

EQUILIBRIUM ADSORPTIVE REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTION USING ACTIVATED CARBONS

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Introduction

Malachite green (MG), a basic triphenyl methane dye is widely used in textile, food, acrylic industries and distilleries. In aquaculture it acts as an anti-fungal, anti-bacterial and antiparasitological agent. It has been classified as Class II health hazard but is still used in some countries because of its low cost. It is difficult to biodegrade and remove it from water. Untreated disposal of water contaminated with the dye into the receiving water body causes damage to aquatic life as well as to human beings by its mutagenic and carcinogenic effects. Among various treatment technologies, adsorption on activated carbon has proven to be one of the most effective and reliable treatment method because activated carbon have a high surface area, microporous structure and high chemical reactivity of their surface. The present paper decreases the influence of surface area and the chemistry of the carbon surface and pH of the solution on the adsorptive removal of malachite green from aqueous solutions.

Experimental

Adsorption of MG from aqueous solution has been studied using four granulated activated carbons namely ACG-100, I-60, I-50 and ICEG having different surface areas and associated with different amounts of carbon-oxygen surface groups. Adsorption studies were carried out by contacting 0.1 g each of an activated carbon with 20 mL of MG solutions of known initial dye concentrations. At equilibrium the dye concentrations were determined spectrophotometrically at a wavelength of 424 nm.

The adsorption studies were also carried out after modifying the surface of the carbons by oxidation with nitric acid and then degassing of the oxidized sample at 400°, 650° and 950°C. The oxidation of the carbon results in enhancing the amounts of carbon-oxygen surface groups while the degassing causes gradual elimination of different amounts of these surface groups. The procedures for oxidation, degassing and determination of carbon-oxygen surface groups have been described elsewhere (1-3).

The amount of equilibrium adsorption, x_e (mg/g), was calculated by

$$x_e = (C_o - C_e) \frac{V}{W} \dots\dots\dots(1)$$

where C_o and C_e (mg/L) are the initial and equilibrium dye concentrations respectively. V is the volume of the solution (L) and W is the mass of activated carbon used (g).

Results and Discussion

Effect of Contact Time

The adsorptive removal of MG as a function to time with an initial concentration of 500 mg/L was carried out using ACG-100 and I-60. There is a rapid adsorption in the beginning and thereafter the adsorption rate decreases gradually and the adsorption reaches equilibrium in about 160 min for the two activated carbons. The time of contact for subsequent studies was kept for 240 min to make sure that equilibrium was attained. ACG-100 has a higher adsorption capacity of 46 mg/g as compared to that of I-60 having adsorption capacity of 42 mg/g at equilibrium. This may be mainly due to higher surface area of ACG-100 (1600 m²/g)

Adsorption Isotherms

The equilibrium adsorption of MG from its aqueous solutions in the concentration range of 100 to 1000 mg/L on all the four activated carbons are Type I of the BET classification. This type of isotherm corresponds to monolayer adsorption. The adsorption is maximum in case of the ACG-100 (1600 m²/g) and minimum in case of ICEG (550 m²/g). The increase in amount adsorbed appears to be in direct proportion to surface areas of these activated carbons. The equilibrium data is followed by both Langmuir and Freundlich isotherm models.

Effect of carbon-oxygen surface groups on adsorption

In order to determine the influence of carbon-oxygen surface groups on the adsorption, two carbons samples ACG-100 and I-60 were oxidized with nitric acid and then degassed at 400°, 650° and 950° temperatures. Oxidation results in an increase in the carbon-oxygen surface groups whereas degassing results in a gradual removal of the carbon-oxygen surface groups. The adsorption isotherms of MG on oxidized and degassed ACG-100 samples are shown in Fig 1. The amounts of carbon-oxygen surface groups present on the oxidized and degassed ACG-100 carbon samples are recorded in Table 1. It is seen that adsorption increases on oxidation and decreases gradually as the temperature of degassing is enhanced. The increase in adsorption of MG on oxidation can be attributed to the increase in carbon-oxygen surface groups.. It is also seen that the decrease in adsorption of MG is only small in the case of 400°- degassed sample and considerably larger on the 650°-degassed carbon sample. The adsorption on the 950°-degassed sample is almost of the same order as the adsorption on the 650°-degassed sample. It appears that the adsorption of MG is determined by the amount of acidic surface groups when are evolved as CO₂ on degassing. As 400°-degassed sample loses only a small portion of this acidic group, the decrease in adsorption is only small. In the case of 650°-degassed carbon sample which loses most of its acidic groups but retains the other surface groups in tact, the adsorption decreases considerably. The acidic surface groups which have been recognized as carboxylic and lactonic ionize in water leaving negatively charged -COO⁻ sites on the carbon surface which show electrostatic attractive interactions towards the cations of the MG molecule.

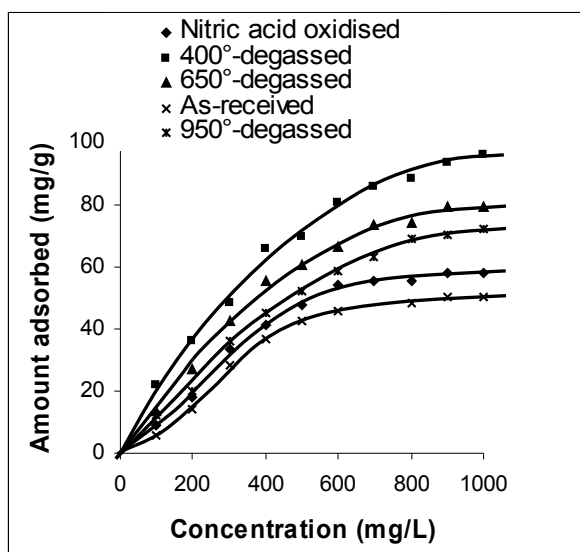


Fig. 1 Adsorption isotherms of Malachite green on ACG-100 before and after degassing

Table 1 Surface acidity and gases evolved on degassing oxidized and degassed ACG-100 carbon samples

Carbon sample	Surface acidity (mEq/100 g)	Oxygen evolved (g/100g) as				Total
		CO ₂	CO	H ₂ O		
As-received	42	0.67	3.42	1.21	5.30	
HNO ₃ -oxidized	395	6.32	4.13	1.32	11.77	
400°-degassed	276	4.41	4.05	1.25	9.71	
650°-degassed	52	0.83	3.85	1.16	5.84	
950°-degassed	traces	traces	traces	traces	traces	

Effect of pH

The effect of solution pH on the adsorption of MG at pH range 1-12 for as-received ACG-100 and I-60 carbon samples at initial concentration of 100 mg/L was determined. It is seen that the adsorption is very small at pH values between 1 and 3. It increases abruptly at pH values in the range 3-6. Maximum adsorption of dye was observed at around pH 6 and no significant change in the amount adsorbed was observed thereafter. It appears that the zero point charge (ZPC) of the two carbons is around pH = 3. It appears that a change in pH of the solution results in a change in the carbon surface charge. At pH values lower than ZPC, there is excessive protonation of the carbon surface which gives it a positive

charge and results in lower adsorption due to their repulsive interactions between the carbon surface and the positively charged MG ions. At pH values larger than ZPC the carbon surface attains a negative charge due to the ionization of carbon-oxygen surface groups. This causes attractive electrostatic interactions between the carbon surface and the MG ions and results in increased adsorption.

Effect of Temperature

The adsorption capacity of the activated carbons ACG-100 and I-60 increases with the increase in the temperature of the system from 30° to 60°. The increase in adsorption of the dye at higher temperatures may be attributed increase in mobility of dye molecules and acquiring sufficient energy to interact with the adsorption sites on the carbon surface. The energy of activation for adsorption on ACG-100 and I-60 is around 80 kJ/mol which is in the domain of physical adsorption but may suggest the formation of stronger hydrogen type bonding.

Kinetic Modelling

The adsorption rate data was analysed using Lagergren pseudo first and second order model. The data fitted well the second order rate model.

Conclusions

The adsorption of MG dye on activated carbons follows Langmuir and Freundlich isotherm equations. The adsorption depends on surface area but is considerably influenced by the presence of acidic carbon-oxygen surface groups. The adsorption increases on oxidation of the carbon surface due to the formation of carbon-oxygen groups and decreases gradually when these surface groups are eliminated on degassing at gradually increasing temperatures indicating that the acidic carbon-oxygen groups enhances the adsorption of MG. Optimum pH for the equilibrium adsorption of MG is around pH 6. The adsorption isotherm follow Langmuir and Freundlich models. The adsorption increases with temperature and the activation energy of adsorption is around 80 kJ/mol. The kinetic study showed that the adsorption followed pseudo-second-order model.

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