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Removal of Acidic Dye (Acid Violet 4bs) From Aqueous Solutions Using Modified Forms of Adsorbents

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Abstract: *This research work deals with the application of using Sawdust (SD), Activated Carbon (AC) and PolyAniline coated SawDust (PAN/SD) produced from the plant of Calotropis Gigantea (CG) for the removal of Acid Violet 4BS dye from aqueous solutions. Adsorption experiments were carried out using batch mode technique. The effects such as adsorbent dose, initial dye concentration, pH and contact time were then studied. The maximum dye removal was found to be at natural pH for all the modified forms of adsorbents. A comparative study was made and it was found that the maximum percentage of dye removed by CGSD was 50.40%, for CGAC was 59.42% and for CGPAN/SD was 84.88%. Hence the study proved that CGPAN/SD is an efficient adsorbent compared to other forms for the removal of Acid Violet 4BS dye from aqueous solutions.*

Key words: *Adsorption, Sawdust, Activated carbon, PolyAniline coated sawdust, Acid violet 4BS.*

I. INTRODUCTION

Water pollution is mainly due to the discharge of the untreated or partially treated waste water from many industries on land or in water bodies¹. Effluents discharged from dyeing industries are highly colored and toxic. Adsorption is an effective treatment method that is widely used in the removal of contaminants from water and wastewater. This method has also been proven to be an important way to treat colored effluents². Activated carbon has been the most commonly used adsorbent due to their high adsorption capacity³. However the high cost of activated carbon restricts its use largely in developing countries. However very little data are available on the adsorption kinetics of sawdust.

In this study, we have introduced the application of using Sawdust (SD), Activated carbon (AC) and PolyAniline coated sawdust (PAN/SD) produced from the plant of Calotropis Gigantea(CG) for the removal of Acid Violet 4BS dye from aqueous solutions. One efficient way of increasing adsorption capacity of saw dust is the polymerization of monomer on the surface of saw dust. Chemical polymerization of aniline in aqueous acidic media can be easily performed using of oxidizing agents such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The principle is based on the switchable chemical structure and ion exchange properties of conducting polymers. The effects such as adsorbent dose, initial dye concentration, pH and contact time has been evaluated to assess the possibility of CGSD, CGAC, CGPAN/SD for the removal of acid violet 4BS. The maximum dye removal was found to be at natural pH for all the modified forms of adsorbents. A comparative study was made and it was found that the maximum percentage of dye removed by CGPAN/SD than CGSD, CGAC. Hence PolyAniline coated sawdust of Calotropis Gigantea(CG) has been used for the better removal of acid violet 4BS from aqueous solution.

II. EXPERIMENTAL WORK

A. Preparation of sawdust (CGSD)

Calotropis Gigantea(CG) stem was cut into pieces, dried in sunlight for 10 days. The dried material was grinded and sieved to a desired particle size and stored in a tight lid container for further adsorption studies.

B. Preparation of activated carbon (CGAC)

Calotropis Gigantea(CG) stem was cut into pieces, dried in sunlight for 10 days. The dried material was soaked in a boiling solution of 10 % H_3PO_4 for one hour and kept at room temperature for 24 hours⁵. After 24 hour, the material was separated, air dried and carbonized in muffle furnace at 400°C. The carbonized material was powdered and activated in a muffle furnace at 800°C for a period of 10 minutes. Then the material was washed with plenty of water to remove residual acid, dried, sieved to a desired particle size and stored in a tight lid container for further adsorption studies.

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C. Preparation of Polyaniline coated saw dust of Calotropis Gigantea (CGPan/SD)

Polyaniline coated Calotropis Gigantea was synthesized on sawdust surface of Calotropis Gigantea. In order to prepare polymer coated sawdust, 5.0 g sawdust immersed in 50 mL of 0.20 M freshly distilled aniline in 1M HCl solution for 6 hours before polymerization. The excess of the monomer solution was removed by simple decantation. Then 50 mL of 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant solution was added into the mixture gradually, and the reaction was allowed to continue for 4 hours at room temperature. The polymer coated sawdust (CGPan/SD) was filtered, washed with distilled water, dried in an oven at about 60 °C and sieved before use⁴. The coating percentage of each polymer onto saw dust determined by weight difference of the dried sawdust before and after coating and it was nearly 5%.

D. Preparation of Acid Violet 4BS dye

The stock solution of 1000mg/L of the Acid Violet 4BS dye was prepared by dissolving 1000mg of the dye in 1 litre double distilled water.

[Molecular Formula: $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_8\text{S}_2 \cdot 2\text{Na}$, Mol.Wt: 483.3834, λ_{max} : 544 nm]

Molecular Structure:

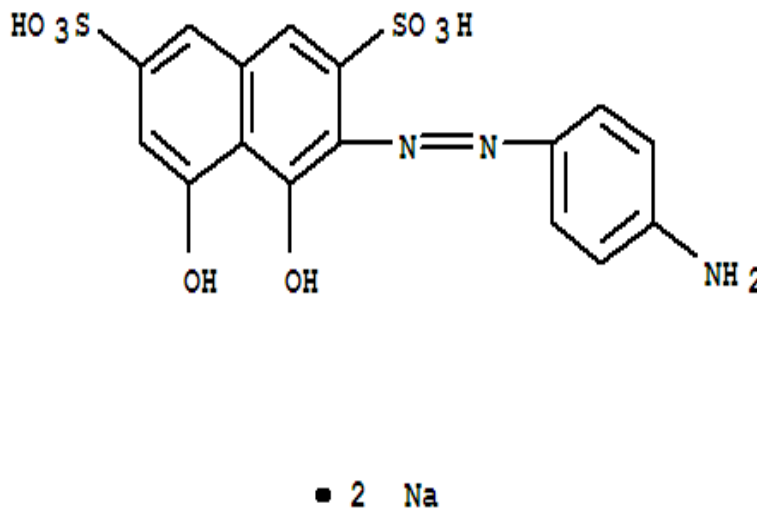


Figure 1- Molecular structure of Acid Violet 4BS

E. Batch mode adsorption experiments

The adsorption experiments were carried out by agitating 100 mg adsorbent with 100 mL of dye solutions of 25 to 100 mg/L concentration at 180 rpm on an Orbital shaker (REMI make). The mixture was withdrawn at specified intervals, centrifuged using electrical centrifuge (Universal make) at 5000rpm for 20 minutes and unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make UV Spectrophotometer (Elico make: BL-198) at λ_{max} of 544 nm. The effect of pH was studied by using dilute HCl and NaOH solutions. The effects of each parameter (initial dye concentration, pH, agitation time) were evaluated in an experiment by varying that parameter, while other parameters are maintained as constant. The amount of dye on various modified forms of adsorbents were calculated from the following equation

$$q_t = \frac{(C_0 - C_e)}{M} V \quad (1)$$

where, q_t (mg/g) is the amount of dye adsorbed at time t, C_0 and C_e (mg/L) are the concentrations of dye at initial and equilibrium respectively. V (L) is the volume of the solution and M (g) is the mass of dry adsorbent used.

III. RESULTS AND DISCUSSION

A. Effect of agitation time and initial dye concentration

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The rate of adsorption is a function of the initial dye concentration and contact time which is an important factor for the effective adsorption. When the initial dye concentration increased from 25 to 100 mg/L, the percentage of dye adsorption decreases from 82.46 % to 41.19 % for CGSD and 91.23% to 50.80% for CGAC and 94.74% to 72.07% for CGPAn/SD because the adsorbent has a limited number of active sites which becomes saturated at a certain concentration.

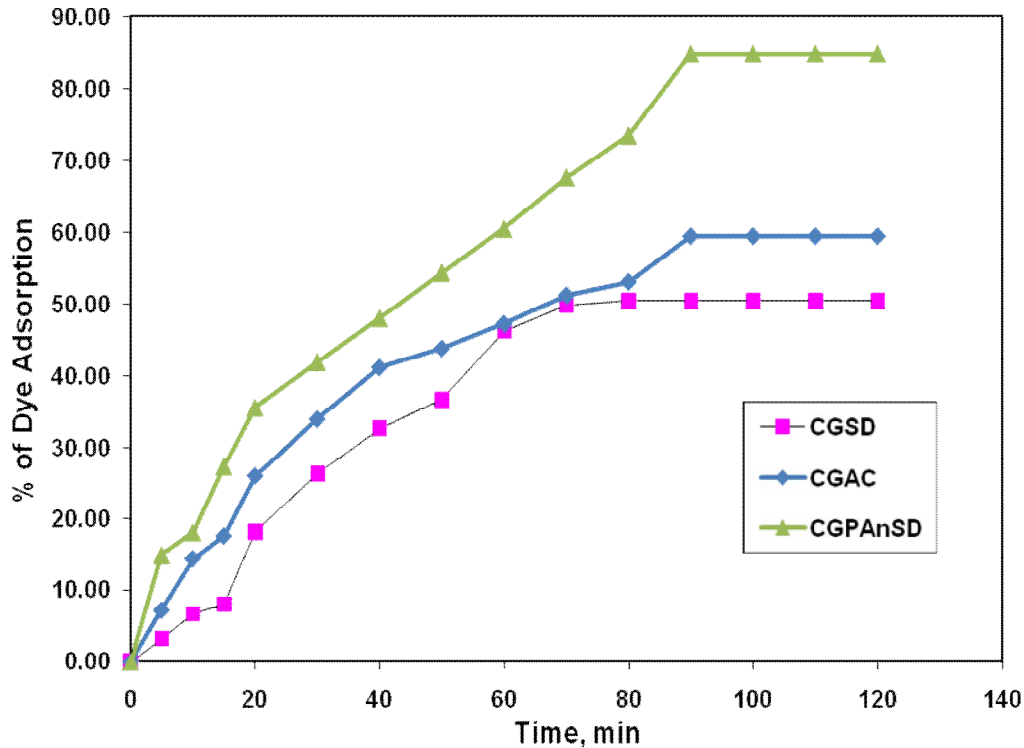


Figure 2 - Effect of agitation time on the percentage removal of acid violet 4BS dye on CGSD, CGAC and CGPAn/SD at 30° C (adsorbent dosage= 100mg; pH = natural pH; initial dye concentration = 50 mg/L)

The equilibrium adsorption increased with rise in contact time and equilibrium reached at almost 90 minutes for Acid Violet 4BS for all the modified forms of adsorbents. Initially the rate of adsorption was rapid, slow and reaches equilibrium, further increase in contact time did not enhance the adsorption. The initial rapid adsorption may be attributed to the presence of large number of available binding sites for adsorption and slower adsorption is due to saturation of binding sites and equilibrium attained.

B. Kinetics studies

In order to determine the adsorption kinetics, the pseudo-first order, and the pseudo-second order models were checked. The conformity between experimental data and the model predicted values is expressed by correlation coefficient (R^2). In order to investigate the mechanism of adsorption, characteristic constants of adsorption were determined using Pseudo-first order equation⁵ based on solid capacity and Pseudo-second order equation⁶ based on solid phase adsorption.

The integrated form of Pseudo-first order Lagergren kinetic equation

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

The dye adsorption described by a modified second order equation is expressed as

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

Pseudo second order plot of t/q_t vs t gives the results of kinetic studies are summarized in Table.1. Based on the values of correlation coefficient, the second order kinetic model was more suitable to describe the adsorption process.

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Table .1 Kinetic Model values for adsorption of Acid Violet 4BS

Dyes	Conc mg/L	First Order Kinetics			Second Order Kinetics		
		k ₁ (min ⁻¹)	q _e (cal) (mg/g)	r ²	k ₂ (g/mgmin)	q _e (cal) (mg/g)	r ²
CGSD	25	0.01958	24.5980	0.8614	0.00020	43.48	0.8897
	50	0.00783	42.8449	0.8211	0.00015	54.64	0.8311
	75	0.01750	43.3810	0.8746	0.00011	77.52	0.8919
	100	0.00737	73.7055	0.9589	0.00025	68.03	0.9947
CGAC	25	0.01865	18.2725	0.9091	0.00142	27.17	0.9744
	50	0.00944	39.5366	0.9555	0.00044	43.86	0.9888
	75	0.04905	52.5775	0.9433	0.00089	52.08	0.9897
	100	0.00898	78.6321	0.984	0.00009	100.00	0.8989
CGPAn/SD	25	0.04122	15.6927	0.9763	0.00432	25.71	0.9994
	50	0.01796	41.1339	0.9913	0.00029	62.89	0.956
	75	0.02073	43.0724	0.9552	0.00105	65.36	0.9948
	100	0.03155	64.1652	0.9912	0.00086	82.64	0.997

C. Isotherm studies

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between adsorbate and adsorbent. The Langmuir type adsorption isotherm indicates surface homogeneity of the adsorbent and hints towards the conclusion that the surface of adsorbent is made up of small adsorption patches which are energetically equivalent to each other in respect of adsorption phenomenon.

Langmuir model is represented by the following equation⁷

$$\frac{C_e}{q_e} = \frac{1}{Q_o b_L} + \left(\frac{1}{Q_o} \right) C_e \quad (3)$$

where q_e the amount is adsorbed at equilibrium (mg/g), Q_o is the monolayer adsorption capacity (mg/g), C_e is the equilibrium concentration of adsorbate (mg/l) and b_L is Langmuir constant related to energy of adsorption. The Langmuir adsorption capacities of Acid violet 4BS dye vary from 131.57 mg/g to 175.43 mg/g for CGAC and 204.08 mg/g to 227.27 mg/g for CGPAn/SD respectively on increasing in temperature from 30° C to 50° C. This indicated that the adsorption was favor at high operating temperature

Table 2: Isotherm Constants for the adsorption of Acid Violet 4BS dye onto CGAC and CGPAn/SD at various Temperatures

Adsorbents	CGAC			CGPAn/SD		
Parameter	Temperature °C					
	30	40	50	30	40	50
Langmuir Isotherm						
Q ₀ (mg/g)	131.57	163.93	175.43	204.08	212.76	227.27
b _L (L/mg)	0.0071	0.0058	0.0055	0.0094	0.0091	0.0086
r ²	0.9795	0.9277	0.9329	0.9855	0.9732	0.9734

IV. CONCLUSION

Adsorption experiments were carried out using batch mode technique with the application of using Sawdust (SD), Activated carbon (AC) and Polyaniline coated sawdust (PAn/SD) produced from the plant of Calotropis Gigantea(CG) for the removal of Acid Violet 4BS dye from aqueous solutions. A comparative study was made for all the modified forms of adsorbents. The kinetic studies revealed that the adsorption data was controlled by surface adsorption. The pseudo-second order kinetic model fitted well with the

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dynamical adsorption behavior of dyes suggested ion exchange adsorption. The experimental adsorption equilibrium data were in good agreement with Langmuir model. Based on the results obtained in this study, it can be concluded that Polyaniline coated saw dust produced from *Calotropis Gigantea* is an effective, economic and efficient adsorbent compared to other forms for the removal of acid violet 4BS dye from aqueous solutions.

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