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Freundlich, Langmuir adsorption isotherms and kinetics for the removal of malachite green from aqueous solutions using agricultural waste rice straw

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ABSTRACT

Malachite (N-methylated diamino triphenyl methane), a green menace, is extensively being used as dye for colouring silk, leather and paper. It is carcinogenic and catalyzes allergic problems. In this work agricultural waste rice straw as adsorbent was employed to remove Malachite green from aqueous solutions. Effects of pH, concentration of the dye, temperature and adsorbent dosage was determined for maximum removal of dye. Equilibrium isotherms for the adsorption of the dye were well fitted to the Freundlich and the Langmuir isotherm models. Thermodynamic parameters, Gibb's free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) have revealed spontaneous and endothermic nature of adsorption process. Kinetic measurements established that the adsorption of Malachite green over rice straw follows first-order kinetics

Keywords: Adsorption, Malachite green, Isotherm, Kinetics, Dye

1. Introduction

Leather, textile, paper and pulp industries discharge a large quantity of highly coloured effluent containing dyes into nearby rivers or land without any treatment because conventional treatment methods are very expensive. Small amount of dye present in water (< 1 mg/L), is highly visible and consequently undesirable (Sun and Yung 2003). Based on the chromophore group, 20 to 30 different groups of dyes are effective pollutant so removal of color from effluents is one of the major environmental problems. Different investigations are focused on effectiveness of low cost adsorbents like pearl mille husk, neam leaf powder, coconut husk, wheat straw, sewage sludge, perlite, maize cobs, wood, peat, natural adsorbent, banana pith and chitin (Poots et al. 1976; Poots et al.1978; Lin et al.1987; Nawar and Doma 1989;Low and Lee 1990; Nassar and Guendi 1991; Namasivayam and Kanchana 1993; Annadurai and Krishnan 1996; Walker and Weatherly 1998; Selverani 2000; Dogan et al. 2000;Robinson et al. 2002; Olereo *et al.*,2003; Verma and Mishra 2006;) for effluent treatment for various application. The dye under investigation, Malachite green is used to colour silk, leather and paper. It is water-soluble and found as contaminant in industrial effluents. Clinical and experimental observations reported so far reveal that malachite green is a multi-organ toxin. Malachite green is highly cytotoxic to mammalian cells (Fessard et al. 1999) and carcinogenic to liver, thyroid and other organs in animals (Rao 1995; Rao and Fernandes 1996; Doerge et al. 1998; Mahudawala et al. 1999; Sundarrajan et al. 2000). Incidences of tumours in lungs, breast and ovary have also been reported from rats exposed to malachite green (Werth and Bioteaux 1958). Because of its hazardous health effects, the present study is devoted to its removal from the wastewater using adsorption technique. The study has been carried out under effect of different variables, like temperature, pH, adsorbent dose and adsorbent concentration for the development of convenient and economically viable process for malachite green removal using a waste material rice straw as potential adsorbent.

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2. Experimental

Malachite green, (N-methylated diamino triphenyl methane) (Figure 1) dye, was obtained from M/s Merck. All other reagents were of A.R. grade. Studies were carried out by preparing the stock solution of 100 mg/L concentration in double distilled water. Concentrations of the dye in aqueous solution was monitored on UV–VIS spectrophotometer, Model 1650 (Shimadhu) over a wavelength range of 624 nm.

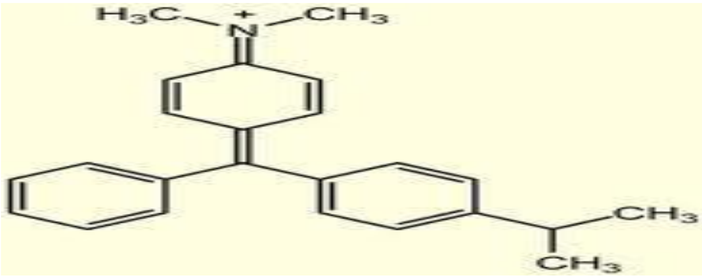


Figure 1: Malachite green, (N-methylated diamino tri phenyl methane)

Adsorbent rice straw was collected from the local agricultural fields. Before using it as adsorbent, rice straw were cut into segment of 10 cm length and washed with water to remove soil and dust, and then dried in hot air oven for overnight. Dried straw was crushed and sieved to retain the 354,500 and 595 nm mesh fraction and stored in desiccators for subsequent use.

2.1 Adsorption studies

The prologue investigations were carried out in batches at different conditions of pH, concentration, time, amount of adsorbent and temperature to check the tendency of adsorption process. In each experiment 250 mL measuring flasks containing 100 mL of dye solution of known concentration was mixed with known amount of adsorbent and mixture was sporadically shaken (100 rpm) and then kept for different time intervals (min) for saturation. The supernatant was harvested by centrifugation at 10000g for 20 min and amount of dye adsorbed was determined spectrophotometrically at the λ_{max} 624 nm.

2.2 Kinetic studies

Kinetic investigations are carried out to measure the rates of reaction under various experimental conditions; dye concentration, pH, temperature and time on the rates of reaction to attainment of equilibrium during the adsorption process. In different measuring flasks, 100 mL of dye solution of known concentration with definite pH and known amount of adsorbent was taken at different temperatures of 25, 30 and 35 ^{0}C with periodic shaking. Dye adsorbed on rice straw was determined by standard procedure.

3. Results and discussion

3.1 Characterization of adsorbent

An untreated rice straw has dry matter, crude protein and ash content 89, 3.3 and 2.9% respectively. Mesh size of matrix 500 and 595 was more effective for the adsorption of dye as compare to 354 nm because decrease in particular size increases available surface area for adsorption (Fig 2a). Different adsorbent dose, revealed that with the increasing dosage of adsorbent the rate of removal of adsorbate increases. There is increase in dye adsorption when amount of adsorbent is increased from 0.5 to 1.0 % but after that it remains constant (2b). So adsorbent concentration of 1% was used for the further adsorption study.

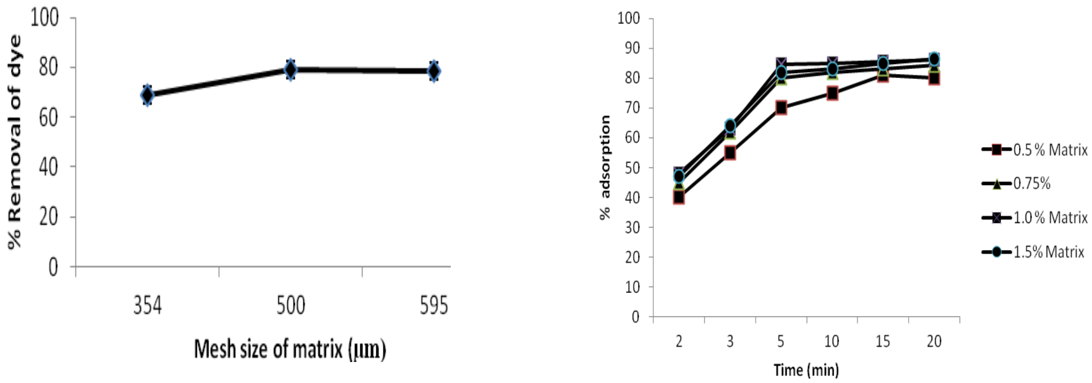
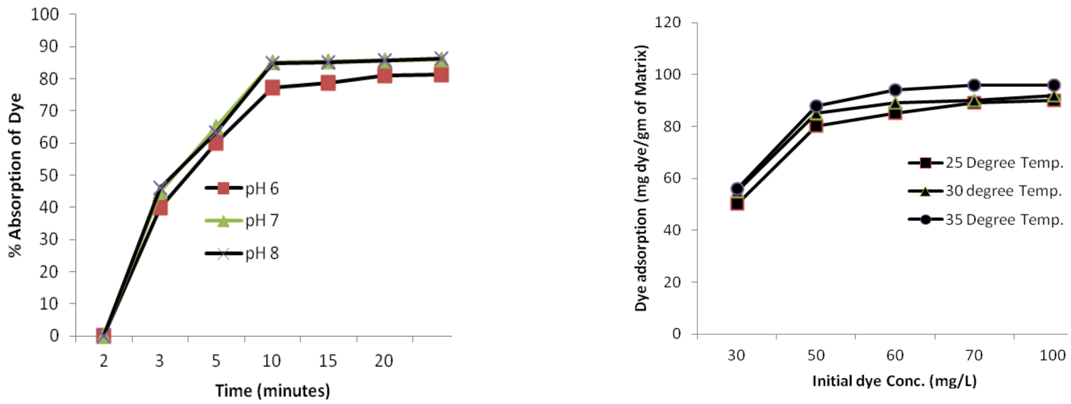


Figure 2: Effect of (a) mesh size and (b) amount of adsorbent for the removal of for malachite green on rice straw system

3.2 Adsorption studies

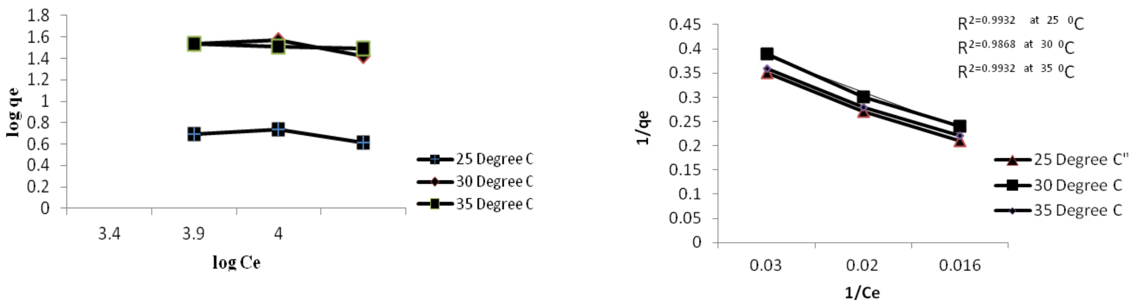
The adsorption characteristics of Malachite green by rice straw were studied at varying pH range from 6, 7 and 8. The profile (Figure 3a) concerning pH shows that in the observed pH range the adsorption capacity was not much affected and remains almost same at lower pH 6, while as the pH increases adsorption enhanced and it was maximum (86.1%) at pH 8. As such all subsequent studies were performed at pH 8.0, which is the optimum value for adsorption. The adsorption of Malachite green was also recorded in the concentration range from (30 to 100 mg/L at a fixed pH of 8.0 and temperatures 25, 30 and 35 ^{0}C (Figure 3b).



(a) (b)

Figure 3: Effect of (a) pH and (b) initial Malachite green concentration for the adsorption

Results specify that the adsorption of Malachite green increases with increase in temperature, indicating endothermic nature of process. It is also observed that the initial removal of dye is fast and with the rise in concentration the percentage uptake gradually decreases. The profile obtained from the study of concentration at different temperatures was used to obtain Langmuir and Freundlich adsorption isotherms by using well-known adsorption isotherm equations (Slejko 1985; Helfferich 1962). In both the cases linear plots were obtained, which reveal the applicability of these isotherms on the ongoing adsorption process. Freundlich and Langmuir plots [Figure 4 (a) and (b)] respectively for the adsorption of Malachite green on rice straw and different Freundlich and Langmuir constants n (87,90 and 92 mg/gm of matrix) and K_f (9.3,10.3 and 11.3) at different temperature 25,30 and 35^{0}C derived from these plots describe the adsorption capacity was found to increase with rising temperature. This reveals the endothermic nature of the ongoing process.



(a) **(b)**

Figure 4: (a) Freundlich and (b) Langmuir adsorption isotherm for malachite green on rice straw at different temperatures

To examine the progression of adsorption dimensionless constant, separation factor *r* (Eagleton 1966) was calculated by following equation:

$$r = \frac{1}{1 + bC_0} \qquad (1)$$

where *b* and C_0 values were derived from Langmuir isotherm. The decline in *r* values with rising temperatures clearly denotes that the ongoing adsorption process is much favourable at higher temperatures. The values of r indicates the nature of the isotherm, if the conditions are r>1, r=1, r<1 and r= 0, the adsorption process is unfavourable, linear, favourable and irreversible respectively. The value of r was less than one which showed that the adsorption process was favourable. The thermodynamic data were evaluated from Langmuir isotherms using following equations:

$$\Delta G^\circ = -RT \ln K \qquad (2)$$

$$\Delta H^\circ = \frac{RT2T1}{T2 - T1} \ln \frac{K2}{K1}$$

$$\Delta S^\circ = \Delta H^\circ - \Delta GT$$

Where *K*, *K*1 and *K*2 are the equilibrium constants obtained from the slopes of adsorption isotherms. Evaluated thermodynamic parameters, change in free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) are presented in Table 1.

Table 1: Thermodynamic parameters for the adsorption of malachite green on rice straw

Thermodynamic Parameters	Thermodynamic Values
ΔG^o (kJ/mol) *at*	
25 ^{0}C	-7.7
30 ^{0}C	-8.5
35 ^{0}C	-9.0
ΔH^o (kJ/mol)	436.83
ΔS^o (J/(mol K)	430

Negative values of ΔG° establish the feasibility of adsorption process. Further, the decrease in the values of ΔG° with the increasing temperature indicates the spontaneity of the process at higher temperatures. The endothermic nature was also confirmed from the positive values of enthalpy change (ΔH°), while good affinity of Malachite green towards the adsorbent materials is revealed by the positive value of ΔS°.

3.3 Kinetic studies

For the effectual designing and representation of the ongoing process, kinetics parameters were calculated. Kinetics of adsorption process at different temperatures (25, 30 and 35°C) exhibited an increase in adsorption with the increase in temperature. The half-life ($t_{1/2}$ =0.693/kd) of each process was also calculated and was found to decrease with increase in temperature. These results once again confirm endothermic nature of the ongoing process.

3.4 Adsorption rate constant study

In order to study the specific rate constant of Malachite green on rice straw, the well-known Lagergren first-order rate equation was employed (Periasamy and Namasvayam 1994). Values of log (qe $-qt$) was calculated for each time interval at different temperatures:

$$\log(q\mathrm{e} - qt) = \log q\mathrm{e} - k_{\mathrm{ad}}\, t/2.303$$

where qe and qt signify the amount adsorbed at equilibrium and at any time t. The graph of log (qe $-qt$) versus t (Figure 5) exhibits straight lines at 25, 30 and 35^{0}C and confirm the first order rate kinetics for the ongoing adsorption process. The k_{ad} values evaluated, from Lagergren plots are found to be 9.4×10^{-3}, 7.0×10^{-3} and 5.6×10^{-3} min^{-1} at 25, 30 and 35^{0}C, respectively.

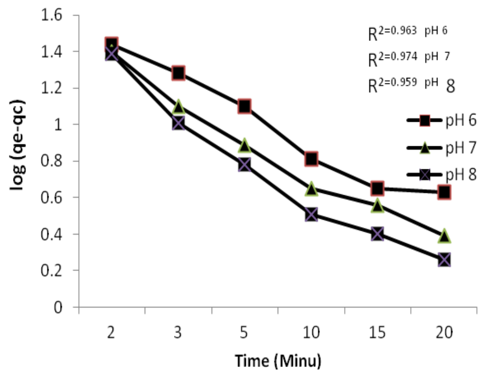


Figure 5: Lagergren's plot of time vs. log(qe $-qt$) for malachite green on rice straw system at different temperatures

3.5 Thermodynamic Equilibrium Constant (K^{0}c)

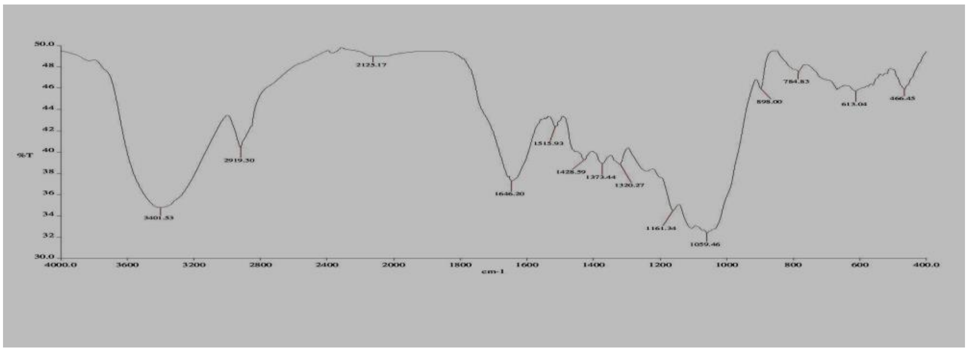
Thermodynamic equilibrium constant for malachite green on rice straw was obtained at 35^{0}C.

$$K^0c = C_a/C_e \tag{3}$$

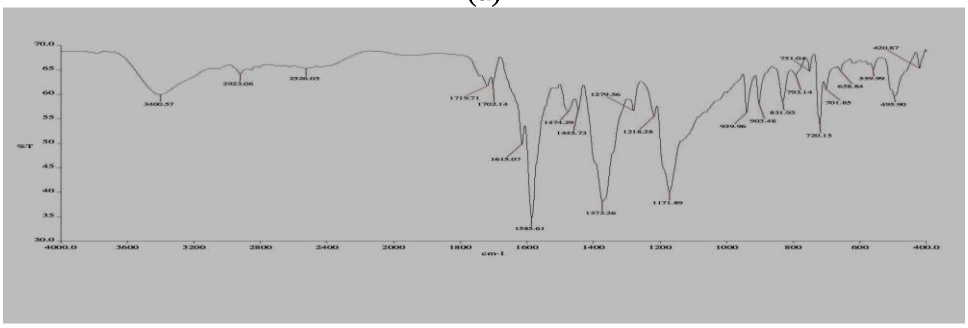
Here C_a was concentration of malachite green on rice straw at equilibrium in mg/L and C_e is the equilibrium concentration of malachite green in solution (mg/L). Thermodynamic equilibrium constants (K^{0}c) was 4.2, 5.7 and 5.72 at pH 6,7 and 8 respectively.

4. The FTIR analysis

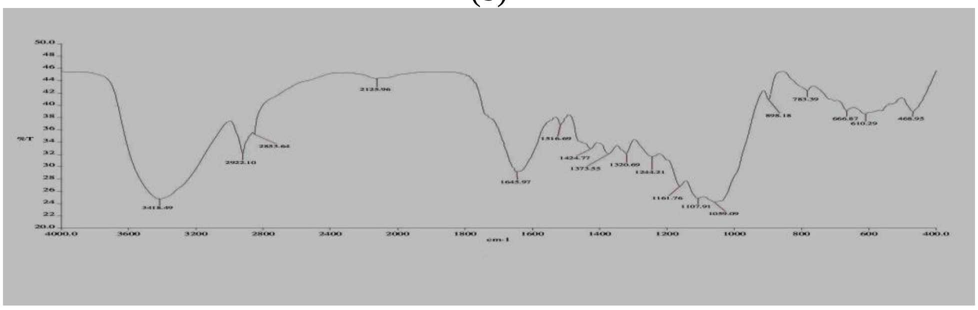
The FTIR spectra of the rice straw, dye and dye adsorbed on rice straw are presented in (Figure 6 a, b, c). The band at 3418 cm $^{-1}$ represents the presence of –OH and –NH groups. The band observed at 2922 cm^{-1} is associated to asymmetric stretches of –CH group. However, a small peak located around 2853 cm $^{-1}$, which is assigned for symmetric stretching vibrations of –CH group. The dual bands at 1645 and 1424 cm^{-1} indicates the presence of –COO, –CO and –NH groups for the untreated and treated ginger waste. Another absorption band appearing around 1161 and 1059 cm^{-1} can be attributed to the C–O stretching and sulphonic group respectively. Spectrum explains that some peaks were shifted or disappeared and that new peaks were also detected. These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of the rice straw adsorption process. It is reflecting the complex nature of adsorbent and shows significant band shifting and intensity changes due to malachite green adsorption.



(a)



(b)



(c)

Figure 6: FTIR spectrum (a) for rice straw(b)dye and (c) dye with rice straw

4.1 Desorption studies

For economical adsorption process, it is necessary to regenerate spent adsorbent, therefore, desorption test on spent rice straw were carried out with 0.1 M solution of sodium hydroxide, sodium chloride, potassium chloride and water (120 rpm for 1 h). It was observed that by using sodium hydroxide higher amount of dye (almost 99%) can be regenerated from the adsorbed rice straw surface after three cycles. Only 0.1M NaOH was used as eluting agent because it was more effective with respect to other desorbing agents. The reversibility of adsorption depends on binding bond such as ionic or covalent bonding or weak binding forces such as Van der Waals' forces or a dipole–dipole interaction formed between the adsorbent surface and the dye molecules. Therefore, different surface characteristics would help to explain the reversibility of adsorption.

4.2 Adsorption consideration for different adsorbent

Many adsorbents for malachite green removal, including activated carbon, various biosorbents, minerals, are reported in the literature (Mittal 2006 ; Bulut et al. 2008; Hamdaouia et al. 2008; Zhang et al. 2008, Kumar and Sivansan 2007;Baek et al. 2010; Rais and Kumar 2010; Shabudeen 2011;). It was found that rice straw is superb adsorbent for malachite green. Activated carbon, was more effective in sorption of malachite green than woody adsorbent. However, activated carbon is cost exorbitant since an enormous energy would be consumed during manufacture of activated carbon. On the contrary, rice straw is very cheap since it has little economic value and can be directly used as adsorbent without any modification. In this sense, rice straw is an excellent adsorbent for malachite green.

5. Conclusion

Removal of malachite green from solution was possible using selected adsorbents. Rice straw was effective for which the removal reached more than 87.27% at concentration of 50 mg/L and at pH 8. Increase in the dose of adsorbent, initial concentration of malachite green and contact time are favourable for increase the adsorption of malachite green. The kinetic of the malachite green on rice straw adsorption was found to follow first order mechanism. The Gibbs free energy was obtained for system and it was found to be -9.0 kJmol for removal of malachite green in synthetic solution. The adsorption data can be satisfactorily explained by Freundlich isotherm. Higher sorption capacity of this sorbent indicates that rice straw can be used for the treatment of malachite green.

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