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Kinetic and isotherm studies for the adsorption of a textile dye using PVA matrix supported activated carbon

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ABSTRACT

Polyvinyl alcohol matrix supported Europhobia antiquorum L activated carbon is analyzed for its applicability as an adsorbent for the removal of Methylene Blue dye from its aqueous solution. Effect of pH, initial dye concentration, dosage and temperature were studied. The PVA matrix supported AC adsorbs 91.67 mg/g of MB at 100 mg/L of initial dye concentration. It was analyzes with the help of pseudo first order, second order models. Collected data also analyzed with the help of Intra particle diffusion model to elucidate the mechanism. These kinetic parameters were compared for various dyes under different condition. Langmuir and Freundlich isotherm models were used to test the equilibrium data. The Langmuir monolayer adsorption capacity increases from 56.49 to 67.12 mg/g on increasing the room temperature from 30 to 50° C. The results this study proves that PVA supported EAC is a promising adsorbent for the remediation of textile effluent in a sustainable manner with a surface area of 739.5 m²/g.

Keywords: Methylene Blue, Adsorption, Kinetics, Isotherm and Effluent.

INTRODUCTION

Pollution in any form is highly hazardous for the living things especially for the mankind. Dyeing industrial waste water is one of the major pollutant adversely affects the environment due to its high toxicity and non-biodegradable nature. Many methods have been successfully demonstrated for the removal of dyes present in the waste water. The methods like electrochemical coagulation, reverse osmosis, nano filtration, adsorption using activated materials etc., are used for the removal of dye from waste water. From these methods, adsorption was proved to be a better method in terms of efficiency and low operating cost.

The recent research is focused on the production of micro and nano adsorbents from agricultural and biological wastes. Preparation of a good quality adsorbent from waste products may contribute for the sustainability of the environment and also gives better benefits in terms of commercial aspects in future.

The major advantage of using the biomaterials and agro based materials are their surplus availability, negligible cost and also they are renewable sources of raw materials for the production of activated carbon. Activated carbon prepared from different materials like agricultural wastes¹⁻², babool seed³, corncob⁴, oil palm waste⁵, orange waste⁶, palm shell⁷, rice husk⁸, Tamarind kernel powder⁹, saw dust¹⁰, eucalyptus bark¹¹, pine saw dust¹², polymerized sawdust¹³, pistachio shells¹⁴, Polyacrylamide-grafted sawdust¹⁵, etc.,

The typical approaches in sorption science is the production of adsorbent containing pre-existing insoluble matrix which will allows the adsorbent can comfortably interact with the pollutants present in the wastewater¹⁶. These type

of adsorbent embedded in a polymer matrix are of great interest because they have many advantages. The matrix gives high mechanical strength and imparts essential physical and chemical properties like surface area and porosity. The adsorbents embedded in a polymer matrix may have the following characteristics (i) controlling and improving the affinity of the material for the pollutant; (ii) changing the selectivity series for sorption; (iii) enhancing sorption kinetics; (iv) improving the stability of the material ¹⁷.

The purpose of the present work is to evaluate the sorption of Methylene Blue from its aqueous solution using Polyvinyl alcohol supported *Euphorbia antiquorum L* wood activated carbon prepared by H_3PO_4 impregnation method (PVAC). To effectively apply this class of sorbents, there is a need to understand the kinetics and mechanism of interaction between the dye molecules and the sorbent particle. The precursor wood used for the preparation of AC is derived from the matured trees of *Euphorbia antiquorum L*. The tree is wide spread throughout peninsular India; it can be found growing up to an altitude of 800 m. One of the largest armed tree in *Euphorbias* with an average height of 5 - 7 m.

MATERIALS AND METHODS

Adsorbent

The *Euphorbia antiquorum* L wood cut into pieces of 2 cm to 3 cm size, dried in sunlight for 10 days. The dried material soaked in a boiling solution of 10 % H_3PO_4 for one hour and kept at room temperature for 24 hours. After 24 hours the wood material separated, air dried and carbonised in muffle furnace at 400°C. The carbonised material was powdered and activated in a muffle furnace at 800°C for a period of 10 minutes. Then the activated carbon is mixed with 1% aqueous solution of Polyvinyl Alcohol (i.e the ratio of carbon & PVA is 1:1) and agitated with magnetic stirrer for 1h, oven dried at 105°C until the complete removal of water. The dried adsorbent powdered well and used for the adsorption studies. The characteristics of the PVAC are studied as per the standard procedures ¹⁷⁻¹⁸ and few important parameters are given in table 1.

Adsorbate

All the chemicals used are reagent grade. Methylene Blue (MB) having molecular formula $C_{16}H_{18}ClN_3S$ (Mol Wt: 319.85), (E. Merck, India) was chosen as the adsorbate. The structure of MB is given in figure 1. A stock solution containing 1000 mg of the dye per litre was prepared by dissolving the dye in double distilled water and was used to prepare the adsorbate solutions by appropriate dilution as required. The percentage purity of dye also considered for the preparation of stock solution.

Adsorption studies

The adsorption experiments were carried out by agitating 100 mg of adsorbent with 200 ml of dye solution of 25 to 100 mg/L concentration at 200 rpm in a temperature controlled orbital shaker (REMI make). The mixture was withdrawn at specified interval then centrifuged using electrical centrifuge (Universal make) at 5000 rpm for 10 minutes and unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make Bio-UV visible spectrometer (BL-198) at 664 nm. The effect of pH was studied by adjusting the pH of the adsorptive solution using 0.1 N NaOH and 0.1 N HCl. All the experiments conducted in duplicate and mean of the two values are taken for calculation.

Kinetics of adsorption

Many scientists have proposed various kinetic models to elucidate the mechanism of solute adsorption. The rate and mechanism of adsorption depends upon various factors like physical and/or chemical properties of adsorbent as well as mass transfer process. The results of these kinetic models are useful for the design and optimization of effluent treatment process in bulk at industrial level. The following three kinetic models were considered for the investigation of the mechanism of MB onto PVAC.

Pseudo first-order kinetic model

The integrated linear form of pseudo first-order kinetic model proposed by Lagergren ¹⁹ is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
(1)

A linear trace is expected between the two parameters, $\log (q_e-q_t)$ and t, provided the adsorption follows first order kinetics. The values of k_1 and q_e can be determined from the slope and intercept.

Pseudo second-order kinetics

The adsorption may also be described by pseudo second-order kinetic $model^{20}$ if the adsorption does not follow the first order kinetics. The linearised form of the pseudo second-order model is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(2)

A plot of t/q_t and t should give a linear relationship if the adsorption follows second order. The values of q_e and k_2 can be calculated from the slope and intercept of the plot.

Intra particle diffusion model

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent. The following kinetic model suggested by Weber and Morris²¹ to investigate adsorption is intra-particle diffusion or not. According to this theory

$$q_t = k_d \cdot t^{1/2} \tag{3}$$

Intercept of a plot of q_t versus $t^{0.5}$ will give the constant k_d .

Adsorption Isotherm

Adsorption isotherm describes the equilibrium existence of adsorbate between the liquid and solid phase. Experimental isotherm data collected at different temperatures were analysed using Langmuir and Freundlich isotherm models.

Langmuir model

The Langmuir model ²² was initially developed to describe the adsorption of gas on to solid surface. It is derived on the assumption of monolayer adsorption and also the surface is energetically homogeneous. The final form of Langmuir isotherm is

$$q_{e} = \frac{Q_{0}.b_{L}.C_{e}}{(1+b_{L}.C_{e})}$$
(4)

The rearranged linear form of Langmuir model is

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \tag{5}$$

The constants Q_0 (monolayer adsorption capacity) and b_L (Langmuir constant) can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e .

Freundlich Model

It is a most popular model for a single solute system derived on the basis distribution of solute between the solid phase and aqueous phase at equilibrium 23 . The Freundlich equation is expressed as;

$$q_e = k_f C_e^{1/n} \tag{6}$$

Linear form of Freundlich equation is

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{7}$$

When 1/n is >1.0, the change in adsorbed dye concentration is greater than the change in the solute concentration.

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RESULTS AND DISCUSSION

Effect of temperature on the adsorption of MB

The Figure 2 represents the uptake of MB onto PVAC at 30, 40 and 50° C as well as various initial dye concentrations. The equilibrium sorption capacity of MB onto PVAC increases from 64.38 to 72.35 mg/g while increasing the temperature from 30 to 50° C. The increase in uptake with increase in temperature indicates that the sorption of MB onto PVAC is an endothermic process. The enhancement in adsorption is due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. This may have caused as a result of increase in the mobility of the dye (due to increase of kinetic energy) with the raise of temperature. At higher concentrations the competition for the adsorption sites are more, which leads to enhanced adsorption with respect to increase in solute concentration.

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Table I –	Important	Physico	Chemical	Properties	of PVAC

S.No	Properties	Values
1	pH	6.72
2	Conductivity, µS/cm	0.712
3	Moisture content, %	6.49
4	Ash, %	11.5
5	Volatile matter, %	16.1
6	Matter soluble in water, %	0.32
7	Matter soluble in 0.25 M HCl, %	1.09
8	Bulk density, g/mL	0.44
9	Specific Gravity	0.81
10	Porosity, %	54.32
11	Surface area, m ² /g	739.5
12	Methylene Blue Value, mg/g	322

Table 2 - Calculated kinetic parameters for the adsorption of MB at various initial concentrations

Parameters	Initial dye	concentra	tion, mg/L	Tem	peratui	e, °C
	50	75	100	30	40	50
q _e exp (mg/g)	36.96	64.38	91.67	64.38	70.35	72.35
Pseudo first order k	cinetics					
$k_1(\min^{-1})$	0.0477	0.0486	0.0491	0.0486	0.0373	0.0428
q _e cal (mg/g)	18.75	33.57	40.09	33.57	28.25	24.53
r ²	0.8829	0.9132	0.8754	0.9132	0.987	0.9669
Pseudo second order kinetics						
k ₂ x 10 ⁻³ (g/mg/min)	0.055	3.2	3.08	3.2	2.57	3.46
qecal (mg/g)	38.91	67.56	95.23	67.56	75.52	76.92
r ²	0.9994	0.9996	0.9994	0.9996	0.9991	0.9997
Intra particle diffusion model						
k_{id} (mg/g/min ^{1/2})	4.90	5.90	5.57	5.90	6.25	9.89

Table 3 - Results of Isotherm Plots

Temperature °C					
Parameters	30	40	50		
Langmuir isotherm					
Qo(mg/g)	56.49	63.29	67.12		
b _L (L/mg)	0.0163	0.0151	0.0145		
r^2	0.9900	0.994	0.9982		
Freundlich isotherm					
n	4.399	4.552	4.789		
k _f	21.46	26.34	30.93		
r^2	0.982	0.9438	0.9321		

Kinetics of Adsorption

The first order kinetic plot at various initial dye concentrations and temperatures are shown in Figures 3 and the results are presented in Table 2. The pseudo first order constant ranged between 0.04767 to 0.04905 min⁻¹ at various concentrations and it varies from 0.03731 to 0.04859 min⁻¹ for the range of temperatures studied. The q_e values calculated from pseudo first order model is in good agreement with the experimental q_e values at various concentrations.

The calculated equilibrium adsorption capacity decreases with temperature in contrary to the experimental q_e (which increases with temperature). This irrelevance between the experimental and calculated q_e values suggests that the first order equation not fit enough to explain the adsorption process.



Figure 2 – Amount of MB Adsorption onto PVAC at various concentrations & Temperatures

The data for the adsorption of MB onto PVAC applied to pseudo second order kinetic model at various concentrations and temperatures as shown in Figure 4, and the results are presented in Table 2.

Initial sorption rate (h) increases on increasing the initial concentration and temperature. The equilibrium sorption capacity (q_e) increases with concentration and decreases on increasing the solution temperature and sorption rate constant (k_2) decreases with increase in the initial dye concentration and decreases linearly with temperature. At higher initial dye concentrations, the number of dye molecules near the vicinity of adsorbent is more, which favours the dense and multilayer accumulation of solute over the sorbent. In this case the increase of temperature increases the kinetic energy of molecule which leads to greater rate of desorption and ultimately leads to decrease of adsorption when the solution temperature is raised.

Even though, the pseudo second order equation gives some marginal deviation in the $q_e(cal)$ and $q_e(exp)$, the data fits very well with good correlation co-efficient for the range of concentrations and temperatures studied. On the basis of r^2 values and resemblance in the $q_e(cal)$ and $q_e(exp)$ it is suggested that the adsorption of MB on to PVAC follows pseudo second order kinetics.

A plot of " q_t " vs " $t^{1/2n}$ " at various initial dye concentrations and temperatures are given in the Figures 5 and the intra particle diffusion constent are given in Table 2. The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through the origin at various concentrations as well as at various temperatures. It indicates the boundary layer control and further show that intra particle diffusion is not the only rate-limiting step, but other kinetics like film diffusion may also be operating simultaneously.



Figure 3 – First order plot of MB Adsorption onto PVAC



Figure 4 – Second order plot of MB Adsorption onto PVAC

Isotherm Studies

Adsorption isotherms were obtained at 30, 40 and 50°C. The Langmuir plot at different temperatures is shown in Figure 6, and the results are given in Table 3. The Langmuir adsorption capacity increases from 56.49 to 67.12 mg/g on increasing the temperature from 30 to 50°.

Analysis of the Langmuir monolayer adsorption capacity obtained for the adsorption of MB onto PVAC agrees well with the other adsorbents reported by the past researchers. The comparative data gives an indication that PVAC has great potential as a sorbent for the adsorption of MB from the effluent.

The Figure 7 shows the Freundlich plot and the results are given in Table 3. The Freundlich constant (k_f) increases from 21.46 to 30.93 mg^{1-1/n} L^{1/n} g⁻¹ on increasing the temperature from 30 to 50°C, the adsorption capacity of the sorbent also increases. High value of k_f shows easy uptake of the dye. The slope 1/n measures the surface heterogeneity and if becomes more prevalent as 1/n gets closer to zero. For n = 1, partition between the two phases is independent of the concentration. Value for 1/n below 1 indicates a normal and favolurable adsorption and the surface is more heterogeneous with more functional groups which favours the adsorption.









Both Langmuir and Freundlich model demonstrates the adsorption of MB onto PVAC very well. In order to decide which type of isotherm fits the experimental data better, the applicability of the model was established from the regression co-efficient (r^2). Langmuir model is more appropriate to explain the nature of adsorption with correlation co-efficient of 0.99 to 0.9982 rather Freundlich model shows little poor fit ($r^2 = 0.932$ to 0.982).



Figure 7 – Freundlich plot of MB Adsorption onto PVAC

CONCLUSION

The PVA matrix supported Activated carbon for the adsorption of dye from its aqueous solution can be conveniently and economically prepared from *Euphorbia antiquorum L* wood. The PVA inert matrix enhances the mechanical stability of activated carbon which will be useful for more number of recycling. The physico-chemical characteristic of the prepared adsorbent is comparable with the commercial activated carbon. The uptake of MB dye increased from 36.96 mg/g to 91.67 mg/g while increasing the initial dye concentration from 25 mg/L to 100 mg/L. The adsorption of MB increases with temperature indicates that the sorption process is endothermic in nature. The pseudo second-order kinetic model describes the adsorption much better than pseudo first-order model. Intra particle diffusion model proves that pore diffusion play a major role for the adsorption MB by PVAC. The Langmuir adsorption capacity varies from 56.48 mg/g to 67.12 mg/g with the range of temperatures studied. Langmuir model is more appropriate to explain the nature of adsorption with high correlation coefficient.

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