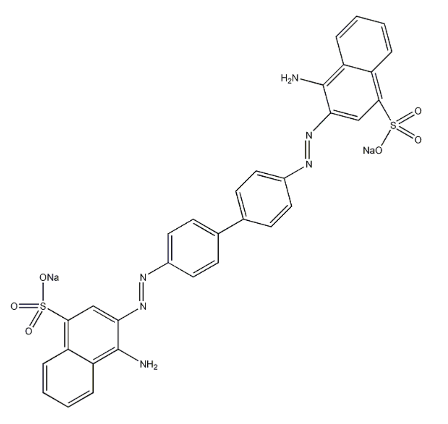

Fig. 1: The structural figure of the dye Congo red.

Fig. 2: SEM micrograph of the camphor sawdust.

6.0, the removal rate of dye Congo red was decreased with increase of pH value in aqueous solution. At pH ≥ 6.0, the removal of rate of dye Congo red has a little change.

Influence of contact time: Fig. 4 presents the influence of contact time on dye Congo red on the camphor sawdust under the condition, such as dye Congo red concentration of 100 mg/L, pH 6.0, temperature 308 K and the camphor sawdust dosage of 0.06 g. The results showed that the adsorption process was rapid for the first 50 min. This was explained by the fact that the adsorption sites were vacant at first stage, and the dye could easily interact with these sites. After 2 h, the adsorption capacity was almost constant and it was considered as the equilibrium time for dye onto the camphor sawdust.

Influence of camphor sawdust dosage: For studying the influence of camphor sawdust dosage on adsorption of dye Congo red, the tests were conducted with different camphor sawdust dosage. The initial concentration of dye Congo red was 100 mg/L and the contact time for adsorption was kept at 3 h to ensure the complete equilibrium. The pH value in aqueous solution was 6.0 and the react temperature was kept at 308 K. The experiment results obtained are shown in Fig. 5.

It can be observed from Fig. 5 that the removal rate of dye Congo red increased with increasing camphor sawdust dosage. The removal rate of dye Congo red increased from 4.05% to 30.12%, with increasing the camphor sawdust dosage from 0.02g to 0.1 g under equilibrium condition.

Influence of dye Congo red concentration: The influence of dye Congo red concentration was investigated. The camphor sawdust dosage was 0.06 g and the contact time for adsorption was kept at 3 h to ensure the complete equilibrium. The pH value in aqueous solution was 6.0 and the react temperature was kept at 308 K. The experiment results obtained are shown in Fig. 6. It can be seen that the adsorption capacity increased with the increasing the dye Congo red concentration. The adsorption was rapid for the first 10 min. This was explained by the fact that the adsorption sites were vacant at first stage, and dye could easily interact with these sites. After 120 min, the adsorption capacity was almost constant for all the studied concentrations and as such it was considered as the equilibrium time for dye on the

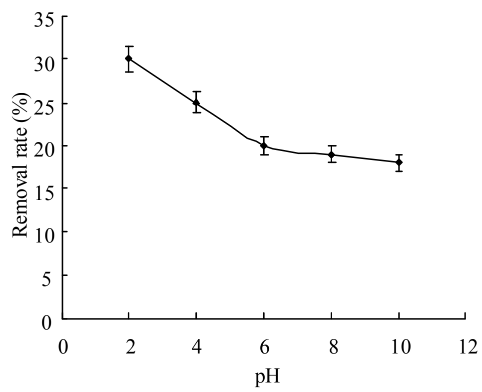

Fig. 3: The influence of the initial pH value in aqueous solution on adsorption.

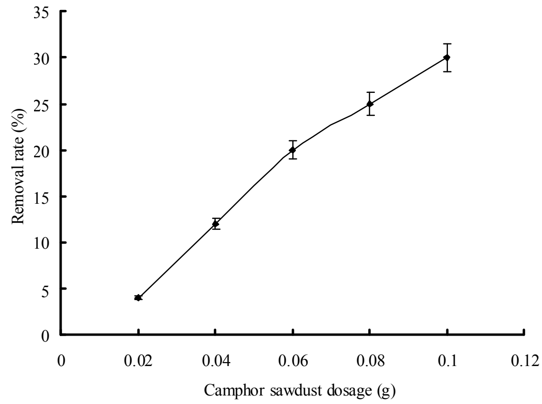

Fig. 5: The influence of camphor sawdust dosage on adsorption.

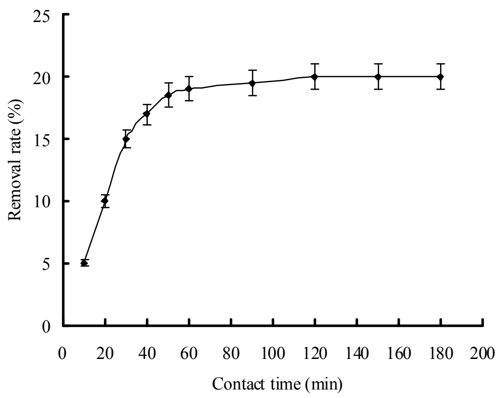

Fig. 4: The influence of contact time on adsorption.

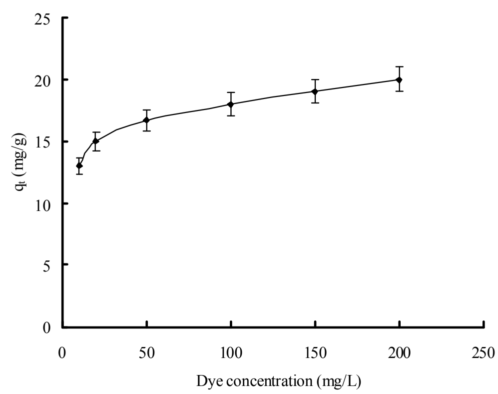

Fig. 6: The influence of dye Congo red concentration on adsorption.

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

Langmuir			Freundlich		
q_{max} (mg/g)	K_L (L/mg)	R^2	K_F ((mg/g)$^{1/n}$)	n	R^2
29.51	0.011	0.9715	1.96	2.12	0.9026

camphor sawdust.

Adsorption isotherm: To examine the relationship between adsorbent and adsorbate at equilibrium, and to search for the maximum sorption capacity of adsorbent, two adsorption isotherm models including Langmuir and Freundlich were applied. The Langmuir model and Freundlich model of linear forms are (Liu & Zhang 2011):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad ...(3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad ...(4)$$

where C_e (mg/L) is the equilibrium concentration in the solution, q_e (mg/g) is the adsorbate adsorbed at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity, n is the Freundlich constant related to adsorption intensity, K_L (L/mg) and K_F ((mg/g)$^{1/n}$) are the adsorption constants for Langmuir and Freundlich models respectively.

Langmuir and Freundlich isotherms were fitted to the experimental data from Fig. 6. The corresponding constants were calculated according to Eq.(3) and Eq.(4), which are listed in Table 1. The results indicated that the Langmuir isotherm fitted better than the Freundlich isotherm for the adsorption of dye Congo red on the camphor sawdust. The adsorption process is heterogeneity of the adsorbents and favourable adsorption. The maximum adsorption capacity obtained from the Langmuir isotherm is 29.51 mg/g.

CONCLUSIONS

In this paper, the potential and effectiveness of the camphor sawdust was studied as an alternative adsorbent for the removal of dye Congo red in aqueous solution. The surface physical morphology of camphor sawdust was observed by a scanning electron microscope. The camphor sawdust has a smooth and compact surface. The reaction factors, such as pH value in aqueous solution, contact time, initial dye Congo red concentration and camphor sawdust dosage, had important influence on the adsorption process. The Langmuir isotherm fitted better than the Freundlich isotherm for the adsorption of dye Congo red on the camphor sawdust. The adsorption process is the heterogeneity of the adsorbents and favourable adsorption.

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