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Removal of basic dyes from aqueous solution by low-cost adsorbent: Wood apple shell (*Feronia acidissima*)

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ABSTRACT

The adsorption of two basic dyes, methylene blue (MB) and crystal violet (CV) on wood apple shell (WAS) were investigated using a batch adsorption technique. A series of experiments were undertaken in an agitated batch adsorber to assess the effect of the system variables such as solution pH, dye concentration and temperature. Removal of dyes was observed to be most effective at higher pH. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The results showed that Langmuir equation fits better than the Freundlich equation. It was observed that the WAS adsorbent showed higher adsorption capacity for crystal violet (130 mg/g) than methylene blue (95.2 mg/g). The FTIR studies indicate that the interaction of dye and WAS surface is via the nitrogen atoms of the adsorbate and oxygen groups of the adsorbent. The adsorption of dyes onto WAS proceeds according to a pseudo-second-order model. Thermodynamic parameters such as free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were also calculated. The studies show that WAS, a lignocellulosic inexpensive material, can be an alternative to other expensive adsorbents used for dye removal in wastewater treatment.

1. Introduction

Water from spent dye baths and dye rinse operations contains unfixed dyes and is highly colored. The persisting colors and the low biodegradable nature of the spent dye baths represent serious problems to the environment [1]. These dyes show harmful effect on living organism on short period of exposure. Ingestion of methylene blue through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea and gastritis. Accidental large dose creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation and methemoglobinemia. Inhalation of crystal violet may cause irritation to the respiratory to the tracks, vomiting, diarrhea, pain, head ache and dizziness. Long-term exposure may cause damage to the mucous membrane and gastrointestinal tract [2].

Several methods such as oxidation with ozone/hydrogen peroxide, biological degradation, membrane filtration, ion exchange, electrochemical oxidation, reverse osmosis, photocatalytical degradation, and adsorption have been used for the removal of dyes [3–10]. All these methods have different color removal capability, capital costs, and operating rates. Among these methods, adsorption has been found to be superior to other techniques in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [11]. Activated carbon has a high adsorption capacity but limited use due to its high cost. This has led to a search for cheaper substitutes. The removal of organic color by adsorption onto agricultural residues has recently become the subject of considerable interest. There are several reports on the removal of dyestuffs by sawdust [12], hardwood [13], bagasse pith [14], banana pith [15] rice husk [16], and maize cob [17].

Wood apple (*Feronia acidissima*) is a native and common fruit cultivated in the dry plains of India and Sri Lanka. It is used in several culinary preparations and a significant amount of outer shell is discarded as waste. Wood apple shell carries the polar functional groups such as alcoholic, carboxylic and ether groups which show that it is a lignocellulosic material.

The study emphasizes on the use of agricultural waste, the shell of wood apple (*F. acidissima*) for the efficient removal of basic dyes from aqueous solution. Batch adsorption studies were carried out systematically in terms of process parameters such as agitation time, initial concentration, and pH.

2. Materials and methods

2.1. Materials

2.1.1. Preparation of the adsorbent

Wood apple shell (Feronia acidissima) was used directly for adsorption experiments without any chemical treatment. The shell was ground in a steel mill and the resulting crumbs were washed thoroughly with deionized water and dried in an air oven at 100 °C for 24 h, ground and passed through British Standard Sieves (BSS) of 240-mesh size and used as such.

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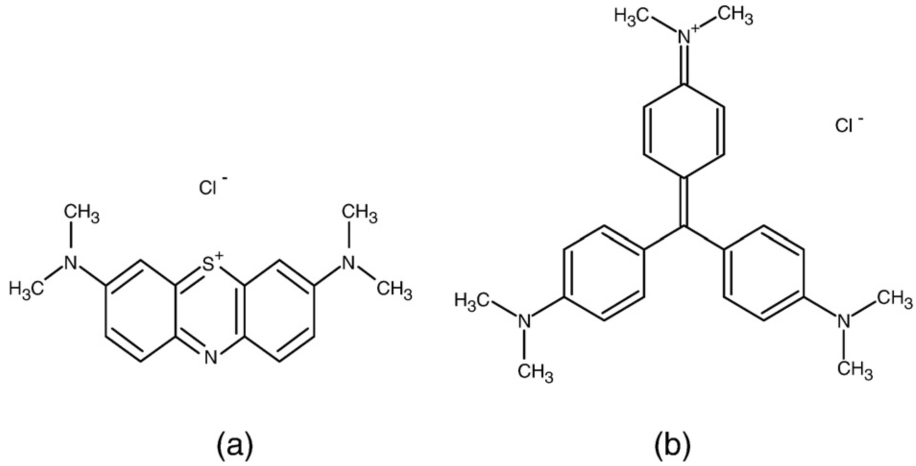

Fig. 1. Structure of methylene blue (a) and crystal violet (b) dyes.

2.1.2. Adsorbates

Methylene blue (MB) (C.I. 52,015, molecular formula $C_{16}H_{18}Cl \cdot N_3SH_2O$, $\lambda_{max} = 664$ nm); and crystal violet (CV) (C.I. 42555, molecular formula $C_{25}H_{30}N_3Cl$, $\lambda_{max} = 590$ nm) dyes were supplied by S.D. Fine Chem. Ltd. India. The dyes' structures are shown in Fig. 1.

2.1.3. Instrumentation

The concentration of dyes in solution was determined spectrophotometrically on a Shimadzu 1650PC UV–Visible spectrophotometer. The pH of the solution was measured with an Elico (India) pH meter. FTIR spectra of different samples were recorded using a Perkin FTIR in absorption mode averaging 32 scans and at a resolution of 4 cm and using KBr pellet method.

2.2. Methods

2.2.1. Adsorption studies

In batch method, a fixed amount of the adsorbent (0.1 g) was added to 100 ml of the dye solution of varying concentration taken in 250 ml stoppered conical flasks, which were placed in a thermostated agitation (32 °C) assembly. The solution was agitated continuously (200 rpm) at constant temperature for 6 h to achieve equilibration. The concentration of the dyes in the solution after equilibrium adsorption was determined spectrophotometrically at λ_{max} 664, and 590 nm for methylene blue and crystal violet respectively. The pH of the adsorbate solution was adjusted using a 0.1 M aqueous solution of either HCl or NaOH.

The adsorbate uptake q_e (mg/g), can be calculated as

$$q_e = (C_o - C_e)V / W \quad (1)$$

where C_o and C_e are the initial and equilibrium adsorbate concentrations (mg/L), V, the volume of the solution and W the mass of the adsorbent (g) and q_e is the amount adsorbed.

Table 1
Physical characteristics of WAS.

Parameters Characteristics	Value	References
pH	6.89	[18]
pHzpc	5.62	[19]
Carbon	45.22%	CHNS analyser
Hydrogen	6.21%	CHNS analyser
Nitrogen	0.077%	CHNS analyser
Moisture	0.07%	[20]
Ash	4.5%	[20]
Bulk density	0.53 g cm^{-3}	[20]

2.2.2. Kinetic studies

Samples of WAS were agitated at 200 rpm with a fixed concentration of adsorbate solution (1000 ml) at the desired temperature in a thermostated bath. The adsorbent was introduced to the reaction flask at zero time and 5 ml of the solution phase was withdrawn at various time intervals. These aliquots were centrifuged to remove particulates and were analyzed for the concentration of dye.

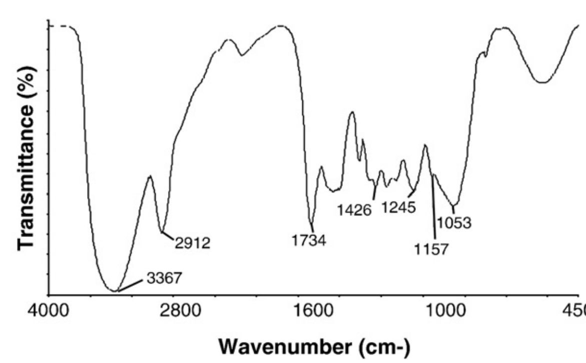

Fig. 2. FTIR spectrum of WAS.

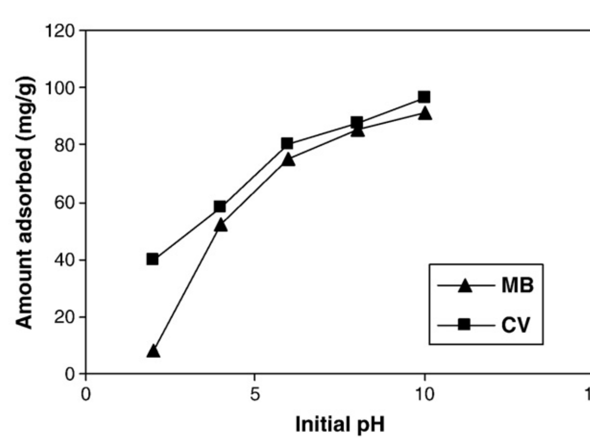

Fig. 3. Effect of pH on the adsorption of dyes on WAS. C_o; 100 mg/L, T; 305 K, WAS; 1 g/L.