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Adsorption Studies of Methylene Blue and Congo Red on The Surface of *Citrus aurantium*

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The adsorption of organic dyes like methylene blue and congo red on *Citrus aurantium* using batch adsorption process has been investigated. The effect of certain parameters on adsorption has been studied. Applicability of Freundlich adsorption isotherm and Langmuir adsorption isotherm has also been tested.

Key Words: Adsorption, Methylene blue, Congo red, *Citrus aurantium*.

INTRODUCTION

Techniques for removal of colour from waste water include biological treatment, coagulation, floatation, oxidation, hyperfiltration and adsorption. Adsorption onto granulated activated carbon or powdered activated carbon is widely practiced, particularly for the organics, which are not easily broken down by biological treatment and by other methods. The technology for manufacturing good quality activated carbon is still cost-prohibitive and regeneration of the used carbon is often problematic. This has prompted the use of many novel materials as adsorbents with a two fold objective to replace activated carbon with cheaper alternatives and to utilize various waste products for the purpose[1,2]. Plant materials are used as a cheap and low cost material for adsorption, for example modified corn starch[3], modified onion skins[4], saw dust[5], phosphate treated saw dust[6], water lettuce[7], *Alterneuthera triandra*[8], *etc*. In the present study, it is demonstrated that fine charcoal powder obtained from *Citrus aurantium* can be a suitable alternative to activated carbon for treating coloured effluents.

EXPERIMENTAL

Congo red was supplied by S.D. Fine Chemicals Ltd., Mumbai, methylene blue was supplied by Qualigens Ltd., Mumbai. These chemicals were used without further purification. The synthetic effluent solutions were made by dissolving the required amount of dye in double distilled water.

Orange fruit peels were collected and washed repeatedly with water to remove dust and soluble impurities and were allowed to dry at room temperature in a shade and then in an air oven at 333-343 K for a long time till the peels become completely dry and crisp. Then peels were burned in presence of incomplete oxygen to peel charcoal powder. The adsorption experiments were carried out in a batch process by using aqueous solutions of the dye in a fixed concentration range. The other variable parameters were adsorbent dose, contact time (1-5 h) and pH of the medium (2.0-10.0). In each experiment, an accurately weighed amount of peel charcoal powder was added to a fixed volume of the dye solution in a 100 mL conical flask and the mixture was agitated on a thermostatic magnetic stirrer for a given length of time at a fixed temperature. The mixture was centrifuged rapidly and the dye remaining unadsorbed was determined spectrophotometrically (Elico-SL 180). The concentrations were determined with the help of carefully prepared calibration curves with standard dye solutions and the amount adsorbed was found by mass balance procedure.

RESULTS AND DISCUSSION

Adsorption at a surface is largely the result of binding forces between the individual atoms, ions or molecules of an adsorptive and the surface, all of these forces having their origin in electromagnetic interactions. The net dispersion, electrostatic, chemisorptive and functional group interactions broadly define the affinity of an adsorbent for a specific adsorption. A number of parameters, specific to a given system, affect adsorption. With respect to the adsorptive, these factors are concentration, molecular weight, molecular size, molecular structure, molecular polarity, steric form or configuration and the nature of background or competitive adsorption. The important characteristics of the adsorbent that determine equilibrium capacity and rate, are the surface area, the physico-chemical nature of the surface, the availability of that surface to adsorptive molecules or ions, the physical size and form of the adsorbent particles. System parameters such as temperature and pH can also markedly influence adsorption to the extent that they effect changes in any one or more of the above mentioned parameters.

Effect of contact time: It was observed that *Citrus aurantium* peels can be used as a low cost adsorbent effectively. The maximum time required for 70 to 85 % adsorption of methylene blue is 1 h. The effect of contact time on adsorption was not much after 1 h. The contact time has a profound impact on adsorption of congo red on peel charcoal powder. The maximum time required for 30 to 45 % adsorption is 1 h, increasing the contact time from 1-5 h greatly enhanced the adsorption of congo red from 45-90 % (Tables 1 and 2).

Effect of pH: The pH of the medium does not have much effect on adsorption of methylene blue on peel charcoal powder. Thus as the pH of the medium changes from 2.0 to 10.0, the adsorption of dye oscillates between 92 to 95 %. This is contrary to what other workers have observed for adsorption of the basic dye on a variety of

TABLE-1
EFFECT OF CONTACT TIME ON ADSORPTION OF METHYLENE BLUE ON PEEL CHARCOAL POWDER AT 300 K. (DYE CONCENTRATION 40 mg/dm^3

Contact time (min)	Amount adsorbed (%) for peel charcoal powder dose of				
	2 g dm^{-3}	4 g dm^{-3}	6 g dm^{-3}	8 g dm^{-3}	10 g dm^{-3}
60	69.0	69.8	70.2	75.6	84.8
120	70.1	70.4	72.4	76.0	85.1
180	71.2	73.4	76.8	79.6	85.6
240	73.4	75.9	77.6	80.8	86.7
300	75.6	76.9	79.5	81.7	87.4

TABLE-2
EFFECT OF CONTACT TIME ON ADSORPTION OF CONGO RED ON PEEL CHARCOAL POWDER AT 300 K

Contact time (min)	Amount adsorbed (%) for peel charcoal powder dose of				
	2 g dm^{-3}	4 g dm^{-3}	6 g dm^{-3}	8 g dm^{-3}	10 g dm^{-3}
60	29.0	30.2	33.6	38.8	45.4
120	32.6	34.9	37.2	40.6	48.7
180	36.8	40.2	45.6	52.8	58.6
240	44.0	48.6	54.5	59.7	66.7
300	55.6	60.2	65.7	78.2	88.9

adsorbents where the pH was shown to have a positive influence[9]. It is likely that the surfaces of peel charcoal powder particles are neither acidic nor basic and the cationic dye, methylene blue seems to have equal preference for the adsorption sites at all pH values. Thus the adsorption can be carried out without a control of the pH. Almost similar observations have been recorded with the congo red.

Adsorption equilibrium: The adsorption process was described by the following isotherms:

Freundlich isotherm: $q_e = k_f c^n_e$

Langmuir isotherm: $C_e/q_e = (1/k_d)\ c_1 + (1/b)C_e$

C_e is the equilibrium adsorptive concentrations in aqueous phase, q_e is the amount of dye adsorbed on unit mass of peel charcoal powder, n and k_f are Freundlich constants, c_1 and k_d are Langmuir constants.

The linear Freundlich and Langmuir plots are obtained by plotting log q_e *vs.* log c_e and c_e/q_e *vs.* c_e, respectively, from which adsorption constants are evaluated.

A further analysis of the Langmuir equation was made on the basis of a dimensionless equilibrium parameter R_L.

$$R_L = 1/(1 + k_d C_{ref})$$

C_{ref} is any equilibrium liquid phase concentration of the solute. The range $0 < R_L < 1$ reflects favourable adsorption. With both methylene blue and congo red, excellent fit with Freundlich isotherm and Langmuir isotherms are obtained. The values of the adsorption coefficients are given in Table-3.

TABLE-3
FREUNDLICH AND LANGMUIR ADSORPTION COEFFICIENTS
FOR THE ADSORPTION OF METHYLENE BLUE ON
PEEL CHARCOAL POWDER (PCP) AT 300 K

PCP Dose ($g\ dm^{-3}$)	Freundlich constants		Langmuir constants		
	n	K_f ($dm^3\ g^{-1}$)	C_1 ($dm^3\ g^{-1}$)	K_d ($mg\ g^{-1}$)	R_L
2	0.59	9.49	0.27	44.84	0.068
4	0.51	5.57	0.30	22.02	0.060
6	0.68	3.72	0.23	21.05	0.080
8	0.52	3.07	0.33	11.51	0.058
10	0.53	2.51	0.30	9.80	0.062
Mean	0.57	4.89	0.29	21.84	0.066

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