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Removal of Malachite Green from Aqueous Solutions by Adsorption on to Timber Waste

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Abstract

Sawdust a timber waste has been used as a bio-sorbent for the removal of a cationic dye, malachite green from aqueous solutions. The process of removal has been optimized for different parameters like initial concentration of dye solution and contact time, pH, adsorbent dose, and temperature. pHzpc of the adsorbent was determined. Elemental analysis of the adsorbent was carried out. FTIR was performed to determine various functional groups attached to the adsorbent surface. The experimental results indicate that 5g/L g of sawdust was able to remove 93% of dye from an initial concentration of 20 mg L^{-1}. Equilibrium was achieved in 100 min. The removal of dye exhibited decreasing trend with increasing temperature and it shows exothermic nature of adsorption. Adsorption data were modelled by Langmuir and Freundlich isotherms. The data was better fitted in Freundlich isotherm model. The maximum adsorption capacity of adsorbent was found to be 13.87 mgg^{-1} at 298 K. The dye adsorption followed the pseudo-second-order kinetics. The results show that saw dust can be a better alternate for the removal of MG from aqueous solutions and effluents.

Keywords: Adsorption, sawdust, malachite green, isotherm.

1. Introduction

Today many dyes are being widely used in different industries which discharge large volumes of wastewater. The wastewater contains large amount of dissolved dyestuff and other products. The disposal of dye wastewater is a big challenge and it causes harm to the aquatic environment (Arulkumar et al., 2011; Wu and Tseng,2008). Some of the dyes present in wastewater even decompose into carcinogenic aromatic amines under anaerobic conditions and cause serious health problems to human beings as well as other animals. Due to the complex molecular structure, dyes are usually very difficult to be biodegraded, and is too hard to eliminate them under natural aquatic environment (McKay et al.,1996). Sawdust is a by-product of timber industry and it is a common source of cellulose and lignin. Sawdust is mainly used in animal feed and paper production, but otherwise it is discarded as a waste material. This polysaccharide has the potential use in a wide variety of applications, such as food and fodder of animals, pharmaceutical and cosmetics industries adhesives and emulsifiers (Asadullah et al., 2010). Among biological materials, agricultural materials usually play an important role due to being widely and easily produced. Different crops are being cultivated all over the world such as rice, wheat, sugar cane, corn, etc. are available for development of activated carbon or itself a good adsorbent for different pollutants like heavy metals or dyes for adsorption experimentation (Sharma and Uma, 2010).

2. Materials and Methods

Biomass sawdust, collected from a local saw mill, Varanasi, was oven dried at 105°C for 24 h, and then sieved to keep average particle size in 150 µm range. The sieved material was collected in desiccator for further studies without any modification.

All the reagents used were of analytical reagent grade chemicals and were obtained from Merck, Mumbai, India. Stock solution of the dye (malachite green) was made by dissolving them in deionized water. The chemical formula of MG: $C_{23}H_{25}N_2Cl$, molecular weight: 365, λmax ; 618 nm. The structure of the dye (MG), C.I. No. 42000.

2.1 Batch mode experiments

50 ml of dye solution of different concentrations were taken in 125 ml of capped reagent bottles. 0.25 g of adsorbent was added in each reagent bottle containing 50ml of MG solution and then agitated at 100 rpm on temperature controlled shaker for various time intervals to observe the saturation time. After saturation time, adsorbent was separated from adsorbate solutions by centrifugation. Analysis of residual concentration of MG in each samples was carried out by Spectrophotometer(Baush and Lomb. USA). Amount adsorbed per unit mass of adsorbent was calculated by following equation.

$$q_e = \left(\frac{C_i - C_e}{W}\right) * V \quad (1)$$

Where C_i and C_e are the initial and equilibrium concentrations of MG respectively (mgL^{-1}), q_e is the amount adsorbed per unit mass of the adsorbent (mgg^{-1}); W is the amount of adsorbent (gL^{-1}).

3. Result and Discussions

3.1Characterization of sawdust

The surface characteristics of the sawdust were determined. Point zero charge of raw sawdust indicates the electrical neutrality of the adsorbent surface at a particular value of pH. Determination of pH_{zpc} was done to investigate the surface behaviour of sawdust (Mall et al.,2005). Point zero charge of raw sawdust was calculated by titrimetric method and that was 7.37.

FTIR of sawdust were identified in the range 0–4500cm^{-1} using a Fourier transform infrared spectrometer (Simadzu, Japan/8400S). For the spectra, ratio of sample and KBr is 4 mg of samples was mixed with 200 mg of spectroscopically pure KBr to prepare pallet of the sample.

Presence of different functional groups shown in figure 2, the main peaks for the samples are at 3395.23, 2923.731661.38, 1022.42, and 566.02 cm^{-1}, surface hydroxyl groups - OH str[1], can be attributed to the stretching vibrations of C-H bonds in alkanes indicative of aldehydic group present on the surface, the siloxane band appears, large amounts of cellulose and the porosity of surface demand that such a material should be used for adsorption studies.

3.2Effect of initial dye concentration and contact time

The effect of different initial concentration of selected dye, malachite green onto saw dust powder is presented in figure 1. The percentage removal of dye decreased with increase in initial dye concentration and showed little decrease by increasing concentrations. This can be explained that all adsorbents have a limited number of active sites, which become saturated after certain concentration (Senthil Kumar et al., 2010).

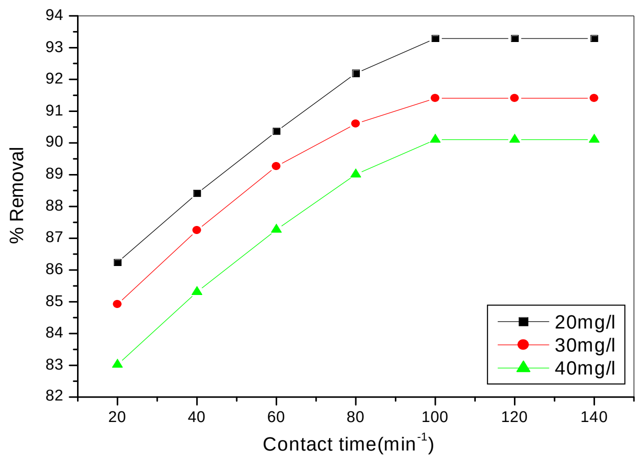

Figure 1: Effect of initial dye concentration on adsorption of malachite green by saw dust.

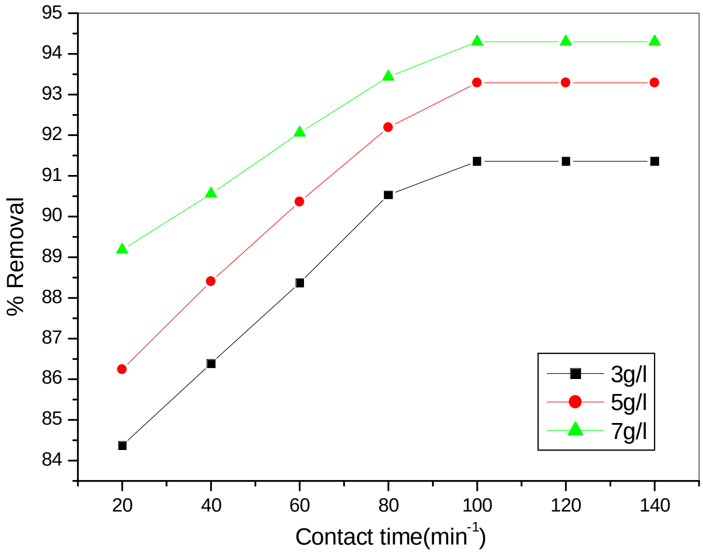

Figure 2: Effect of adsorbent dose on adsorption of malachite green by saw dust

3.3Effect of adsorbent dose

Figure 2 shows the adsorption profile of malachite green versus different saw dust dose in the range of 3–7.0 g L^{-1}. It was observed that percentage of dye removal increased with increase of adsorbent dose. Such a trend is mostly attributed to an increase in the adsorptive surface area and the availability of more active adsorption sites (Ghaedi et al., 2011).

3.3 Effect of pH

pH has been recognized as one of the most important parameters that affects any adsorption process. Thus the effect of pH on the removal efficiency of malachite green was studied at different pH ranging from 4.0 to 8.0. The maximum adsorption of malachite green occurred in the higher (alkaline) pH range. The increase in dye removal capacity at higher pH may also be attributed to the reduction of H^+ ions

4. Adsorption Kinetics

4.1Pseudo first order and pseudo second order kinetics

For evaluating the adsorption kinetics of malachite green, the pseudo-first-order kinetic models have been used and found fit to the experimental data:

$$\log (q_e - q) = \log q_e - \left(\frac{K_{ad}}{2.303}\right) t \quad (2)$$

$$\frac{dq_t}{dt} = k_2(q_e - q)^2 \quad (3)$$

$$h = k_2 q_e^2$$

The log ($q_e - q_t$) versus t plot (figure7) were linear with R^2 0.949. However, equilibrium adsorption capacities, q_e obtained from these plots varied widely, The plot of t/qt against t at different temperatures is shown in Figure 3. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.99$) over the temperature range of 298–318 K. The value of q_e and k_2 can be determined by the slope and intercept of the straight line of the plot of "t/q_t versus t". k_2 ($gmg^{-1}\ min^{-1}$) is the rate constant of pseudo-second order reaction. (Ho and McKay,2009).

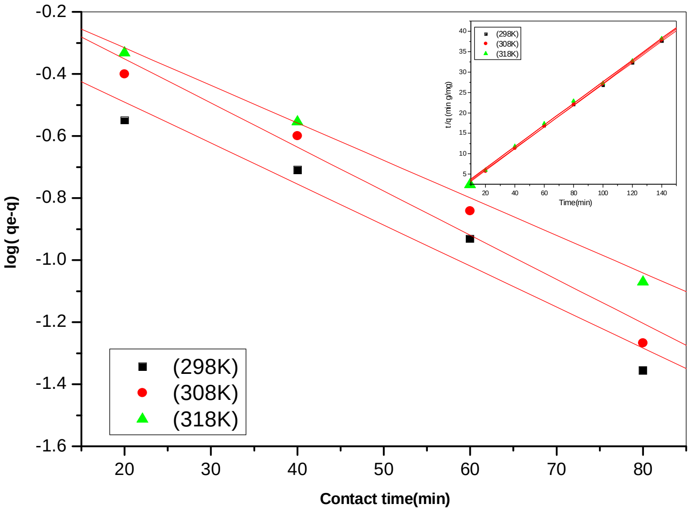

Figure 7: Pseudo-first-order kinetic for adsorption of malachite green onto sawdust at different temperatures.

5. Equilibrium Sotherm

5.1 Langmuir isotherm

The linear form of Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption without interaction between adsorbed molecules commonly expressed as (Uma et al., 2013;Hameed,2009):

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \qquad (4)$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium respectively, Q^o and b are Langmuir parameters related to the capacity and energy of adsorption respectively. The constants b and Q^o can be determined from the slope and intercept of the plot between C_e/q_e and

C_e and at different temperature showing the formation of monolayer coverage of the adsorbate at the outer surface of adsorbent. Values are presented in Table 1.

Table 1: Values of constants of Langmuir and Freundlich, adsorption isotherm for adsorption of malachite green on sawdust.

Isotherms	**Temperature(K)**	**Parameters**		
Langmuir		Qo (mg/g)	b(l/mg)	R2
	298	13.87	0.02	0.988
	308	14.54	0.03	0.888
	318	14.71	0.03	0.987
Freundlich		Kf(l/g)	1/n (l/g)	
	298	0.49	0.60	0.999
	308	0.35	0.64	0.982
	318	0.34	0.59	0.996

5.2Freundlich isotherm

The Freundlich isotherm is applicable to non-ideal adsorption on heterogeneous surfaces result of the assumption that the adsorption occurs and non-uniform distribution of the heat of adsorption over the adsorbent surface takes place (Freundlich,1885). The linear form of the isotherm can be represented as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

where q_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), K_f (mg g^{-1}) (Lg^{-1}) 1/n is the Freundlich constant related to sorption capacity and n is the heterogeneity factor. K_f and 1/n are calculated from the intercept and slope of the straight line of the plot log q_e versus log C_e. Higher correlation coefficient (R^2) values of the straight lines obtained at each temperature confirm the validity of Freundlich adsorption isotherm for both adsorbents on the basis of correlation factor are depicted and values are presented in Table 1.

6. Conclusions

Saw dust was characterized by different techniques. Removal efficiency of adsorbent was found to be quite significant. It was observed that dye removal decrease with increasing concentrations of dye solution. Maximum removal for each concentration ranges can be achieved within 100 minutes only. Removal process was endothermic in nature. Pseudo second order model fitted best in this system. Various isotherm models were applied to investigate the removal process and it was found that Freundlich isotherm is the most suitable isotherm for this process. The isothermal data of

Langmuir model indicate that the adsorption capacity 13.87 mg/g of this biomaterial is significant. On the basis of this study it can be concluded that application of low cost adsorbent for the removal of malachite green from aqueous solutions.

7. Acknowledgement

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