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Research Paper

Removal of Methyl Violet and Cadmium from Aqueous Solution by Using Activated Carbon

***Indhumathi P. [1], Syed Shabudeen S.P. [2], Saraswathy C.P. [3]**
[1]Govt. Arts College, Coimbatore-641 018, Tamil Nadu, INDIA
[2]Dept of Chemistry, Kumaraguru College of Technology, Coimbatore-641 018, Tamil Nadu, INDIA
[3]Dept of Chemistry, Govt. Arts College, Coimbatore-641 018, Tamil Nadu, INDIA

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Abstract: *The present study was focused on removal of methyl violet and cadmium from aqueous solution by using activated carbon. The activated carbon was prepared from the pods of delonix regia. The activation is carried out by different methodologies - Pyrolysis activation, Sulfuric acid activation, Calcium chloride activation, Ammonium carbonate activation, Sodium sulphate activation, Sulfuric acid with ammonium per sulphate activation. The characteristic of this activated carbon was determined. The batch mode of studies carried out for methyl violet and Cd. The effective removal of dye solution was attained at 60 mins. The effect of optimum dosage, pH and initial concentration of adsorbate on the effective removal of cadmium has been studied. The maximum removal of Cd was observed at pH 6. Removal of cadmium increased from 75 to 100 % with increasing adsorbent dosage from 50 to 200 mg. It is revealed that the adsorbent follows the Longregan's first order equation, Longmuir and Frendlich isotherm models. This study reveals that this activated carbon prepared from the parts pots of "Delonix regia" is following adsorption phenomena and it can be employed economically as an alternate to commercially available activated carbon.*

Keywords: Low cost activated carbon, AAS, Longregan's, Langmuir, Freundlich isotherm.

Introduction

The contamination of water by toxic chemicals such as heavy metals is a worldwide problem. Heavy metal Solutions are widely used in industrial activities such as metal finishing, electroplating, painting, Dyeing (textile units), photography, surface treatment and printed circuit board manufacture.

There are several methods of effluent treatment. Primary treatment involves sedimentation, equalization, neutralization etc. In secondary treatment, the dissolved and colloidal organic matter present in wastewater is removed by biological processes involving bacteria and microorganisms. The secondary treatment involves aerated lagoons, trickling filters, activated sludge process, oxidation ditch, oxidation pond, anaerobic digestion etc. Tertiary treatment aims at improving the waste water quality to the point at which it can be used. Other commonly employed treatment methods include: Ion Exchange, Electrodialysis, Evaporation, Chemical Precipitation, Reverse Osmosis, Electro deposition, Chemical Reduction, Adsorption etc.

Activated carbon has been found to be an effective adsorbent though it suffers from the disadvantage of possessing high cost. Several adsorbents like discarded automotive tyres, human hair, starch, xanthate and oxides of manganese etc. have been successfully tried. They are not easily and widely available, therefore low cost [1], agricultural products and by products like crushed coconut shell[4], saw dust[2], peat mass [3], banana pith[5], biogas residual slurry [6] , Coirpith[8] have been employed, as these adsorbents have a distinct advantage over activated carbon because of their low cost and easy availability[7]. The present study is focused on removal of methyl violet and cadmium form aqueous solution using an eco-friendly adsorbent- activated carbon prepared from the pods of *Delonix regia.* The effect of optimum dosage, pH and initial concentration of methyl violet and cadmium on the effective removal of methyl violet and cadmium has been studied.

Material and Methods

Plant profile

Common Name:	Gulmohur
Kingdom:	Plantae
Division:	Phanerogams
Class:	Dicotyledoneae
Subclass:	Polypetalae
Series:	Calyciflorae
Order:	Rosales
Family:	Leguminosae
Sub-Family:	Caesalpineaceae
Genus:	*Delonix*
Species:	*Regia*

Preparation of activated carbon: The pods of Delonix regia (Flame of the forest) was cut into small pieces, dried in sunlight, then 60°C for 24 hours in hot air oven. The dried material is subjected activation by pyrolysis, acid treatment, $CaCl_2$, NH_4CO_3, Na_2SO_4, H_2SO_4+$NH_4S_2O_8$, to obtain various forms of Activated carbon. Then these were washed with doubled distilled water to remove the excess acid and kept in hot air oven at 110°C for 12 hours. Then it was taken in an iron vessel in muffle furnace and the temperature was gradually raised to 550°C for an hour, ground well by using ball mill and then sieved. The characterization of the pods of Delonix regia was carried out and the results were tabulated in Table 1.

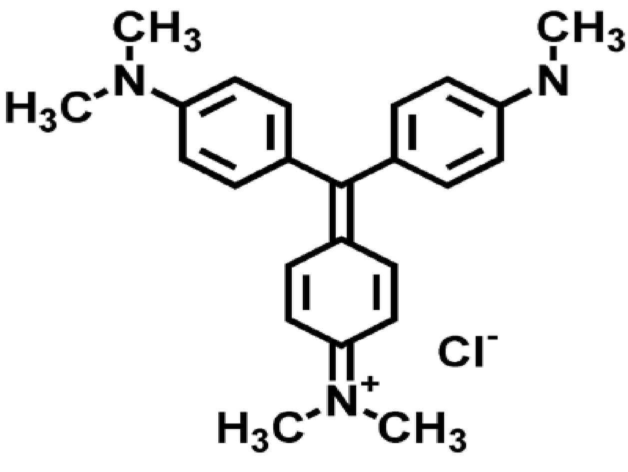
Preparation of adsorbate

Dye solution: Stock solution of dye was prepared by dissolving 1gm of dye in 1000ml of double distilled water to give the concentration of 1000mg/L. The stock solutions were diluted with known initial concentrations say 20mg/L in accurate proportion. Methyl violet is a family of organic compounds that are mainly used as dyes. Depending on the amount of attached methyl groups, the color of the dye can be altered. Its main use is as a purple dye for textiles and to give deep violet colors in paint and ink. The term methyl violet encompasses three compounds that differ in the number of methyl groups attached to the amine functional group. They are all soluble in water, ethanol, diethylene glycol and dipropylene glycol.

Table 1

Characteristics of activated carbon prepared from the pods of Delonix regia by various methods

S. No.	Name of the Experiment	Pyrolysis	H_2SO_4	$CaCl_2$	NH_4CO_3	Na_2SO_4	H_2SO_4+ $NH_4S_2O_8$
1	pH	7.9	7.12	8.9	7.86	8.82	6.83
2	Conductivity ms/cm	0.05	0.09	0.0371	0.01	0.027	0.0403
3	Na(ppm)	0.192	0.26	0.015	0.012	0.045	0.0172
4	K(ppm)	0.81	0.04	0.7	0.15	0.4	0.55
5	Fe(ppm)	0.507	0.12	0.47	0.212	0.28	0.113
6	Ash content (%)	0.2413	0.98	0.20	0.4	0.5	0.5021
7	Moisture content (%)	0.82	0.3	0.73	0.703	0.4	0.94
8	Volatile matter (%)	10.2	17	17.88	26.71	5	5.0
9	Fixed carbon	84.9	90	88	89	90	91.71
10	Porosity (%)	92	90	97.04	88.25	95.7	91.35
11	Matter soluble in water (%)	0.9	0.35	2.21	2.04	0.84	0.211
12	Matter soluble in acid (%)	Nil	1.5	2	2.9	3.1	3.98
13	Surface area (g/cm^2)	180	230	188	196	220	218



Methyl Violet Structure

Cadmium Solution Preparation: Cadmium (II) solutions were prepared by dissolving a weighed quantity of cadmium chloride monohydrate (Merck, Germany) in deionized distilled water. Before the adsorption study, the pH of the Cd(II) solution was adjusted to required value with 0.1M HCl and 0.1M NaOH solutions using a pH meter.

Batch mode of adsorption studies: Batch biosorption experiments were carried out in 100 ml conical flasks containing 0.1g of activated carbon and 20mg/l methyl violet solution, 40 ml of cadmium solution at varying pH 2-8. The flasks were placed on shaker incubator with constant shaking at 150 rpm and 25 °C. After the separation of used adsorbent by centrifugation, the residual concentration of cadmium in solution was analyzed using atomic absorption spectrophotometer. The amount of adsorbed metal ions per gram of activated carbon was obtained using the following equation:

$$q = \frac{[(Ci - Ce) \times V]}{M}$$

where q is the metal uptake (mg/g), Ci is the initial metal concentration (mg/L), Ce is the residual metal concentration (mg/L), V is the volume of metal solution (l) and M is the mass of adsorbent.

Desorption Studies: The exhausted activated carbon was used for desorption studies. The carbon loaded with dye was separated and gently washed with distilled water to remove any unabsorbed dyes. The dye-laden carbons were agitated with 100ml of neutral pH water, 1M Sulphuric acid, 1M Sodium hydroxide, 10% acetic acid (v/v) and 50% acetic acid (v/v) separately for 60 min.

Results and Discussion

Effect of agitation time and initial concentration: For this study methyl violet and cadmium known concentration of 20,40mg/L were separately agitated with 0.1mg/L at 25°C. The percentage removal of methyl violet and cadmium with variation in initial concentration of methyl violet and cadmium solution is shown in figure 1. The increase in percentage removal methyl violet and cadmium when the adsorbate concentration was varied from 0.2 to 0.8 mg/L. The rapid adsorption at the initial contact time can be attributed to the availability of the positively charged surface of activated carbon and the contact time needed for MV solution to reach equilibrium was 60 minutes and cadmium to reach 80 minutes.The results indicated that there was no change in the sorption capacity after 60 (MV) and 80(Cd) minutes, its shown figure 1. Therefore 120 minutes was fixed as the agitation time for isotherm.

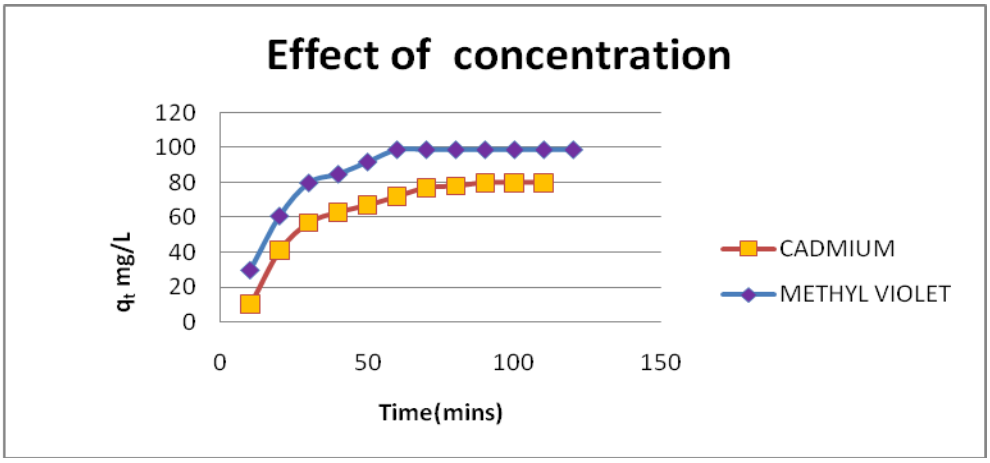


Figure 1: Effect of agitation time on adsorption concentration

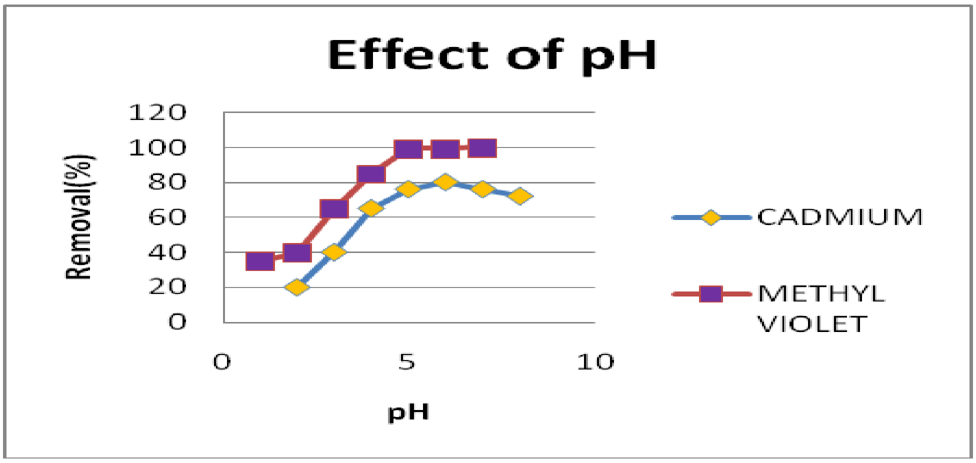


Figure 2: Effect of pH on the removal of Cd and Methyl Violet

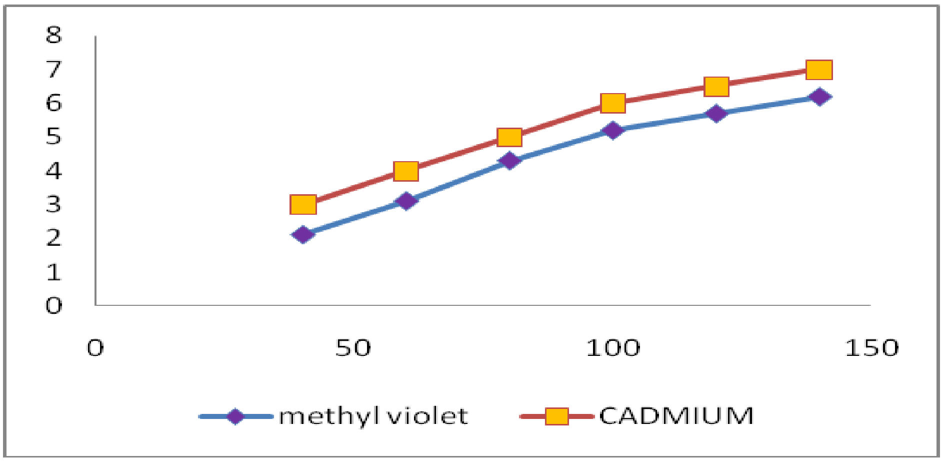


Figure 3: Langmuir isotherm model for Cd and Methyl Violet

Effects of pH variation on methyl violet and cadmium removal from aqueous solution: In order to optimize the pH for maximum methyl violet and cadmium removal, experiments were conducted with 100ml of 0.1 mg/L of Cd solution with 100 mg adsorbent by varying the pH 2 to 8 .The results indicated a maximum adsorption of methyl violet (99%) at 60minutes and cadmium (80%) at120 mins its shown figure 2 .The decrease in adsorption at higher pH may be due to the negative charges on the surface of the adsorbent repelling the negatively charged.

Adsorption isotherms: Adsorption isotherms parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis and the important isotherms, Langmuir, Freundlich isotherms are applied in this study.

Langmuir isotherm: Langmuir adsorption isotherm is based on the assumption that, "Adsorption is a type of chemical combination in which adsorbate is adsorbed on the adsorbent surface and the adsorbed layer is unimolecular".

Langmuir equation, $$q_e = \frac{Q_0 \text{ x b x Ce}}{(1 + (\text{b x Ce})}$$

where, q_e is equal to the quantity of dye adsorbed in mg/g of the adsorbent, Q_0 is the maximum quantity of dye adsorbed in mg/gram of the adsorbent, b and C_e is the constant of Langmuir adsorption and the dye concentration at equilibrium in mg/l respectively. Langmuir adsorption parameters are determined by transforming the equation, which is in linear form. The Linear plot of C_e/q_e Vs C_e showed that the adsorption followed Langmuir isotherm model (Figure 3). The values of monolayer capacity 'Q_0' and Langmuir constant 'b' had been evaluated from the intercept and slope of these plots by using graphical techniques.

The effect of isotherm shape has been taken into consideration with a view to predict whether the studied adsorption system is favorable or unfavorable. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimension less constant referred to as separation factor or equilibrium parameter

$$R_L = \frac{1}{(1 + bC_0)}$$

Where C_0 is the initial concentration and 'b' is the constant related to the energy of adsorption (Langmuir constant) table 2. The values of R_L indicate the nature of the isotherm, if the conditions are ($R_L>1$, $R_L=1$, $0<R_L<1$ and $R_L= 0$) are unfavorable, linear, favorable and irreversible respectively. The value of R_L was less than one which showed that the adsorption process was favorable.

Table 2
Langmuir and Freundlich isotherm constant for methyl and cadmium

Models	**Isotherm Constant**			
Langmuir	Q0 (mg/g)	b x 10-3 (L/ mg)	RL	r2
Methyl violet	43.6	16.6	0.28	0.996
Cadmium	80	0.064	0.945	0.992
Freundlich	kf (mg/g)	n		r2
Methyl violet	3.4	2.2		0.982
Cadmium	17.89	3.26		0.912

Freundlich Isotherm: Freundlich isotherm model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. Linear form of Freundlich model was expressed by

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where, qe is dye concentration in solid at equilibrium (mg/g),Ce is dye concentration in solution at equilibrium (mg/L), Kf is the Freundlich isotherm constant related to adsorption capacity(L/mg) and n is the Freundlich isotherm constant related to adsorption intensity. The linear plot of log qe versus log Ce and the values of n and kf calculated from the slope and intercept are given in table 2.The value of n was greater than one indicating the favorable adsorption of MV.

Adsorption kinetics: Kinetic studies are necessary to optimize different operation condition for the sorption of dyes. The kinetics of MV and Cd onto AC was analyzed using pseudo-first order, and Intraparticle diffusion kinetic models.

Pseudo – first order kinetic model: The pseudo-first order equation of Lagergren is generally expressed as follows, $dq / dt = K_{ad} (q_e – q_t)$, where q_e and q_t are the sorption capacity at equilibrium and sorption capacity at time and K_{ad} is the rate constant of pseudo – first order sorption (1/min). After integration and applying boundary condition t = 0 to t = t and q = 0 to q = q_t, the integrated form becomes,

$$\log (q_e – q_t) = \log q_e – [K_{ad} / 2.303]\, t$$

The linear plots of $\log (q_e – q_t)$ Vs t showed that adsorption followed the pseudo first order rate expression given by Lagergren. The K_{ad} value for Reactive orange was calculated from the slope of linear plots. The rate constants for adsorption (1/min) of dye at ambient temperature of different particle size are presented in the Figures. From these observations, the pods of Delonix regia activated carbon follows Lagergren pseudo first order kinetics.

Conclusion

The carbon derived from the *Delonix regia* pods can be used as an efficient adsorbent for the removal of methyl violet and cadmium from aqueous solution. The adsorption is faster and the rate is mainly controlled by intraparticle diffusion based on sorption phenomenon. The adsorption is controlled only by particle size because small particles will have more surface area for adsorption it is proved in the above studies. The maximum removal of methyl violet 100% and cadmium 80%. Langmuir and Freundlich isotherm models were proved it is favorable. It is technically feasible, low cost, economically it is very useful.

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