

REMOVAL OF METHYLENE BLUE BY ADSORPTION ON LOW-COST CARBONACEOUS ADSORBENT

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Abstract

The removal of color from aquatic systems caused by presence of synthetic dyes is extremely important from the environmental viewpoint because most of these dyes are toxic, mutagenic and carcinogenic. In this present study the kinetics and mechanism of methylene blue adsorption on commercial activated carbon (CAC) and indigenously prepared activated carbons from *Enicostema Axillare*, Lam. Carbon (EAC), have been studied. The effects of various experimental parameters have been investigated using a batch adsorption technique to obtain information on treating effluents from the dye industry. The extent of dye removal increased with decrease in the initial concentration of the dye and particle size of the adsorbent and also increased with increase in contact time, amount of adsorbent used and the initial pH of the solution. The adsorption capacities of indigenous activated carbons have been compared with that of the commercial activated carbon. The results indicate that such carbons could be employed as low cost alternatives to commercial activated carbon in wastewater treatment for the removal of colour and dyes.

1. Introduction

Effluents from the dyeing and finishing processes in the textile industry are known to contain colour, high amounts of surfactants, dissolved solids and possibly heavy metals such as Cr, Ni and Cu [1]. The effluents from the dyestuff manufacturing and some similar industries are also generally highly coloured with a large amount of suspended organic solids and hence are the

important sources of water pollution. From an environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic and, consequently, their treatment cannot depend on bio-degradation alone [2,3]. Hence, decolourisation of dye house effluent via the removal of dyes has become an important aspect of textile wastewater treatment. The environmental issues surrounding the presence of colour in effluent is a continuing problem for dyestuff manufactures, dyers, finishers

and water companies, because increasingly stringent colour consent standards are being enforced by regulatory bodies to reduce the quality of colour in effluent and water courses. At present, the problem is considered to be solely aesthetic rather than eco toxicological. Even so, the problem of colour in wastewater is common to many dye houses. Many studies have been conducted on the toxicity of dyes and their impact on the eco system [4,5], as well as the environmental issues associated with the manufacture and subsequent usage of dyes [6,7]. Biological treatment processes are reported to be efficient in the removal of suspended solids and reduction of chemical oxygen demand but are largely ineffective in removing colour from wastewater [8]. Hence, investigations have been conducted on physico-chemical methods of removing colour from textile effluent. These studies include the use of coagulants [9], oxidising agents [10], ultra-filtration [11], electro-chemical [12,13] and adsorption [8] techniques. The advantages and disadvantages of each technique have been extensively reviewed [14]. Of these methods, adsorption has been found to be an efficient and economic process to remove dyes, pigments and other colourants and also to control the bio-chemical oxygen demand [14]. Activated carbon (AC), inorganic oxides, natural adsorbents (such as clays and clay minerals, cellulosic materials, chitin and chitosan) have been extensively used as adsorbents [15–20]. AC adsorption has been found to be an effective and widely employed means of water and wastewater treatment [21]. Despite its prolific use in water and waste water industries, commercial AC (CAC) remains an expensive material. This has led to a search for low-cost materials as alternative adsorbent materials [17,18]. The purpose of this work was to study the removal of The purpose of this work was to study the kinetics and mechanism of adsorption of

methylene blue (MB), on various indigenously prepared SCs (IPACs) from agricultural wastes and to compare their adsorption capacity for the removal of MB under optimum experimental conditions. Thus, this investigation is aimed at to study the kinetics and dynamics of adsorption of a basic dye viz., methylene blue (MB) on CAC and (IPACs) such as *Enicostema Axillare*, Lam. Carbon (EAC), and to find out the possibility of using these carbonaceous materials as low-cost adsorbents for the removal of dyes in general and MB, in particular

2. Materials and methods

The material commercial AC (CAC) was supplied by E.Merck, India. Raw materials for the preparation of indigenously prepared activated carbons from *Enicostema Axillare*, Lam. Carbon (EAC), carbon are procured locally, washed, dried and Powdered. The powdered raw materials (500g) have been carbonised and sulphonated by con. sulphuric acid, washed to remove excess free (tested with BaCl_2 solution) acid and dried at 70°C for 12 h. It was labeled as Activated Carbons (ACs). The method followed was similar to the reported one for preparing ACs from plant materials [6-8]. Methylene blue (MB) supplied by BDH was used as an adsorbate and was not purified prior to use. All the other chemicals used in this study were reagent grade and supplied by BDH (India). Double distilled water was employed for preparing all the solutions and reagents.

2.1. Adsorption studies

A stock solution of MB (1000 mg/l) was prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out at room temperature ($30 \pm 1^\circ\text{C}$) under batch mode [22]. The initial concentrations (C_i) of MB were obtained by measuring O.D. at 663 nm (max) using Elico UV-visible spectrophotometer (Model: SLI59). Exactly

50 ml of MB solution of known initial concentration (C_i range: 100–500mg/l) was shaken at the constant agitation speed(200 rpm) with a required dose of AC (range 8–11.6 g/l) for IPACs, except CAC), of a fixed particle size (range: 90–250 mm for ACs except CAC) for a specific period of contact time (range: 5–120min) in a thermostatic orbit incubator shaker(NEOLAB, India), after noting down the initial pH of the solution (pH=7.2). The pH of the solutions were adjusted to the required value (range: 2–10) by adding either 1MHCl or 1MNaOH solution. After equilibration, the final concentrations (C_f) were measured at 663 nm by spectrophotometric method (Elico UV visible spectrophotometer—Model: SL159).

The percentage removal of dye and amount adsorbed (in mg/g) were calculated using the following relationships:

$$\text{Percentage removal} = 100 (C_i - C_e) / C_i \quad (1)$$

$$\text{Amount adsorbed (q)} = (X/m) = (C_i - C_e) \times V / m \dots\dots\dots (2)$$

where C_i and C_f are the initial and final concentrations(in mg/l) of dye, respectively and ‘m’ is the mass of AC (in mg/l)V is the volume taken. Blanks containing no dye were used for each series of experiments as controls. The average values of duplicate runs were obtained and analysed. Error in data: $\pm 1-2\%$ for percentage removal $\pm 0.005-0.01$ mg/g for amount adsorbed.

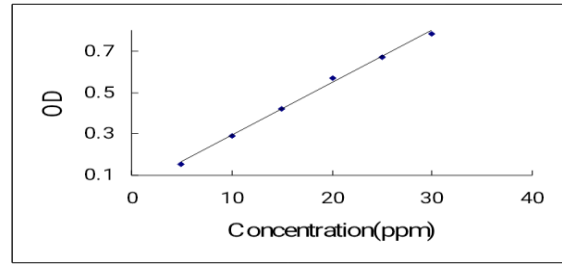


Fig. 1. Standard graph

3. Result and Discussion.

The values of the Physico-Chemical parameters are given in Table 3.1 The moisture content though does not affect the adsorption power, it dilutes the adsorbent and therefore necessitates the use of additional amount of adsorbent for the treatment process. The moisture content is higher in the case of EAC suggesting that extensive porosity has been introduced in to the structure. The electrical conductivity values decreases from CAC to EAC. Based on the various Physic – Chemical properties, it is concluded that EAC can be used in the treatment of water and waste water,

The absolute density in both hydrated (wet) and dehydrated (dry) pure EAC are presented in Table 3.1.It is found that the absolute density in both wet (hydrated) and dry (dehydrated) status decrease steadily from CAC to EAC indicates that ACs more closely packed. Gravimetric swelling percentage of CAC and EAC is given in Table 3.1. A close look at the data given in Table 3.1 indicates adsorbent materials are macro reticular having non-gel pores.

The percentage of attritional breaking for CAC and EAC are presented in Table 3.1. From the data revealed that ACs has more mechanical stability.

Table.3.1. Physico – chemical properties of Adsorbents.

Properties		CAC	TFC
Absolute Density (g mL ⁻¹)	Dry	0.925	0.8891
	Wet	0.964	0.9134
% of Gravimetric swelling		32.33	30.0
% of Attritional breaking		4.02	3.45
pH		9.4	6.13
Conductivity(ohm/cm)×10 ⁻³		4.6	4.0
% of Moisture		10.1	1.63
Zero point charge(pH _{ZPC})		7.25	4.76
Surface Area m ² g ⁻¹		875	703
Decolourising Power mgL ⁻¹		12.0	5.6

Table.3.2. Effect of [MB]_i on the % removal and amount adsorbed by ACs

Contact time-35 min, pH-7.2, Particle size- 90 μ, Dose- CAC:2g/L EAC :10. g/L

Adsorbent	Parameter	Concentration in(ppm)				
		Methylene Blue dye				
CAC	C _i	300	350	400	450	500
	C _e	16	27	42	48	78
	% of Removal	94.6	92.2	89.5	89.3	84.4
	Amount Adsorbed(q _e)	118.3	134.5	149.2	167.5	175.8
EAC	Methylene Blue dye					
	C _i	200	250	300	350	400
	C _e	1.2	2.4	4.6	7.2	9.5
	% of Removal	99.2	99.0	98.4	97.9	97.6
	Amount Adsorbed(q _e)	19.8	24.8	29.6	34.3	39.1

Table.3.3. Effect of Particle size of CAC and EAC on the amount adsorbed (mg g^{-1}) and the % removal of various experimental dyesContact time-35 min, pH-7.2, C_i ; optimum, Dose- CAC:2g/L EAC :10. g/L

Adsorbent	Parameter	Concentration in(ppm)				
		Methylene Blue dye				
CAC	C_i	300	350	400	450	500
	C_e	16	27	42	48	78
	% of Removal	94.6	92.2	89.5	89.3	84.4
	Amount Adsorbed(q_e)	118.3	134.5	149.2	167.5	175.8
EAC	Methylene Blue dye					
	C_i	200	250	300	350	400
	C_e	1.2	2.4	4.6	7.2	9.5
	% of Removal	99.2	99.0	98.4	97.9	97.6
	Amount Adsorbed(q_e)	19.8	24.8	29.6	34.3	39.1

Table.3.4 Effect of pH of CAC and EAC on the amount adsorbed ($'q_e'$ mg g^{-1}) and the % removal of various experimental dyesContact time-35 min, particle size;90 micron, C_i ; optimum, Dose- CAC:2g/L EAC :10. g/L

CAC	Methylene Blue dye									
	pH	2	3	4	5	6	7	8	9	10
	% of Removal	90.1	90.6	91.6	92.5	93.4	96.7	98.9	99.2	99.6
	Amount Adsorbed	257.9	259.3	262.2	264.7	267.3	276.7	283.0	283.9	285.1
EAC	Methylene Blue dye									
	pH	2	3	4	5	6	7	8	9	10
	% of Removal	97.4	97.6	97.8	98	9.6	99	99.3	99.4	99.92
	Amount Adsorbed	19.5	19.52	19.56	19.60	19.72	19.80	19.86	19.88	19.92

Table 3.5. Effect of dose of adsorbent on the amount adsorbed of MB by CAC. and EAC

CAC		ACs*	EAC
Dose (g l ⁻¹)	q _e in mg g ⁻¹	Dose (g l ⁻¹)	q _e in mg g ⁻¹
1.0	336.1	8.0	16.5
1.2	321.4	8.8	17.6
1.4	312.5	9.6	18.3
1.6	297.3	10.0	19.3
1.8	290.2	10.8	20.0
2.0	285.04	11.6	20.8

*ACs –Activated Carbons Viz., EAC and RAC

Effect of Initial concentration of metal ion

The effect of initial concentration of dye on the percentage removal of MB dye using indigenously prepared ACs is presented in Table 3.2. It was observed that the percentage removal decreased with the increase in dye concentration. For ACs, the percentage removal of dye) was found to be 99.2% at the initial concentration of 200 mg/L for EAC and of 300 mg for CAC. The adsorbent dose and a contact time of 35 minutes, at the optimum pH were fixed.

Effect of Particle Size of Adsorbents

The effect of particle size of adsorbents on the extent of removal of dye (% and q) was studied, the equilibrium value of amount adsorbed was observed to decrease with the increase in particle size of adsorbents (Table.3.3.). The percentage removal of dye (MB) decreased exponentially with the increase in particle size of both the adsorbents. This may be due to the decrease in the activated sites of adsorbents molecules, especially at higher particle.

In the adsorption system, particle size plays a vital role, irrespective of the other experimental parameters which affect

the rate of adsorption parameters and to study the kinetics of adsorption of dye (MB), batch adsorption experiments were carried out and relevant experimental data are given in Table 3.3.

The particle size at which the maximum percentage removal of MB occur was fixed as the optimum particle size (90µ for both EAC and CAC). The removal of MB by adsorption on EAC and CAC was found to be slow for increasing particle size.

Effect of pH

Table show the effect of initial pH on the removal of MB from aqueous solution by AC. It was found that adsorption of MB ions increases with increase in pH value from 4 to 9 and thereafter it maintain a constant % removal. Adsorption of dye ion depends upon the nature of both the adsorbent surface and the dye in solution. The later depends on pH. Above pH 4, adsorption of MB dye is increased because Maximum dye sequestration from the aqueous solution of MB dye achieved within 15 minutes after start of the experiment at all studied concentrations. Above this 7 pH, adsorption process decreased due to weakening of electrostatic force of

attraction between the oppositely charged adsorbate and adsorbent. Maximum adsorption occurs at the optimum pH of 7.29 and hence pH was maintained constant at 7.2 for all other studies.

Effect of dose of adsorbent

Table 3.5 shows the effect of carbon dosage on the percentage removal of dye. The removal of metal ions increased with increase in carbon dosage and attained a maximum (99.2%) at a dosage of 10 g/L for EAC and 99% at a dosage of 2.4g/L for CAC. This is also given in table. The increase in the percent removal of dye with the increase in carbon dosage is due to the availability of larger surface area with more active functional groups. Saturation occurs as a result of non-availability of active sites on the adsorbent. With just 10g/L of the adsorbent, 99.2% adsorption was found to occur at room temperature which reflects the efficiency of the indigenously prepared AC viz., EAC.

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