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ADSORPTION OF ACID BLUE- 40 (A TEXTILE DYE) USING *PROSOPIS JULIFLORA* ACTIVATED CARBON EMBEDDED IN POLYANILINE MATRIX

N.Gopal* and M. Asaithambi
PG and Research Department of Chemistry, Erode Arts and Science College (Atonomous),
Erode- 638 009, TamilNadu, India
*E-mail: chemgopal@yahoo.com

ABSTRACT

An activated carbon was prepared by $ZnCl_2$ activation method using Prosopis juliflora seeds. The prepared AC was embedded in polyaniline inert matrix (PPAC). It was used for the adsorptive removal of Acid Blue 40 (AB 40) dye. The PPAC has exceptionally well developed porosity with a surface area of 1028 m^2/g. The maximum percentage (92.7%) of adsorption observed at a pH of 3 and the percentage of adsorption decreased on increasing the pH. The kinetics of AB40 adsorption analyzed using pseudo-first order and pseudo-second order kinetic equations. The study revealed that the adsorption initially follows second order and in the later stages it follows pseudo-first order kinetics. The activation energy obtained for the adsorption of AB40 by PPAC is 77.30 kJ/mol, indicating the weak forces of attraction between solute and sorbent. Standard enthalpy change $\Delta H°$ is 61.214 kJ/mol (less than 80 kJ/mol) substantiate the physisorption and the positive sign indicate the endothermic nature of AB40 adsorption by PPAC.

Keywords: *Prosopis Juliflora*, Acid Blue 40, Kinetics, Thermodynamics and Acid dye.

INTRODUCTION

Most of the developing countries face severe water scarcity due to pollution caused on the ground water sources. This pollution mainly caused by the discharge of untreated effluents. The main reason for the discharge of untreated effluents is the high cost involved for the treatment process. Of all the industries, textile processing consumes and discharges large amount of water[1]. It is estimated that about 40-65 L of textile effluent is generated per kg of cloth produced[2]. Untreated textile effluents contain synthetic dyes, which causes severe environmental concern due to their high visibility and recalcitrance. Presence of dye molecules and their degradation products in water leads to acute toxicity and mutagenicity to living things.

Numerous technologies have been tried in the past for the effective treatment of dye bearing wastewater. Every technology has some limitations either in the form of ineffectiveness or high cost. Among these technologies adsorption using activated materials was proved to be effective in terms of quality of treatment. It has a very complex structure, with pores ranging from micropores to macropores. It has been reported that the surface area, pore volume, porosity and pore size distribution of AC have significant effects on the adsorption of organic pollutants[3,4]. However, commercially available activated carbon considered as expensive for many small scale industries in the developing countries. Expensive and non-renewable nature of the starting materials like coke is unjustified for pollution control applications.

Exploration of an AC from renewable resources is highly warranted in the present scenario. Utilization of waste biomass for the production of AC can minimize the burden of solid waste disposal. Many agro wastes like pine bark[5], rice husk[6], babassu coconut epicarp[7], cottonseed hull[8], olive-based activated carbon[9], agricultural waste[10], bamboo[11], deoiled mustard[12] etc., have been tried as a precursor for the preparation of AC in the recent past.

Anthraquinone dye is the second most important class of commercial dyes after azo dye, which are based on 9, 10-anthraquinone. Different colors can be made by introducing powerful electron-donor groups such as amino or hydroxyl into one or more of the four alpha positions. They are characterized by their brightness and good fastness, and gamed wide applications in textile industry[13]. These classes of dyes pose serious problems to flora and fauna when they are discharged into the environment. Thus, keeping the hazardous nature and harmful effects in view, it was considered worthwhile to make systematic efforts to remove AB 40 from wastewater using *Prosopis Juliflora* Activated carbon embedded in Polyaniline matrix. About the precursor, *Prosopis Juliflora* has invaded millions of hectares of land in the arid and semi-arid continents of Asia, Africa, Australia and Americas. These species threatening crop production, depleting the water resources and displacing native flora and fauna. The seeds of *Prosopis Juliflora* are high in protein, are not easily digestible by animals, requiring some form of grinding and processing by humans.

EXPERIMENTAL

Adsorbent Preparation

The seeds of *Prosopis Juliflora* were collected from in and around the rural regions of Erode District of Tamilnadu, India. The collected seeds were cut in to pieces of 2 to 4 cm size sun dried for one week. The dried material was used for the preparation of adsorbent as per the following procedure.

Carbonization with chloride salts

The material to be carbonized is impregnated with a boiling solution of zinc chloride for 2 hrs and soaked in the same solution for 24 hrs so that the solution gets well adsorbed for a period of 24 hours. At the end of 24 hours, the excess chloride solution decanted off and air-dried. Then the material was placed in muffle furnace, carbonized at 400°C. The dried material was powdered and activated in a muffle furnace at 800°C for a period of 10 minutes. After the activation, the carbon washed sufficiently with 4N HCl to remove the cations. Then the material was washed with plenty of water to remove excess acid, dried and powdered.

Preparation of Polyaniline Composite

The poly aniline was synthesized on the surface of above mentioned AC, which was previously soaked in monomer aniline solution (0.2 M) for 12 hour at room temperature followed by slow addition of chemical oxidants 0.2 M Ammonium per sulphate in 1.2 M HCl for poly aniline at room temperature for 4 hours.[14]
The textile dye, Acid Blue 40 (Molecular Formula of $C_{22}H_{16}N_3NaO_6S$, CI No. 62125, λmax of 615 nm, FW. 473.43) was procured from E. Merck, India and used without further purification. Its chemical structure is shown in Fig. 1. A stock solution containing 1000 mg of the dye per liter was prepared by dissolving appropriate amount of dye (based on percentage purity) in double distilled water and was used to prepare the adsorbate solutions by appropriate dilution as required.

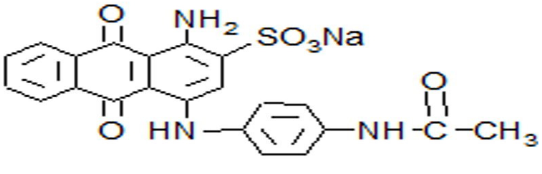

Fig.-1: Structure of AB40

Characterization of adsorbent

Physico-chemical characters of the activated carbon samples were studied as per the standard testing methods. The N_2 adsorption-desorption isotherms of activated carbon were measured at 77K using N_2 gas sorption analyzer (Nova 1000, Quantachrome Corporation) in order to determine the surface area using the BET equation.

Adsorption Studies

The adsorption experiments were carried out in 200 ml tight lid glass bottle (Borosil-R) by agitating 100 mg of adsorbent with a 200 ml of the aqueous dye solution. The effect of pH was studied by adjusting the pH of the adsorptive solution 2 to 11 using 0.1N HCl and 0.1N NaOH. All other kinetic experiments were carried out at the normal pH of the dye solution. The contents of the flasks were agitated with the help of a temperature controlled orbital shaker (REMI Make). After the specified time, the sample is taken out from the shaker 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 615 nm. All the experiments were conducted in duplicate and mean of the two values were taken for calculation. Maximum deviation is 4 %.

The amount of adsorbed AB 40 q_e (mg/g) was calculated as follows:

$$\text{Amount of adsorbed dye per g of adsorbent } (q_e) = (c_0 - c_e)\frac{V}{W} \quad (1)$$

$$\text{Percentage of dye removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

Where, C_0 and Ce (mg/L) are the liquid-phase concentrations of dye initially and at equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

Desorption Studies

After adsorption experiments the dye loaded carbon washed gently with double distilled water to remove any un-adsorbed dye if present. Desorption studies were conducted using several such carbon samples. 500 mg of the dye loaded carbon agitated above the equilibration time with 50 ml of double distilled water of various pH.

RESULTS AND DISCUSSION

Adsorbent Characteristics

The physico chemical properties *Prosopis juliflora* seed carbon embedded in polyaniline matrix (PPAC) is given in table 1. Modest amount of ash and volatile matter makes PPAC as good candidature for the wastewater treatment applications. The PPAC has exceptionally well developed porosity and very high surface area of 1028 m^2/g. High value Methylene Blue adsorption capacity indicates that the AC has tremendous potential towards the adsorption of large organic molecules.

Batch Mode Adsorption

Effect of pH on dye Adsorption and Desorption

The role of pH for the adsorption and desorption of AB40 on to PPAC is represented in the fig. 2. At lower pH, there is an excessive protonation leads the carbon surface with more positive which attracts the negatively charged dye (Dye-SO_3^-) from the solution phase considerably by significant electrostatic attraction. The maximum percentage (92.7%) of adsorption observed at a pH of 3. As the pH of the system increases, the amount of H^+ ions decreases in the system. When the pH of the solution is equal to pH_{ZPC} the surface of carbon is neutral and the adsorption is only because of pore diffusions. When the pH goes beyond the pH_{ZPC} the carbon surface becomes negatively charged and this will repel the nagativelly charged dye molecules which ultimately results in the decrease of adsorption at higher pH values.

Table-1: Physico-Chemical Characteristics of PPAC

S.No.	Properties	Values
1	pH	7.48
2	Conductivity, mS/cm^2	0.273
3	Moisture content, %	11.4

4	Ash, %	16.4
5	Volatile matter, %	15.5
6	Matter soluble in water, %	0.44
7	Matter soluble in 0.25 M HCl, %	1.27
8	Bulk density, (g / ml)	0.46
9	Specific Gravity	0.93
10	Porosity, %	50.54
11	Surface area, m^2 / g	1028
12	Methylene Blue Value, mg/g	443
13	pH $_{ZPC}$	6.8

In the case of desorption, usage of HCl as a desorbing agent, the surface of adsorbent become positively charged and it will not allow the dye molecules to leave from its surface. Where as NaOH makes the surface adsorbent to be negative there by the negative dye molecules experiences a repulsive force and leaves from the surface of adsorbent. The high % of desorption gives an insight that very weak forces of attraction holds the dye molecules on the surface of adsorbent. Further this has to be confirmed with the bonding energy studies like activation energy and enthalpy changes.

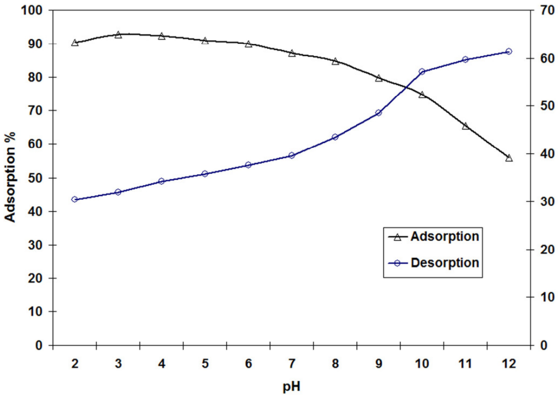

Fig.-2: Effect of pH on the adsorption and desorption of AB40

Effect of Initial Concentration and Temperature

Effect initial dye concentration and temperature for the adsorption of AB40 by PPAC were plotted in fig.-3. The amount of dye adsorption increases linearly with time and reaches equilibrium at a contact time of 100 min. Adsorption of AB40 dye was very fast initially and nearly 50% of dyes were adsorbed in less than 30 min. Though, the percentage of adsorption decreases while increasing the initial dye concentration from 25 to 100 mg/L, where as the quantity of adsorption increases linearly from 23.91 to 85.16 mg/g. At higher concentration the velocity of solutes diffusing towards the interior pores will also be high due to high concentration gradient between the solid and liquid phase. Another fact is that the increase in initial dye concentration provides necessary driving force to overcome the mass transfer resistance.

Increase in solution temperature enhances the amount of dye adsorption from 46.28 to 49.47 mg/g. The adsorption of AB40 dye by PPAC was enhanced with raising the temperature from 30 to 45°C indicating that a high temperature favored the dye removal by adsorption. The results indicate that the adsorption of AB40 by PPAC is endothermic in nature. Though the adsorption increases with temperature but the quantity of solute adsorbed is very marginal.

The increase of adsorption with temperature may be attributed to increase in the number of active surface sites available for adsorption on each adsorbent, increase in the porosity and in the total pore volume of the adsorbent. The enhancement in adsorption could be also 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 also be a result of an increase in the mobility of the dye molecule with an increase in their kinetic energy, and the enhanced rate of intraparticle diffusion of sorbate with the rise of temperature.

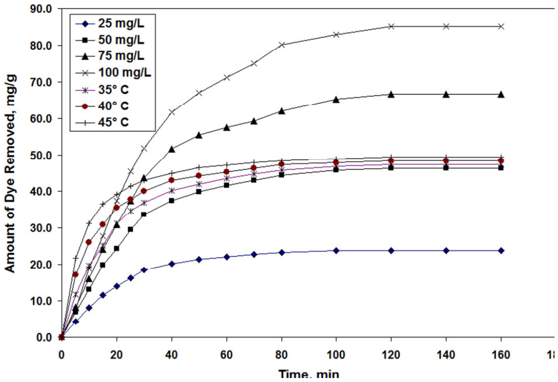

Fig.-3: Effect initial dye concentration and temperature for the adsorption of AB40 by PPAC.

Kinetics of Adsorption

The competition between the solute and the solvent molecules for adsorption sites makes the solute to be adsorbed on to the adsorbent. The tendency of a particular solute to get adsorbed is determined by the difference in adsorption potential between solute and the solvent. In order to evaluate the number of molecules which actually determines the velocity of adsorption process it is essential to analyze the adsorption data using pseudo-first order and pseudo-second order kinetic models. The linear from of pseudo-first order kinetic model expressed by Lagergren[15] is given in equation (3).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

A linear trace is expected between the two parameters, $\log(q_e\text{-}q_t)$ and t, provided the adsorption follows pseudo-first order kinetics. The values of k_1 (pseudo-first order rate constant, min^{-1}) and q_e (calculated adsorption capacity, mg/g) were determined from the slope and intercept of the plot (Figure not shown) and the results are presented in Table-2.

Table-2: Results of Various kinetic models for the adsorption of AB40 onto PPAC

	Initial dye concentration, mg/L				Temperature, °C			
	25	50	75	100	30	35	40	45
$q_e$exp.(mg/g)	23.91	46.28	66.74	85.16	46.28	47.34	48.40	49.47
Pseudo first order kinetics								
k_1 (min^{-1})	0.0313	0.0375	0.0359	0.0368	0.0426	0.0419	0.0424	0.0417
$q_e$cal(mg/g)	16.79	43.61	71.29	100.35	50.21	41.54	35.07	28.07
r^2	0.8752	0.9568	0.9888	0.9895	0.9879	0.9923	0.9869	0.9705
Pseudo second order kinetics								
k_2 (g/mg/min)	0.0019	0.0007	0.0004	0.0002	0.0007	0.0014	0.0021	0.0032
h	1.496	2.274	2.521	2.663	2.274	3.771	5.724	8.489
$q_e$cal(mg/g)	27.62	55.56	84.75	114.94	55.56	52.63	51.81	51.81
r^2	0.9927	0.9883	0.9826	0.9632	0.9883	0.9982	0.9996	0.9999

Lagergren equation represents the pseudo-first order kinetics for the whole adsorption reaction, with a one-partial order with respect to the free concentration sites and a zero-partial order with respect to the solute in the solution. This behavior was expected if the external diffusion is not the rate determining step in the adsorption process because since its linear expression has a similar form as that of the traditional model of external diffusion. Besides, the pseudo-first order was generally used in case of physical adsorption onto homogeneous adsorbents. The pseudo-first order rate constant (k_1) increases on increasing the initial dye concentration and it decreases while increasing the solution temperature. At higher concentration the competition for the adsorption sites by the solutes increase which hinders the rate of adsorption. Where as increase of solution temperature favors the adsorption of AB40 onto PPAC hence the entire adsorption process is endothermic in nature.

The kinetic data for the adsorption of AB40 by PPAC is also analyzed using pseudo-second order kinetic model. The linear expression suggested by Ho and McKay^{16} is-

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (4)$$

$$h = k_2 . q_e^2 \qquad (5)$$

Where k_2 (g/mg/min) is the rate constant, and h is known as initial sorption rate. The value of q_e and k_2 for the adsorption of AB40 by PPAC was determined from the slope and intercept of the straight line plots of ''t/q_t vs t'' (fig. 4) and the results are given in Table-2.

The adsorption of AB40 onto PPAC in not in good agreement between the extrapolated kinetic values and the experimental dye removal results, at various initial dye concentrations. Therefore, this model is valid for a small interval of contact time only. The initial sorption rate (h) increase linearly on increasing the initial dye concentration as well as the solution temperature. At the beginning of the adsorption process many solute molecules compete for bare surface which gives higher initial sorption rate. Raise in the temperature also increase the kinetic velocity of solute molecules there by enhances initial sorption rate. The adsorption capacity and linear regression coefficient suggests that the adsorption of AB40 by PPAC does not follow pseudo-second order model for the entire range of concentration and temperature.

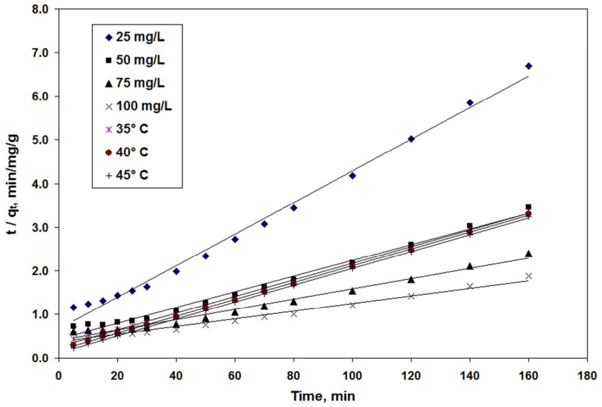

Fig.-4: Second order kinetics plot for the adsorption of AB40 onto PPAC

The adsorption of AB40 by PPAC follows pseudo-second order at the beginning of adsorption and in the later stages one-partial order with respect to the free concentration sites and a zero-partial order with respect to the solute in the solution (i.e follows pseudo-first order rate expression).

Thermodynamic parameters

The activation energy for the adsorption of AB40 onto PPAC was evaluated using the following form of Arrhenius equation.

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (6)$$

Where, k_2 (g/mg/min) is the rate constant derived from pseudo-second order kinetic model, Ea (kJ/mol) is the Arrhenius activation energy of adsorption and A is the Arrhenius factor, R is the gas constant which is equal to 8.314 J/mol/K, and T (K) is the system temperature.

Table-3: Thermodynamical parameters for the adsorption AB40 onto PPAC

Temperature, °C	ΔH°, kJ/mol	ΔS°, J/K/mol	ΔG°, kJ/mol	Ea, kJ/mol
30	61.214	214.58	- 4.012	77.30
35			- 4.685	
40			- 5.686	
45			- 7.275	

The Activation for the adsorption and the Arrhenius factor were calculated from the plot of ln k_2 vs 1/T (figure not shown) and the results were summarized in table 3. The activation energy obtained for the adsorption of AB40 by PPAC is 77.30 kJ/mol, indicating that the solute molecules are held onto the surface of adsorbent by weak forces of attraction.

The thermodynamic parameters such as Gibbs free energy change ΔG°, standard enthalpy ΔH°, and standard entropy ΔS° were also calculated to identify the influence of temperature on the adsorption process. These parameters were calculated based on the isotherm data collected for 50 mg/L of AB40 solution at various temperatures. The thermodynamic parameters were evaluated using the following mathematical relationship.

$$K_c = \frac{C_{ads}}{C_{sol}} \tag{7}$$

$$\Delta G^0 = -RT \ln K_c \tag{8}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{9}$$

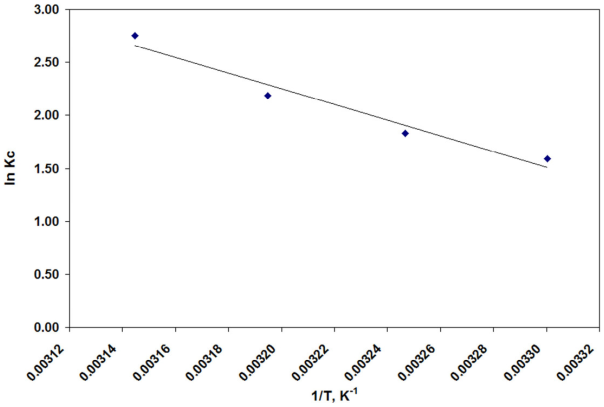

Fig.-5: Vant Hoff plot for the adsorption of AB40 onto PPAC.

Where, K_c is the equilibrium constant, C_{ads} is the amount of AB40 (mg/L) adsorbed on PPAC at equilibrium, C_{sol} is the equilibrium concentration of AB40 (mg/ L) in the solution, T is the solution temperature in K and R is a gas constant (8.314 J/mol/K). The values ΔH° and ΔS° were evaluated from the slope and intercept of vant Hoff plot of ln Kc vs 1/T as shown in fig. 5 and the results were presented in Table-3.

The negative standard Gibbs free energy change depicts the spontaneous nature of adsorption. The adsorption of AB40 by PPAC is more favored by high temperature as indicated by the more negative

Gibbs free energy during the temperature increase. Standard enthalpy change ΔH° is 61.214 kJ/mol (less than 80 kJ/mol) substantiate the physisorption and the positive sign indicate the endothermic nature of AB40 adsorption by PPAC. The randomness increases at the interface during the adsorption of AB40 by PPAC as indicated by the positive ΔS° (214.58 J/K/mol).

CONCLUSION

The seeds of *Prosopis Juliflora* were conveniently made into an activated carbon and the same is embedded in polyaniline matrix (PPAC). The polyaniline embedded AC has a surface area of 1028 m^2/g. The PPAC was conveniently applied for the adsorptive removal of Acid Blue 40 through batch mode analysis. The PPAC can adsorb 85.16 mg of dye per gram of adsorbent at 100 mg/L of initial dye concentration. The adsorption kinetics follows pseudo-second order during the beginning of the adsorption processes and in the later stages, it becomes pseudo-first order. The spontaneity of adsorption, endothermic nature, and randomness increases at the interface during the adsorption were demonstrated using ΔG°, ΔH° and ΔS° respectively.

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