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Removal of Dyestuffs from Aqueous Solutions Using Maize Cob

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The adsorption of the dyes, malachite green, congo red and methyl red onto maize cob, an agricultural waste, was studied. Isotherm studies were carried out to find out the maximum adsorption capacity of maize cob for the dyestuffs. Adsorption was found to follow Freundlich isotherm model. Contact-time experiments were carried out in an agitated batch adsorber to assess the effect of temperature and maize cob particle size on adsorption.

INTRODUCTION

Synthetic dyes are used extensively in almost all industries. The wastage accompanying the dyeing process results in effluents contaminated with harmful dyesstuffs, contributing to environmental pollution[1]. These wastewaters also impart undesirable colour to the waterways. Hence it is necessary to remove these dyestuffs from the effluents before they are released into waterways. Many physical and chemical methods are employed to remove the dyestuff from the effluents. Of these, adsorption technique is very widely used. However, most systems use activated carbon as adsorbent whuch is expensive. In addition, such a technique also requires costly regeneration plant[2]. Hence, a search for efficient and cost-effective adsorbent has intensified in recent years[3]. Maize cob, an agricultural waste, is one such adsorbent. It the present work, the ability of maize cob to adsorb dyestuffs from aqueous solution is studied.

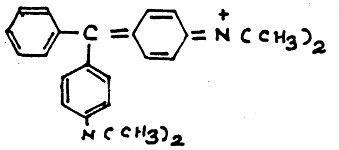
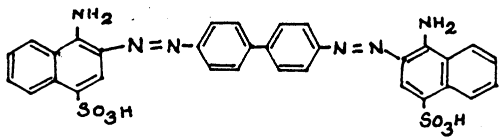
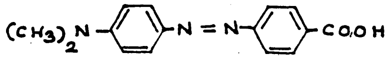
EXPERIMENTAL

The seeds of fully grown maize were removed and the stalk part of the maize was dried first in sunlight and then in an air oven at about 60 to 70°C. The dried maize cob was crushed into small lumps and then mechanically pulverised using a disintegrator. The powdered maize cob was sorted into different particle sizes by sieve analysis and kept in a desiccator before use.

The adsorbates used in this work and the structure are listed in Table-1.

The concentration of the colouring matter was determined using a spectrophotometer and the wavelength was selected so as to obtain a maximum adsorbance for each dyestuff.

Method: The equilibrium isotherms were determined by contacting a mass of maize cob with 0.050 dm^3 of the dye solution in sealed glass bottles in a constant temperature bath. The solutions were stirred at constant speed using a magnetic stirrer. Aliquots of the dye solution were withdrawn at known time intervals and centrifuged. The clear centrifugates were filtered with a millipore filter of the size 2–3 μm and then the adsorbance was determined.

Commerical Name		Structure
1.	Malachite Green	
2.	Congo Red	
3.	Methyl Red	

Several contact time experiments were carried out to study the effect of a number of variables such as the effect of initial concentration of dyestuff, the effect of maize cob size, the effect of temperature and the effect of maize cob mass.

RESULTS AND DISCUSSION

Effect of initial concentration of dyestuff: The equilibrium liquid phase concentrations of the dyes were determined by contacting a constant mass of maize cob (5 g/dm^3) of particle size 500 μm with 0.050 dm^3 of dye solution of different initial concentrations. The percentage of adsorption was obtained from the equilibrium concentration from the following relationship:

$$\text{Percentage of adsorption} = \frac{100(C_0 - C_e)}{C_0}$$

where C_0 is the initial concentration of the dye solution and C_e is the equilibrium concentration of the dye in the liquid phase. The results are given in Table-2.

TABLE-2
PERCENTAGE ADSORPTION OF DYESTUFFS
Maize cob mass: 5g/dm^3, Temperature: 305 K, Particle size: 500 μm

Dyestuff	C_0 (mg/dm^3)	C_e (mg/dm^3)	Per cent adsorption
Malachite green	1.85	0.18	90.3
	4.69	0.98	79.1
	7.42	1.95	73.7
	17.08	4.44	74.0
Congo red	6.97	0.83	88.1
	17.17	3.08	82.1
	22.77	4.62	79.7
	41.80	10.79	74.2
Methyl red	26.93	21.00	22.0
	53.86	44.80	16.8
	80.80	69.00	14.6
	107.70	91.20	15.3

Malachite green and congo red were adsorbed to a greater extent while methyl red was adsorbed comparatively to a smaller extent.

Equilibrium isotherm: The adsorption was found to follow Freundlich isotherm model. The Freundlich equation for a linear plot (Fig. 1) is represented as:

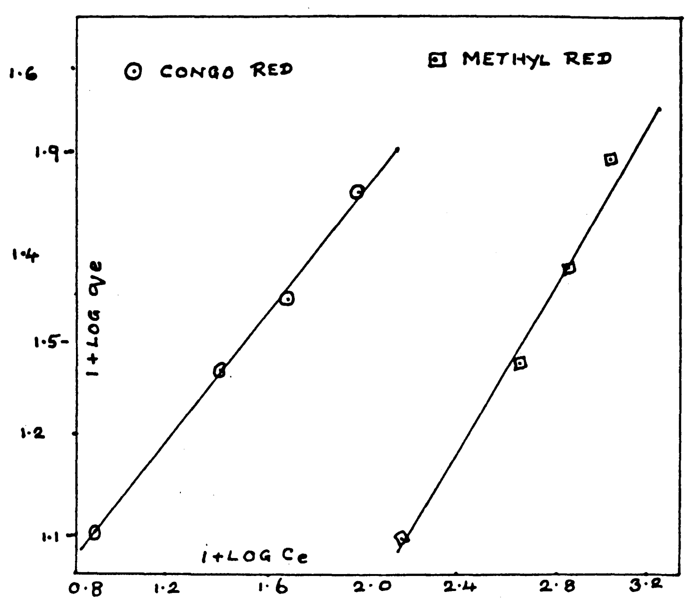


Fig. 1. Freundlich Isotherm

$$\log_{q_e} = \log K_F + 1/n \log C_e \tag{1}$$

where q_e = equilibrium concentration of the dye in solid phase

K_F = Freundlich constant

n = Freundlich exponent

and C_e = equilibrium concentration of dye in liquid phase

The value of q_e is calculated from the equation

$$q_e = \frac{(C_0 - C_e)}{m} \tag{2}$$

where C_0 is the initial concentration of dye and m is the mass of the absorbent.

The plots of log C_e *vs.* log q_e were found to be linear over a wide range of concentrations of the dye solution (Fig. 1).

The various parameters in Freundlich isotherm at 305 K have been calculated and are given in Table-3.

TABLE-3
FREUNDLICH CONSTANTS FOR VARIOUS DYES

Dye	Particle size (μm)	Temp (K)	K_f (dm^3/g)	n	Concentration range (mg/dm^3)
Malachite green	500	305	2.14	1.67	1.5–18
Congo red	500	305	1.39	1.59	6.0–42
Methyl red	500	305	0.15	1.51	26–108

The value of K_F gives a measure of adsorption capacity of maize cob for the dyestuff concerned and the value of n gives the intensity of adsorption[4]. Malachite green and Congo Red were adsorbed to a greater extent as indicated by their higher K_F values. This is attributed to the basic groups present in these two dyes. The amino groups in these dyes are positively charged. The surface of the maize cob is cellulose based and the surface of cellulose in contact with water is negatively charged[5]. The cationic dye base will thus undergo attraction on approaching the anionic maize cob structure. On the other hand, the approach of an acidic dye like methyl red will suffer coulombic repulsion due to the presence of carboxylate group.

The intensity of adsorption values are found to be almost same for these dyes. This fact suggests that once the dye molecule approaches the active sites on the surface of the maize cob, it is held by van der waals forces of equal magnitude. However, the ease of approach is determined by the acidic or the basic nature of the dye.

Effect of particle size: The influence of the particle size of maize cob on the rate of adsorption has been investigated for malachite green and congo red. The experimental results are shown in Fig. 2 as a plot of $(C_t - C_0)$ against time for the adsorption of malachite green. The data show an increase in the rate of dye uptake as the mean diameter of the adsorbent decreases. This observation is

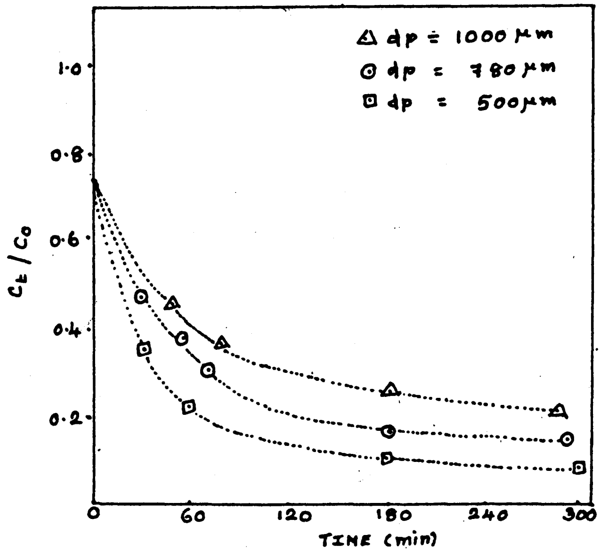


Fig. 2. Effect of particle size on the adsorption of malachite green

in agreement with the proposed isotherm model, since the large external surface area removes more dye in the initial stages of the adsorption process than the large particles.

Effect of temperature: The temperature effect on the rate of adsorption of malachite green has been studied. The plot of C_t/C_0 *vs.* time at different temperatures is given in Fig. 3. The adsorption rate is found to decrease with an

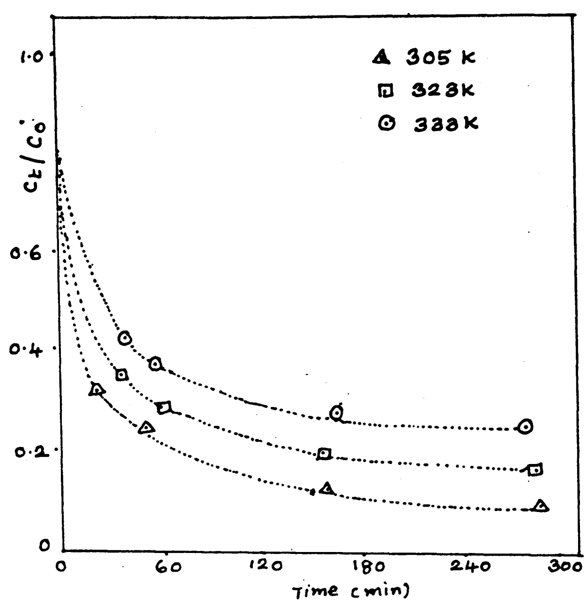


Fig. 3. Effect of temperature on the adsorption of malachite green

increase in temperature. This trend suggests that the adsorption process is exothermic in nature.

Effects of maize cob mass: The effect of maize cob on the adsorption rate was studied when other experimental conditions were maintained constant. The rate of adsorption of the dye increased with increasing maize cob mass, till it reached the limiting value. These results are given in Table 4.

TABLE-4
EFFECT OF MAIZE COB MASS

Malachite green: 37.08 mg/dm^3, Contact time: 30 min., Temperature: 305 K, Particle size: 200 μm

Maize cob (g/dm^3)	C_t (mg/dm^3)	C_t/C_0
0	37.08	1.00
2	19.54	0.53
5	11.01	0.30
10	3.73	0.10
15	3.55	0.10

Figure 4 gives a plot of (C_t/C_0) against time for the adsorption of malachite green.

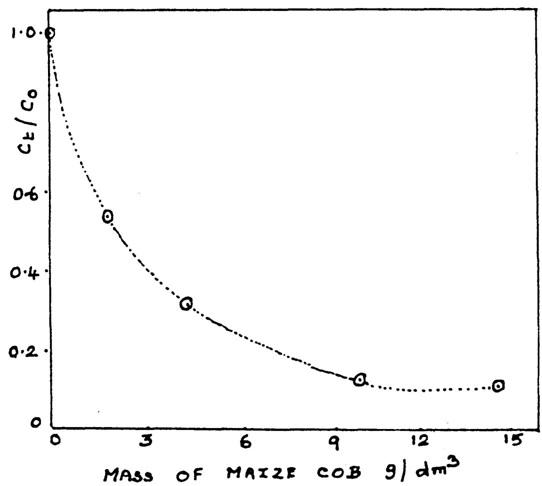


Fig. 4. Effect of maize cob mass on the adsorption of malachite green

The rate of adsorption depends on the driving force per unit area and in this case, since the initial dye concentration is constant, increasing the mass of maize cob increases the surface area for adsorption and hence the rate of dye adsorption increases. Since the particle size is constant, the surface area will be directly proportional to the mass of the maize cob in the system. However, the monolayer saturation capacity is reached faster at the optimum concentration and hence the limiting value.

Conclusion

The adsorption of the dyestuffs malachite green, congo red and methyl red onto maize cob was studied. An overall agreement with Freundlich isotherm had been found. Malachite green and congo red were adsorbed to a greater extent and thus maize cob could be used as an adsorbent for the removal of these dyes from wastewater. However, methyl red was adsorbed comparatively to a lesser extent.

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