The Asian Review of Civil Engineering
ISSN: 2249-6203 Vol.6 No.1, 2017, pp.21-37
© The Research Publication, www.trp.org.in
DOI: https://doi.org/10.51983/tarce-2017.6.1.2233

Adsorption Kinetic and Isotherm Studies of Azure-A on Various Activated Carbons Derived from Low Cost Agricultural Wastes

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Abstract - **The present study narrates the eminent role of agricultural wastes as adsorbents viz., Sorghum Vulgare Carbon (SVC), Zea Mays Carbon (ZMC), Sorghum Vulgare Varity Carbon (SVVC), Ceiba Peutandra Carbon (CPC), Projobis Juliflora Carbon (PJC) for the removal of Azure-A (AA) dye from waste water. Experimental parameters such an effect of initialconcentration, contact time, dose, pH and particle size have been analyzed. The experimental results are there analyzed using Freundlich, Langmuir, Temkin, Redlich–Peterson and Dubinin–Radushkevich isotherm models. Multiple kinetic equations (first order, pseudo first order and pseudo second order) were applied to the adsorption kinetics of AA on various activated carbons. Surface morphology of the adsorbents before and after adsorption is studied by Scanning Electron Microscopy (SEM-Edax). FT-IR analyses revealed the presence of functional groups of dye on the adsorbents. It is inferred from the experimental result that the activated carbons (SVC, ZMC, SVVC, CPC and PJC) from agricultural wastes can be applied as an adsorbent in the removal of AA dye from waste water.**

Keyword: **Azure-A, Low Cost Carbon, Kinetics, Isotherm, SEM-Edax, Adsorption**

I. INTRODUCTION

Dye is a chemical substance which contains chromophore and auxochrome. The colour of the dye is due to presence of chromophore and its fixing properly is due to presence of auxochromes. The auxochromes are colour enhancing groups and classified into acidic and basic auxochromes. The basic auxochromes are amine, alkyl amine and di alkyl amine etc. Azure -A (AA) belongs to thiazine class which is the most commonly used dye for dying fabrics. It is used in paper, colouring and medical applications. Although it is not considered as a hazardous agent, it can cause some harmful effects. Acute exposure to dye causes vomiting, jaundice and increased heart rate. Hence it is an urgent need to remove dye. Methylene blue also produces same hazardous effect as that of AzureA (AA) and differs in structure by one amine group. Synthetic dye is difficult to biodegrade due to their complex aromatic structures, which provide them physco-chemical, thermal and optical stability [1]. Some dyes have been reported to cause allergy, irritation, cancer and even mutation in humans [2].

Water and waste water treatment is an emergent need to provide sustainable environment to humans and aquatic life. Recently different methods have been employed to purify water. Methods like electro dialysis [3], Reverse osmosis [4,5], ion exchange [6-18], oxidation reduction [19-21], solvent extraction [22], coagulation techniques [23-27] Ultra filtration [28] and adsorption [29-31] are used in water and waste water treatment. Activated carbon is the most effective adsorbent widely employed to treat waste water containing different types of dyes [32].

A wide variety of activated carbons have been prepared from agricultural wastes, Plentiful agricultural and wood by-products give an inexpensive and renewable additional source of adsorbents. Some of the adsorbents developed from agricultural wastes were banana pith [33], groundnut shell [34], Poplar Wood [35], neem leaves [36], mango seed shell [37], mosambi peel [38], apricot stone [39], mango leaf powder [40], palm kernel shell [41], beet pulp [42], rice husk [43], date stones [44], Atti leaf [45], wood apple outer shell [46], sugar cane stalks [47], Thespesia populanea pods [48], Azadirachta indica bank [49], grounded rice hull [50], palm flower [51], Terminalia Catappa Linn [52], nilgiri (eucalyptus globulus) leaves [53], Phaseolus trilobus, Leucena leucocephala and casuarina [54], Miswak leaves [55], Cocoa (Theobroma cacao) shell [56], bamboo [57], comcob [58], shells of bittim [59], coconut husk [60], oil palm shell [61], palm ash [62], patherium [63], wheat bran [64], coconut tree flower and jute fibre [65], cereal chaff [66], thevetia peruviana [67], seeds of martynia annua L and Xanthiyam strumarium plant [68], fruits of mimusops elengi [73], efukwa shells, marula fruit stones, jackalberry seeds, combe seeds and eembu seeds [74], cashew nut shell [75], Tapioca peel [76], punica grantum (pomegranate rind) [77], Polygonum orientale linn [78], jatroph husk [79], plum kernel and jacaranda [80], peanut shells [81], locust bean tree bark [82], husk of bhagar seeds [83], sunflower seed hull [84], melon seed shell [85], areca nut pod [86], yam peels [87], flamboyant pod back, milk bush kernel shell [88], Diospyrous melanoxylon leaf waste [89], red seaweed Laurencia papillosa [90], Bidi [91], Achyranthes aspera linn [92], jack fruit seed [93], cotton plant wastes [94], barley straw [95], oak sawdust [96], bottle ground [97], syzygium cumini seed [98], amla seed [99], coconut oil cake [100], caussia aunculata bark and emblica officinalis bark [101] etc.

This research is an attempt to remove hazardous dye Azure -A by using SVC, ZMC, SVVC, CPC and PJC as adsorbents.
The aim of this chapter is as follows:

1. To study the effect of various process parameters on the extent of removal of AA.
2. To optimize the process parameters.
3. To apply various adsorption isotherms to the adsorption data.
4. To study kinetic and dynamics of adsorption.

The adsorption experiments were carried out at different experimental conditions (Table 2) and the results obtained are discussed.

II. ADSORBENTS

A. Preparation of Activated Carbon

The collected plant material was washed and air dried two or weeks. The preparation of carbon material was made according to the literature method [102].scheme 3.1.represents the illusrations of the IPACs preparation and activation. The raw material were locally collected, cut in to the small species, washed with water, dried and carbonized at the temperature range of 300-800^{o}C, in muffle furnace in the absence of air. During carbonization, volatile products were removed.After the carbonization the carbons were collected and for activation by 4N H_2SO_4 at 80^{o}C for 60min. Then, ACs were thoroughly washed with double distilled water until the washings were free from acid and others ions (tested with Erichrome black-T indicator).after the activation adsorbent materials were then subjected to thermal activation by heating them at 120^{o}C for 2h in an air-oven and cooled, stored in separate brown bottles. The activated carbon materials such as Sorghum Vulgare Carbon (SVC), Zea Mays Carbon (ZMC), Sorghum Vulgare Varity Carbon (SVVC), Ceiba Peutandra Carbon (CPC), Projobis Juliflora Carbon (PJC) were then sieved into different discrete particles size in a machnicalsiever. The IPACs were sieved into different particle size (90-250microns) collected and stored separately. Batch Adsorption Experiments

1. Experiments for removal of AA-dye

To study the effect of experimental parameters like initial concentration, contact time, adsorbent dosage and pH for the removal of dyes. Adsorption experiments were carried out at room temperature (30 +10C) under batch mode [103]. The 25mL of 10 mg/L of AA solution with 100mg of particle size 90 to 250μ were shaken on Kemi shaker (model RS-12 plus, rpm 250) for 5, 10, 20, 40, 60, 80, 100, 120, 140 and 160 minutes in different flasks of 100ml capacity at solution pH 5. The solutions were withdrawn at different time intervals and the adsorbent was removed from the solution by centrifugation using centrifuge machine (Kemi 1ml) [104]. The absorbance of the supernatant solution predicted to determine the remaining dye concentration and measured before and after adsorption process by single beam spectrophotometer (Systronics Visiscan 167).The adsorption efficiency qe (mg/g) at various times was amount calculated using following equation-1.

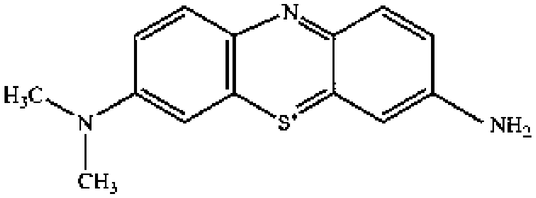
$$q_e = (Ci - Ce)\, V / W \qquad (1)$$

Where, Ci is the initial AA concentration (mg/L), Ce is the concentration (mg/L) of AA solutions at given time t, V is the volume (L) of the MG solution and W is the weight (g) of low cost carbon. The percentage removal of AA from solution was estimated using the following equation.2

$$\text{Percentage removal} = (Ci - Ce) / Ci \times 100 \qquad (2)$$

Where, Ci and Ce are initial and final absorbance of AA solutions before and after adsorption. The consequences of different parameters such as effect of pH, adsorbent dose and agitation time were studied. The obtained kinetic data were applied to various kinetics models: pseudo –first-order, pseudo-second-order, intraparticle, Elovich, Natarajan-Khalaf, Bhattacharya and Venkobachar.

TABLE I PHYSICOCHEMICAL CHARACTERISTICS OF USED DYE

Name	Molecular structure	Nature	M_w (g/mol)	λmax (nm)
AZURE-A DYE (N,N-Dimethylthionine)		Cationic dye	291.797	625-634

2. *Characterization of Spectra (SEM-Edax images of ACs)*

The textural / morphological characteristics of the surface of the adsorbents are studied by Scanning Electron Microscope (SEM) [105-107]. The scanning electron micrographs (SEMs) of the AC samples Edax studies and after SEM adsorption of dyes are recorded. The typical SEM photographs of AC samples, Edax studies and after SEM adsorption of dyes are shown in Fig 4.5-4.10.The SEM photographs of AC samples clearly provide the information regarding the surface texture and porosity of the samples. The SEM photographs also show that the particles can be roughly approximated as spheres or globules, if the roughness factor is included to account for the irregularities. At higher magnification (viz., 1 × 3000) the globules are distinctly visible and they appear to be quite uniform with internal porous structures or holes.

The SEM photographs indicate the presence of holes or internal pores on the particles of the ACs. The size of the internal pores of ACs is roughly of the order of 15-30 microns. Thus SEM photographs depict the porosity nature of the carbonaceous materials and the presence of grains in it. The adsorbed dye molecules are either engulfed or surrounded by the porous adsorbent particles.The color of ACs is found to be black and blackish-grey and when viewed under powerful microscope, the presence of the spherical particles is also noted. The results of the SEM studies indicate that the dye molecules are adsorbed on the surface of the ACs, and Edax studied was after with dye various elements in Fig.1-5 which are indigenously prepared from agricultural wastes/by products.

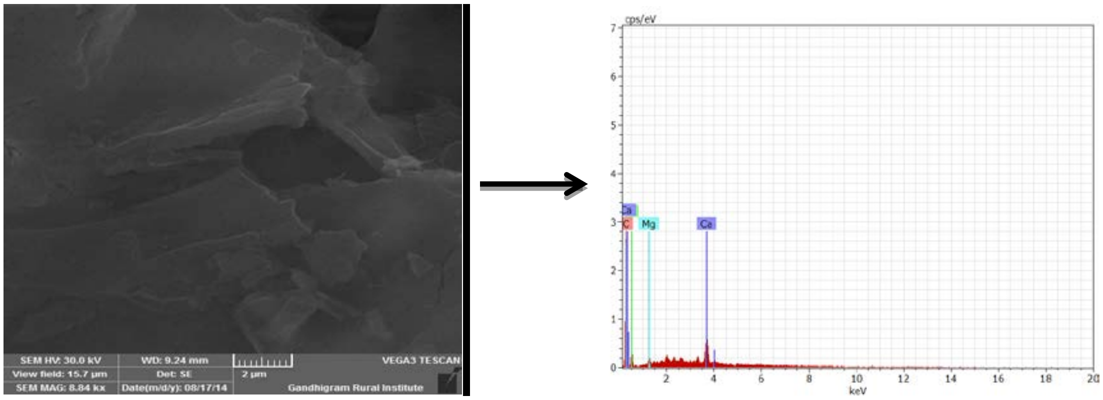


Fig.1 After SEM SVC and Edax

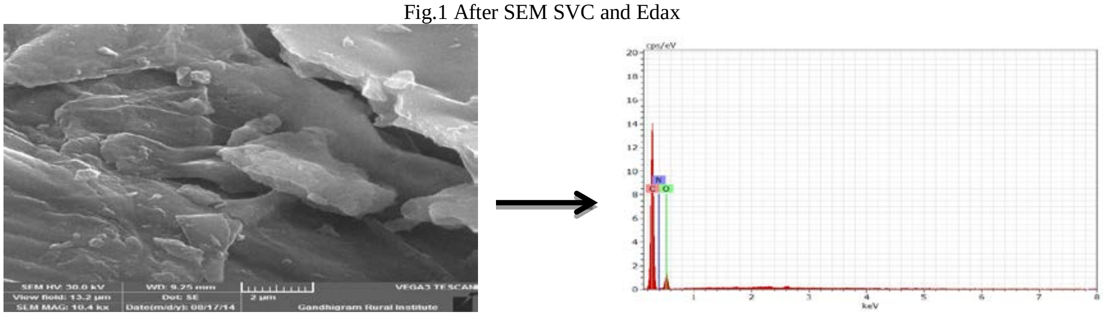


Fig.2 After SEM ZMC and Edax

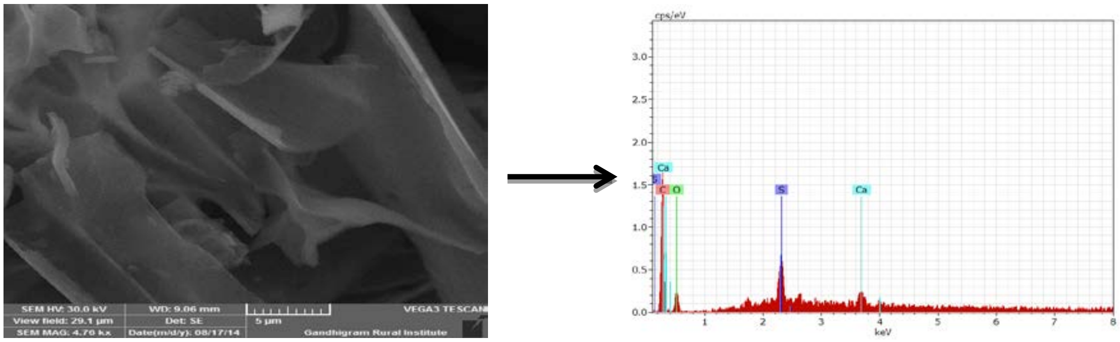


Fig.3 After SEM SVVC and Edax

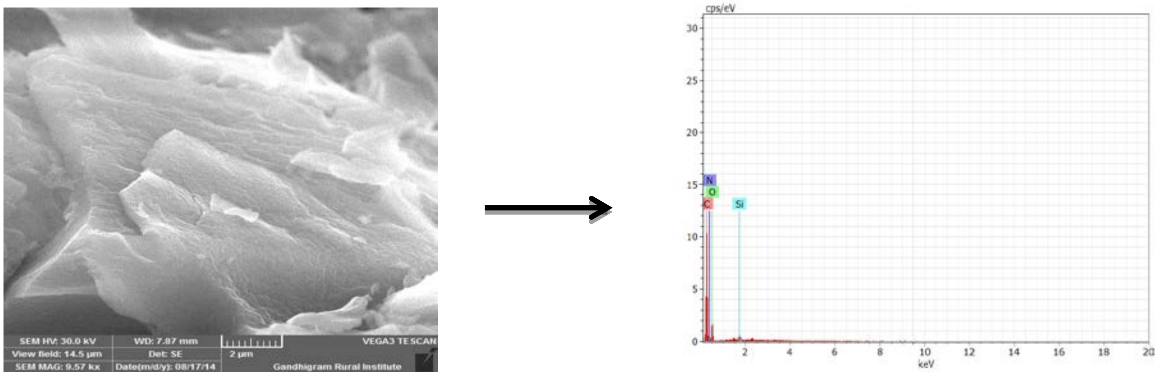


Fig.4 After SEM CPC and Edax

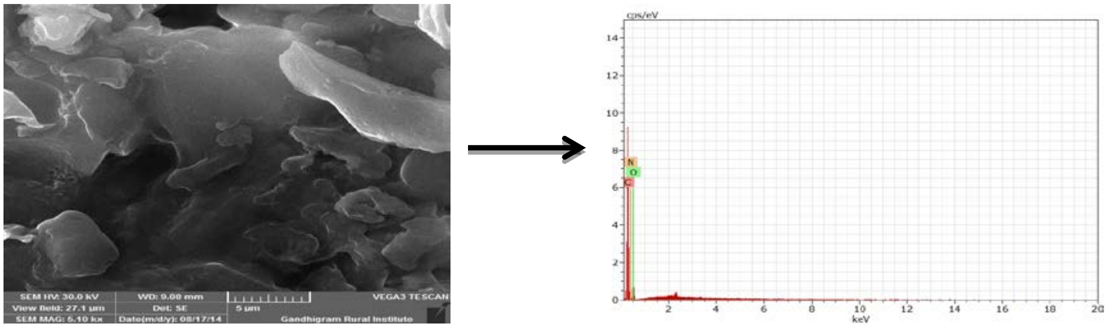


Fig.5After SEM PJC and Edax

It is concluded that these ACs could be employed adsorbent materials for the removal of dyes by adsorption from water and wastewater
.

3. FT-IR Studies

The Fourier Transform Infra-Red (FT-IR) spectra of AA loaded SVC and unloaded SVC are shown in Fig.6. The peak of unloaded SVC at 752.2 may be due to N-H bending. The highest peak at 1122.5 may be due to C=S stretching and peak at 1672.2 could be due to C=N stretching. The FT-IR spectra of AA loaded SVC indicate that there is a slight shift in the frequency of peaks at 754.1, 1120.6, and 1670.2 which may be due to adsorption of AA on the surface of SVC. The functional groups present on the surface of SVC are responsible for adsorption of AA (Table 2)

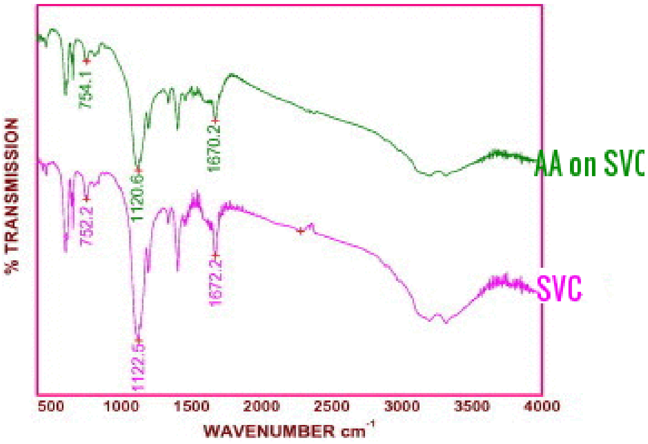


Fig.6 FT-IR Loaded with Dye AA on SVC and Free SVC

TABLE II EFFECT OF EXPERIMENTAL PARAMETERS ON THE EXTENT OF REMOVAL OF AZURE -A (AA) BY ACS

Experimental Parameters	**Adsorbents**					
		SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
Concentration (ppm)	ppm	52-66	52-66	52-66	52-66	52-66
	% R	98.9-97.9	92.8-87.5	92.4-86.8	91.2-84.4	87.3-77.8
Contact time (min)		5-60	5-60	5-60	5-60	5-60
	% R	98.7-85.0	91-94.6	88-92.2	84-88.6	74-90.3
Dosel (hL^{-1})		0.4-1.6	0.4-1.6	0.4-1.6	0.4-1.6	0.4-1.6
	% R	97.4-99.8	92.6-94.8	88.2-94	86.6-92.2	82.6-90.6
Initial pH		2-11	2-11	2-11	2-11	2-11
	% R	99.1-99.8	74.1-97.5	69.2-98.4	69-97.4	50-92.3
Particle size		---	90-250	90-250	90-250	90-250
	% R	---	94.1-88.3	92.4-89.4	92.2-81.2	88.3-75.3
Temperature		30-60	30-60	30-60	30-60	30-60
	% R	97.9-99.2	92.8-98.7	92.2-98.2	91.2-97.9	87.3-97.1

III. EFFECT OF INITIAL CONCENTRATION

The effect of initial concentration of the extent of removal of dye Azure-A (in terms of percentage removal and amount adsorbed (q) on various adsorbents was studied. The percentage removal is found to decrease exponentially, while the amount of dye adsorbed increases exponentially with the increase in initial concentration of Azure- A (AA) Fig.7. This may be due to lack of available active sites required for the higher initial concentration of AA. At lower concentrations substantial amount of AA got adsorbed leaving behind more number of active sites are available. Similar results have been reported in literature on the extent of removal of dyes [108, 109], metal ions [110] and carboxylic acids [111, 112].

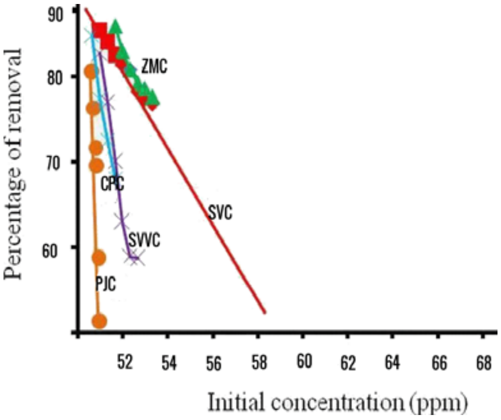


Fig.7 Effect of Initial Concentration

A. *Adsorption Isotherms*

The adsorption isotherms explain the distribution of adsorption molecules between liquid phase and solid phase at an equilibrium state. The surface model that can be used for design purpose [113] is evaluated by fitting isotherm data to different isotherm models. Adsorption isotherm is critical in optimizing the use of adsorbents and describes the interaction of solutes with adsorbents. At low concentrations, the equilibrium adsorption isotherms of Azure-A on the prepared low activated carbon show a sleep increase which indicated the high affinity towards the solute. The linearized forms of Freundlich and Langmuir isotherms [114] are used to analyze the adsorption data. Those data are given in Table 1.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [115]. An isotherm is appropriate for a highly heterogeneous surface. This application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorptional centre of the adsorbent.

Freundlich isotherm: log qe = log K+1 (1/n) log Ce (3.1)

The constants K and 1/n is calculated from the plot of log q_e versus log C_e Fig 1.2. According to Hall [116], the mathematical calculations show that the value of 1/n lower than unity present that Azure-A was beneficial adsorption, adsorbed by the adsorbents such as SVC, ZMC, SVVC, CPC and PJC. Many adsorption processes have been successfully explained by Langmuir adsorption isotherm and it has been used here to describe the sorption of dye onto carbon. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogenous sites within the adsorption takes place.

Langmuir isotherm: $(C_e / q_e) = (1 / Q_o b) + (C_e / Q_1)$ (3.2)

TABLE III RESULTS OF ANALYSIS ON TESTING THE APPLICABILITY OF ADSORPTION ISOTHERM FOR THE REMOVAL OF AZURE -A DYE BY ADSORPTION ON SVC, ZMC, SVVC, CPC AND PJC.

Isotherm	**Adsorbents**					
	Parameters	**SVC**	**ZMC**	**SVVC**	**CPC**	**PJC**
Freundlich	Slope(1/n)	0.730	0.278	0.437	0.262	0.261
	Intercpt(Icgk)	0.371	0.022	0.637	0.741	0.676
	n-Value	0.999	0.901	0.981	0.964	0.971
Langmuir	Slope (1/Qα)	0.001	0.008	0.010	0.016	0.021
	Intercpt(1/Qα/α)	0.006	0.045	0.033	0.063	0.054
	n-Value	0.997	0.986	0.984	0.982	0.988
	Qα(mgg-^{1})	834.0	114.2	106.8	92.8	53.1
	b(gL^{-1})	0.183	0.196	0.277	0.266	0.393
	R1=1/(1+Coα)	0.013	0.092	0.056	0.069	0.079
Temkin	A(Lg^{-1})	1.505	1.868	3.600	5.850	5.715
	B	197.9	25.5	21.6	10.3	8.9
	n-Value	0.996	0.986	0.957	0.948	0.970
Redlich-Peterson	K_R	153.90	22.47	39.57	15.74	18.24
	αR	0.487	0.414	0.466	0.360	0.528
	β	0.891	0.872	0.722	0.759	0.639
	n-Value	0.999	0.990	0.996	0.969	0.953
Dubinin-R	Xm(mgg^{-1})	528.00	62.15	75.88	46.06	31.05
	E(kJmcl^{-1})	5.60	10.38	9.69	9.04	15.54
	K(jmcl^{2} KJ^{2})10^{-7}	-1.6	-4.6	-5.3	-6.1	-2.1
	n-Value	0.967	0.924	0.842	0.849	0.838

Langmuir parameters have been obtained from the linear correlation between the values of (Ce / Qe) and Ce Fig.3. Based on the correlation coefficient (r), adsorption isotherm with SVC, ZMC, SVVC, CPC and PJC can be better described by Langmuir equation. The applicability of the Langmuir isotherm suggests the mono-layer coverage of the Azure-A dye on the surface of the carbons. The mono-layer adsorption capacities (Qe) of the adsorbents are found to be of the order given below:

SVC < ZMC < SVVC < CPC < PJC

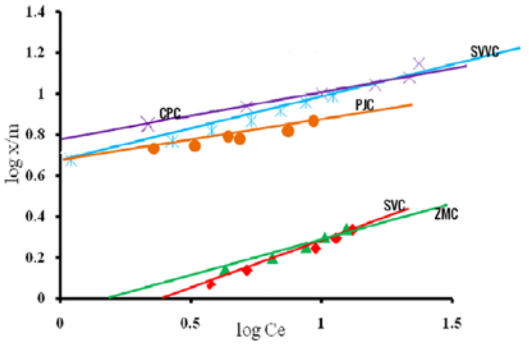


Fig.8 Freundlich Isotherm for the removal of AA on ACs

Table 3 Results of correlation analysis on testing the applicability of adsorption isotherm for the removal of Azure-A dye by adsorption on SVC, ZMC, SVVC, CPC and PJC. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation [110]:

$$R_L = [1/(1+bC_1)] \quad (3.3)$$

Here Ci = optimum initial concentration of AA (mgL^{-1})
b = Langmuir Constant (Lmg^{-1})

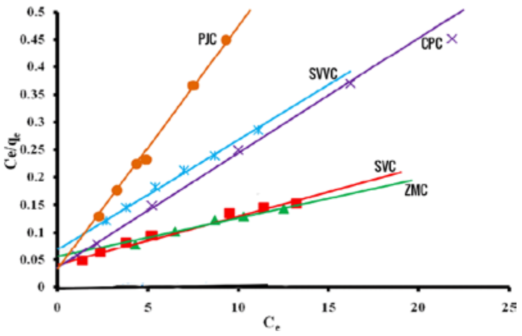


Fig.9 Langmuir Isotherm for the removal of AA on ACs

The values of separation factor, R_L indicate the nature of the adsorption process are given here,

R_L Values	Nature of the Adsorption Process
$R_L > 1$	Unfavorable
$R_L=1$	Linear
$0<R_L<1$	Favorable
R1=0	Irreversible

The value of R_L (Table 1) calculated from the adsorption isotherms is the range of zero to one (0.013-0.092), which indicates that the adsorption process is favorable for all these adsorbents. Temkin isotherm contains a factor that explicit takes in account according species-adsorbate interactions. This isotherm assumes that

1. Adsorption is characterized by uniform distribution of binding energies on some maximum binding energy [117].
2. The heat of adsorption of all the molecules in the dye increases intensity with coverage due to adsorbate – adsorbate interactions

$$Q_e = B \text{ In } A + B \text{ In } C_e \qquad (3.4)$$

The plot of qe versus Ce enables to determine the constants A and B Fig 9. Constant B is associated to the heat of adsorption and A is the equilibrium binding constant corresponding to the concentrated binding energy. The values of the parameter appeared in Table 3.The Redlich-Peterson isotherm (R-P) is a combination of features of both Langmuir and Freundlich isotherms. It can be used to describe adsorption of both homogeneous and heterogeneous surfaces [118]. The linearizer form of R-P isotherm is to be given as [119]:

$$\log [(K_R C_e / qe) -1] = \beta \log C_e + \log K_R \quad (3.5)$$

By plotting the values of log [(K_R C_e / qe)-1] against log C_e the values of β log C_e can be determined from the intercept log (αR) and the slope αβ respectively Fig 10.

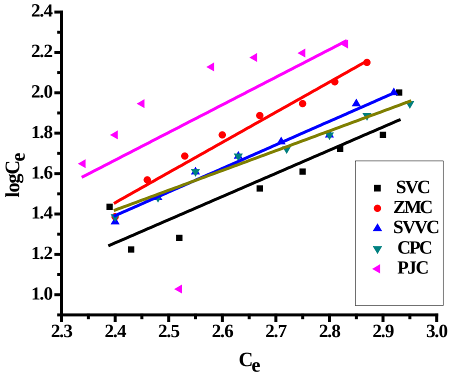


Fig.10 Temkin Isotherm for the removal of AA on ACs.

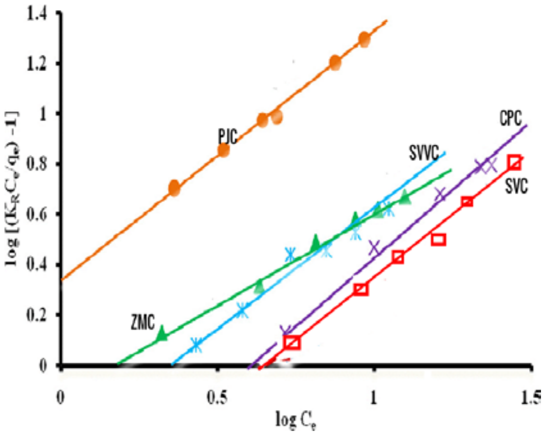


Fig.11 Redlich- Peterson Isotherm for the removal of AA on ACs.

Many researches have applied the Dubinin-Radushkevich isotherm for the adsorption of metal ions and dyes from aqueous solution. The magnitude of E is useful for approximating the mechanism of the adsorption reaction. In the case of E < 8 kjmol-^{1}, physical forces may affect the adsorption. In the case of E < 16 kjmol-^{1}, adsorption may be dominated by particle diffusion [120]. From the experimental values (Table 3) it is confirmed that these processes are carried out through particle diffusion.

$$\text{In } q = \text{In } X'_m - K'_{\epsilon}{}^2 \qquad (3.6)$$

The D-R plots (Inq against $_{\epsilon}{}^2$), give the parameters X'_m and K' from the values of intercept and slope (Fig 11). The mean energy of adsorption (E, in kjmol^{-1}), can be calculated from the K' value using the following equation:

$$E = (-2 K')^{-0.5} \qquad (3.7)$$

IV. EFFECT OF CONTACT TIME

The effect of contact time on the amount of dye adsorbed was observed at the optimum initial concentration of dye. The extent of removal of Azure-A by these adsorbents is found to increase exponentially and reach a maximum value with increase in contact time Fig.13 The relative increase in the extent of removal of dye after 30 min., of contact time is not significant and hence it is fixed as the optimum contact time. The relevant data are given in Table 1.3. Similar results have been reported in literature for the removal of Gentian Violet dye, metal ions and carboxylic acids [121].

A. Kinetics of Adsorption

The Kinetics and dynamics of Adsorption of Azure -A (AA) on various adsorbents have been studied by applying the various kinetic equations [122]:

First Order Equation:

$$(1/ q_t) = (k/ q_{max}) (1/t) + (1/q_{max}) \qquad (4.1)$$

Natarajan and Khalaf Equation:

$$\text{Log} (C_i / C_t) = (K/ 2.303)\, t \qquad (4.2)$$

Bhattacharya and Venkobachar Equation:

$$\text{Log} [1- U(t)] = - (k_{ad} / 2.303)\, t \qquad (4.3)$$

Pseudo First Order Model:

$$\text{Log} (q_e-q_t) = \log\ q_e - (k_{ad} / 2.303)\, t \qquad (4.4)$$

Pseudo Second Order Model:

$$t / q_t = 1 /k_2\, q_e^2 + t / q_e \qquad (4.5)$$

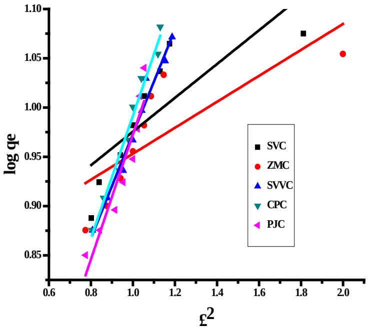


Fig.12 Dubinin-Radushkevich Isotherm for the removal of ACs

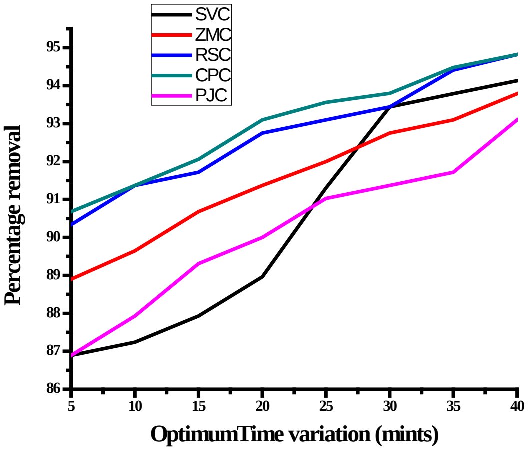


Fig.13 Effect of Contact Time for the removal of AA on ACs

Ci and C_t = Concentration of AA at time zero and time t respectively (mgL^{-1})

q_e and q_t = amount of AA adsorbed at equilibrium time and time t respectively (mgg^{-1})

U (t) = $[(C_i - C_t) / C_i - C_e)]$

C_e = equilibrium AA concentration (mgL^{-1})

K = first order adsorption rate constant (min^{-1})

TABLE IV KINETICS AND DYNAMICS OF ADSORPTION OF AZURE A DYE ON SVC, ZMC, SVVC, CPC AND PJC

Kinetic Equation	**Adsorbents**					
	Parameters	**SVC**	**ZMC**	**SVVC**	**CPC**	**PJC**
First Order	K min^{-1}	0.137	0.177	0.237	0.561	1.145
	r-value	0.850	0.818	0.951	0.778	0.806
Natarajan and Khala	K min^{-1}	0.294	0.155	0.140	0.116	0.096
	r-value	0.973	0.996	0.944	0.916	0.963
Bhattacharya and Venkobachar	K min^{-1}	0.362	0.238	0.247	0.168	0.145
	r-value	0.992	0.995	0.981	0.903	0.903
Pseudo First Order	K min^{-1}	0.362	0.238	0.247	0.198	0.145
	r-value	0.897	0.995	0.981	0.932	0.903
Pseudo Second Order	K min^{-1}	24.55	3.413	2.774	2.492	1.452
	r-value	0.999	0.999	0.999	0.999	0.998
Intra particle diffusion	K_p	0.918	0.575	0.441	0.387	0.350
	Intercept	394.20	53.60	43.51	36.76	24.00
	r-value	0.987	0.994	0.968	0.944	0.968

The values of (i) 1/qt, (ii) log (Ci/Ct), (iii) log [1-U (t)], (iv) log (qe-qt) and (v) t/qt were linearly correlated with time (t). The values of first order rate constant and correlation co-efficient(r-values) are given Table 4 (Fig.14-Fig.18). All the linear correlations were to be statistically significant, indicating the applicability of these kinetic

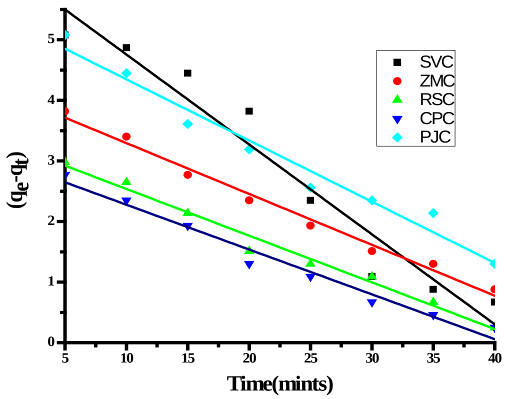


Fig.14 First Order Kinetic Plot for the removal of AA on ACs

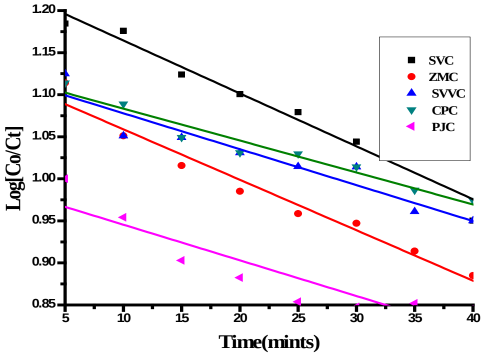


Fig.15 Natarajan and Khala Plot for the removal of AA on ACs

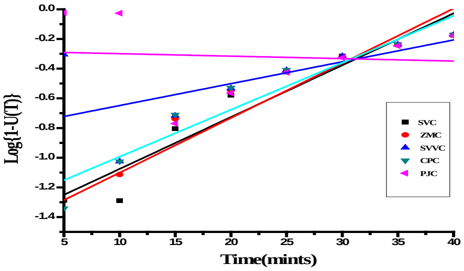


Fig.16 Bhattacharya and Venkobachar Plot for the removal of AA on ACs

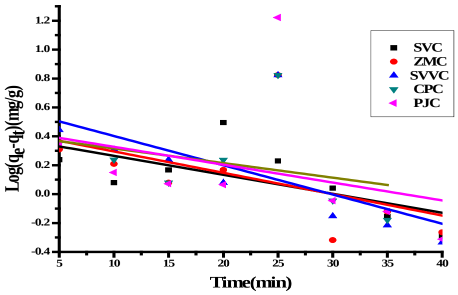


Fig.17 Pseudo First Order Plot for the removal of AA on ACs

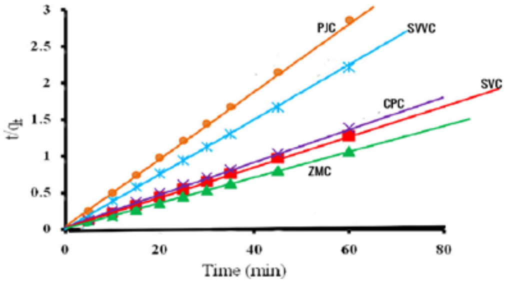


Fig.18 Pseudo Second Order Plot for the removal of AA on ACs

Equations and the pseudo second order nature of the adsorption process of Azure A on these low cost adsorbents. The results of the kinetic studies are presented in Table 4. The straight lines for all the initial concentrations with extremely high correlation coefficients for pseudo second order model compared to those for the entire first order kinetics model for the adsorption of Azure- A dye onto ACs strongly suggest that all the adsorption systems are of pseudo second order model. Based on the assumption the rate limiting step may be chemical adsorption of chemisorption involving valance forces through sharing or exchange of electrons between the active sites of carbons and polar dye ions. The calculated values Qe found from pseudo first order kinetic model gives less reasonable values for all the adsorbents,ACs tan those from the pseudo second order kinetic model. For all the adsorbents, Qe calculated agreed well with experimental Qe in the pseudo second order kinetics.

It is inferred that each dye adsorption system using ACs follows the second order kinetics which provides a better correlation data. In order to compare the validity of each model more efficiently a normalized standard deviation Δq(%) is calculated using the following equation:

$$\Delta q(\%)=100\times\{[(q_t^{exp}-q_t^{cal})\;/\;q_t^{exp}]2)\;/\;(n-1)\}^{1/2} \qquad (4.6)$$

Where the superscripts, exp and cal are the experimental and calculated values of qt viz., the amount adsorbed at different time t and n is the number the Δq(%) values are given in Table 4. Based on the low values of Δq(%), it is concluded that the adsorption of Azure-A can be best described by the pseudo second order model.

B. Intra - Particle Diffusion Model

Besides adsorption at the outer surface of the adsorbent there is also possibility of intra-particle diffusion of dyes from the bulk of the solution to the solid phase through intra particle diffusion which is frequently the rate controlling step in many adsorption processes. The intra particle diffusion process in the present adsorption system is also tested by applying the intra-particle diffusion model [123].

$$q_t = K_p t^{1/2} + C \qquad (4.7)$$

Where qt = Adsorbent of AA, adsorbent at time t (mgg^{-1}), C = Intercept, K_p = Intra Particle Diffusion rate constant (mgg^{-1} min $^{1/2}$). The values of qt were create to be linearly associated with values of $t^{1/2}$. The K_p were to be calculated by using correlation analysis.

TABLE V COMPARISON OF CAL AND EXP VALUES OF AZURE -A WITH ACS

Kinetic Equation	**Adsorbents**					
	Parameters	**SVC**	**ZMC**	**SVVC**	**CPC**	**PJC**
Pseudo First Order	Exp (mgg^{-1})	56.3	46.3	43.2	27.1	21.0
	Cal (mgg^{-1})	2.7	2.7	12.6	13.3	28.5
	R^2 value	0.991	0.962	0.870	0.815	0.823
	Δq(%)	99.16	99.19	99.52	98.96	98.30
Pseudo Second Order	Exp (mgg^{-1})	56.3	46.3	43.2	27.1	21.0
	Cal (mgg^{-1})	56.9	46.1	43.2	27.1	21.0
	R^2 value	0.999	0.999	0.999	0.998	0.999
	Δq(%)	0.988	0.398	1.316	0.696	1.455

The values are found to be close to unity, indicating the application of this model. The presence of intra - particle diffusion process [124, 125]. The calculated values Cal (mgg^{-1}) for adsorbents for SVC (0.575) minimum for PJC (0.176). This result indicates that the intra particle diffusion process values CPC and shows in PJC. The intra particle diffusion plot is given in Fig.19 The values t intercept Table 6.given an idea about the boundary layer thickness i.e., the A value of C is greater is the contribution of surface adsorption in the rate limiting time.

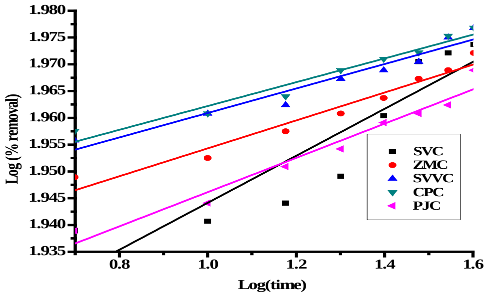


Fig.19 Intra – Particle Diffusion Plot For The Removal Of Aa On Acs

The intercept C value of adsorbents in SVC (53.60) and minimum in PJC (19.74) indicating that the boundary layer effect is maximum in SVC and minimum in PJC among the adsorbents other than PJC.

$$\text{Log (\% removal)} = C + m \log (\text{time}) \qquad (4.8)$$

Where C = Intercept and m = Slope.

TABLE VI STATISTICAL RESULTS OF INTRA-PARTICLE MODELS FOR THE ADSORPTION OF AA DYE ON ACS

Kinetic Model	**Adsorbents**					
	Parameters	**SVC**	**ZMC**	**SVVC**	**CPC**	**PJC**
Intra Particle Diffusion	K_p	0.575	0.441	0.397	0.350	0.178
	Correlation Coefficient (r)	0.994	0.968	0.944	0.976	0.974
	Intercept (c)	53.60	43.51	36.77	24.00	19.74
	Δq(%)	0.127	0.334	1.243	0.703	0.324
Log(% removal) vs log (time)	Slope	0.014	0.018	0.027	0.093	0.179
	Correlation Coefficient (r)	0.961	0.991	0.840	0.941	0.954
	Intercept (c)	1.946	1.932	1.895	1.789	1.645

The correlation of the values of log (% removal) and log (time) also resulted in linear relationship in (Fig.20) which indicates that the process of intra particle diffusion is leading place in these adsorption system Table 6. The values of slope indicates the presence of intra particle diffusion process as one of the rate limiting steps, besides many after processes controlling the rate of adsorption all of which may be operating simultaneously [126].

C. Effect of dose of adsorbent

The effect of different doses of adsorbent for the removal of Azure A by adsorption on various indigenously prepared ACs (Viz., SVC, ZMC, SVVC, CPC and PJC) at the optimum initial concentration (C_i) of dye, 30min of contact time and 90 microns particle size at solution pH itself [127] were studied at 30 ± 1^{0}C. The adsorption data for

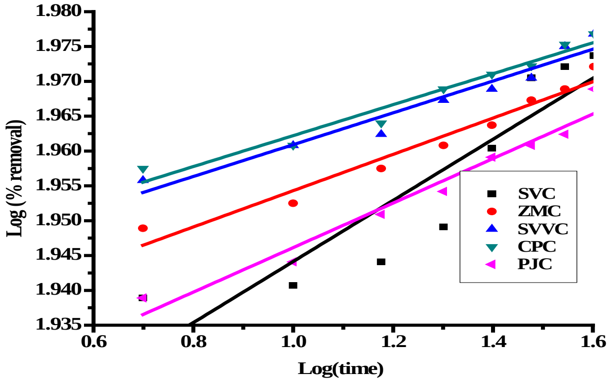


Fig.20 Log (%removal) Vs Log (Time) Plot for the removal of AA on ACs.

The removal of Azure -A by various indigenously prepared ACs presented Chapter-2.The experimental variation of the percentage removal of dye with dose of the adsorbent a represented in a Table 7.

TABLE VII EFFECT OF ADSORBENT ON THE EXTENT OF REMOVAL OF AA BY ACS AT 30^0 ± 10^C

Dose of Adsorbents gL^{-1}	**% Removal (Amount Adsorbent in mgg^{-1})**				
	SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
0.4	97.4(3.5)	92.7(2.7)	88.2(2.2)	86.17(2.17)	82.7(1.24)
0.6	98.3(3.7)	93.2(2.73)	91.4(2.26)	88.4(2.21)	84.7(1.27)
0.8	98.4(3.8)	93.5(2.80)	91.8(2.27)	90.8(2.27)	87(1.31)
1	98.5(3.9)	94.1(2.82)	92.2(2.31)	91.2(2.28)	87.7(1.32)
1.2	98.6(4.2)	94.2(2.83)	92.8(2.32)	91.4(2.29)	88.7(1.33)
1.4	98.7 (4.3)	94.5(2.85)	93.2(2.33)	91.8(2.29)	89.7(1.34)
1.6	98.8 (4.4)	94.83(2.9)	94(2.43)	92.2(2.31)	90.5(1.36)

Initial Concen = Optimum pH=7.2
Contact Time = 30 min Particle size = 90 microns

The values of percentage removal of dye by adsorption onto various ACs are time to increase experimentally with the increase in dose of the adsorbents and then dye of a higher increase of adsorbents ACs. The amount of dye unit mass of the adsorbent (AC) increases, the surface area proportionality increases (as the species size of AC remains almost constants, 90microns), which has resulted in an increases in the percentage of removal of dye, owing to greater availability of surface achieve in Fig.21.

The percentage removal of dye by adsorbents increases with increase in doses of adsorbents. This may be due to increase in the availability of surface active sites and also due to the increase in the effective surface area resulting from the configuration of the adsorbent, especially at higher adsorbent doses [128], [129]. These results are found to be in harmony with the available reports in literature on the study of the effects of dose of various adsorbents on the removal of dyes by adsorption [130], [131]. Similar trend on the effect of dose of adsorbent is also available in literature based on the studies on the removal of dyes [132-135], pesticides [136] other organic substances like phenol, toluene, xylene etc., [137-139] and metal ions [140, 141] by various adsorbents.

TABLE VIII RESULTS OF THE LINEAR REGRESSION ANALYSIS OF LOG AMOUNT ADSORBED WITH LOG DOSE FOR THE REMOVAL OF AA BY ADSORPTION ON ACS.

Parameters	**SVC**	**ZMC**	**SVVC**	**CPC**	**PJC**
Slope(n)	0.054	0.088	0.097	0.144	0.008
Correlation Coefficient (r)	0.934	0.964	0.936	0.989	0.980
Intercept (c)	0.340	0.184	0.161	0.171	0.187

The optimum does is fixed as $2gL^{-1}$ for various indigenously prepared ACs. The values of amount of dye adsorbed are found to vary exponentially with the fractional power term of the dose of adsorbent [142] according to the following model.

$qe = [dose]^{-n} + C$ (4.9)

$Log\ qe = -n \log [dose] + C$ (4.10)

Where,

qe = amount of dye adsorbed (in mgg-1) at equilibrium contact time

n = fractional value of the slope obtained from the plot of log qe versus log [dose]

C = intercept value and c´ and C are constants in equations 4.9 and 4.10 respectively.

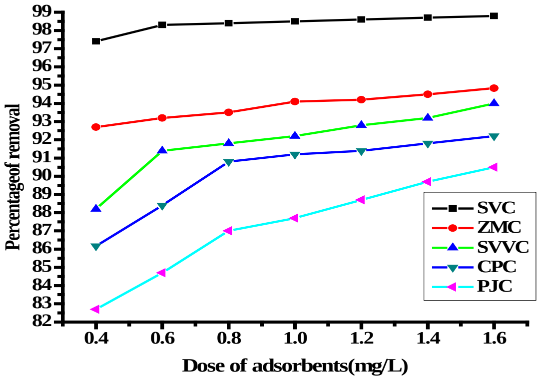


Fig.21 Effect of Dose for the removal of AA on Acs

D. Effect of Initial Ph

The effects of initial pH on adsorption process for dye Azure A (AA) on ACs were studied at different pH values range from 2-11. The experimental conditionals like optimum initial concentrations of dye AA, 30 mins of contact time dose of adsorbent $2gL^{-1}$ and 90 microns particle size were maintained. The outcomes are presented in Table 9.

TABLE IX EFFECT OF PH ON THE EXTENT OF REMOVAL OF AA BY ACS AT 30 ± 1^0C

Dye pH	**% Removal (Amount Adsorbent in mgg^{-1})**				
	SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
2	74.2(2.07)	69.2(1.73)	69(1.72)	50.0(0.75)	37.5(0.45)
3	76.6(2.16)	73.0(1.83)	72.2(1.81)	54.0(0.81)	41.6(0.50)
4	86.2(2.5)	87.8(2.19)	80.0(2.0)	69.0(1.04)	58.3(0.70)
5	88.8(2.59)	88.4(2.21)	86.2(2.06)	73.0(1.1)	62.0(0.75)
6	91.8(2.71)	89.2(2.23)	86.2(2.15)	79.3(1.19)	65.8(0.79)
7	92.5(2.73)	90.2(2.25)	89.8(2.24)	86.6(1.3)	73.7(0.88)
8	93.2(2.75)	90.8(2.26)	90.4(2.26)	88.3(1.32)	84.2(1.01)
9	93.5(2.76)	91.0(2.28)	90.8(2.27)	89.6(1.34)	85.4(1.02)
10	94.5(2.18)	91.6(2.29)	91.4(2.28)	91.3(1.37)	85.8(1.03)
11	97.5(2.91)	92.2(2.31)	92(2.3)	92.3(1.38)	87.1(1.04)

Initial Concen = Optimum Particle size = 90 microns
Case = 2 gL-1 Contact Time = 30 min

The change of pH decides the dye binding capacity of each sorbent. The pH value changes slightly after adsorption and a decrease in pH value is noted (ΔpH = pH final-pH initial). Dyes are complex aromatic organic compounds having different functional groups and unsaturated bonds on their structures. The surface of adsorbent may include many functional groups such as carbohydrates, amines, hydroxyl, carboxyl, sulphonic acid and their carbonaceous O2, OH groups [143], which may take part in binding mechanism. Therefore, the interaction between dye molecules and sorbent is basically a combined result of changes on dye molecules and the surface of sorbent.

At low pH, the surfaces of activated carbons may become positively changed the process of H^2 ions in solution. The electrostatic repulsion between AA and surface of adsorbents decreases the amount of AA adsorbed. At high pH, the surface of activated carbons may become negatively charged due to excess of OH ions in solution. Accordingly electrostatic attraction between cationic dye and anionic surfaces of activated carbons rises the amount of AA adsorbed. Thus pH affects the surface charge on the adsorbent and acidic or basic nature of dyes. Thus pH is noted to be highly favorable for the removal of AA by adsorbents. The maximum percentage removal of AA occurs at pH 10.11. Similar results have been reported from the literature study [144, 145]. The plot of percentage removal of dye AA against pH is shown in Fig 21.

E. Effect of Particle Size

The effect of particle size on adsorption process for Azure A dye on SVC, ZMC, SVVC, CPC and PJC carbons were studied by varying particle sizes. The experimental conditions like optimum initial concentration of dye AA, 30 mins of contact time, dose of sorbent $2gL^{-1}$ and initial pH are shown in Table 9. The adsorption capacity for dye increased with decrease in the particle size of adsorbents Fig 23.

TABLE X RESULTS OF THE LINEAR REGRESSION ANALYSIS OF PARTICLE SIZE VARIATION WITH % REMOVAL OF AA BY ADSORPTION ON ACS.

Parameters	**SVC**	**ZMC**	**SVVC**	**CPC**	**PJC**
Slope(n)	0.039	0.019	0.059	0.075	0.094
Correlation Coefficient (r)	0.932	0.978	0.909	0.945	0.945
Intercept (c)	97.71	94.08	95.17	93.30	91.63

For the particle size range from 90-212 µm, the amount of dye adsorbed linearly increases with the decrease in particle size of the adsorbent. The decrease in particle size sorbents to increase in surface area and increase the changes of adsorption at the outer surface of the ACs. In addition to this, there may be a possibility of intra-particle diffusion from the outer surface into the pores of the material. For larger particles, the diffusion resistance to mass transfer is greater. This may be due to different factors such as diffusional path length or mass transfer resistance, contact time and blockage section of the particle may not be utilized for adsorption. As a result the adsorption capacity of large particles may be low [146, 147].

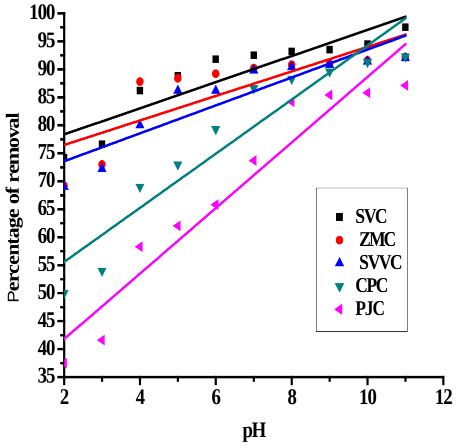


Fig.22 Effect of pH for the removal of AA on Acs

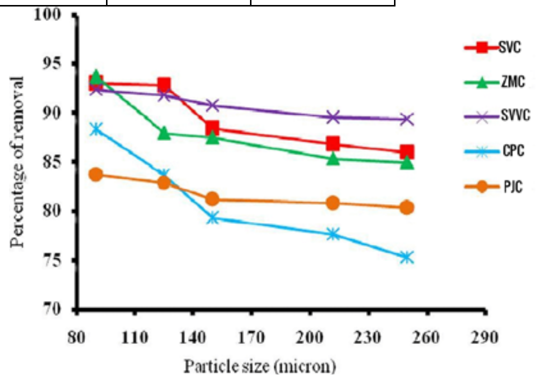


Fig.23 Effect of particle size for the removal of AA on Acs

F. Effect of Temperature

The effect of temperature on the adsorption of Azure -A dye by SVC, ZMC, SVVC, CPC and PJC carbons were studied at temperature 30^0C, 40^0C, 50^0C and 60^0C. The adsorption of Azure A dye increased with increase of temperature up to 60^0C indicating that a high temperature favors the dye removal by adsorption onto all these sorbents. The enhancement in adsorption with temperature may be attributed to increase in number of active surface sites available for adsorption on each adsorbent, increase in the porosity an in the total pore volumes 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.

The enhanced adsorption at high temperature may be the result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo interaction with active sites at the surface. It is clear that the sorption of Azure A on the six sorbents is an endothermic process and AA dye sorption may involve not only physical but also chemical sorption [148].

V. THERMODYNAMIC PARAMETERS

The thermodynamic parameters such as ΔH^0 and ΔS^0 could be obtained from the vaunt Hoff plots viz., the plots of log Keqm vs 1/T, respectively from the slope and intercept values. The ΔH^0 and ΔS^0 values (Calculated by least squares method) are reported in Table 1.10. The positive values of ΔH^0 indicate that the adsorption process is endothermic nature. The negative values of ΔG^0 indicate that the adsorption process (for removal of dyes by ACs) is spontaneous and favourable i.e., the adsorptive forces are quite strong enough to overcome the potential barrier between the adsorbate species in solid liquid interface. The positive values of ΔS^0 suggest that randomness or disorder increases at the solid liquid interface, during the adsorption process of dyes on ACs.

The thermodynamic parameters determined from the equilibrium studies indicate from the dye adsorption on ACs is favourable and spontaneous and the adsorption is mostly chemisorption with some extent of physisorption. The negative values of ΔG^0 indicate the feasibility and spontaneity of the adsorption process. The enhancement of adsorption at higher temperature may be due to the process in the diffusion rate of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the solution [149]. The positive value of ΔS^0 (8.56 to 22.50 Jmole-^{1}K-^{1}) suggests that randomness or disorder increases at the solid solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent.

TABLE XI THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF AA WITH ACS

Parameters	**Adsorbents**				
	SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
ΔH^0 KJmol^{-1}	-25.35	-17.74	-16.15	-14.80	-12.15
ΔG^0 KJmol^{-1}	17.86	14.45	13.24	12.10	11.95
ΔS^0 Jmole-^{1}K-^{1})	21.20	17.16	12.35	10.72	8.56

The positive values of ΔH^0 indicate that the adsorption process is endothermic value. The energy of physical adsorption, which is due to the vander waals forces is basically around 5-20 KJmol^{-1}, which could not efficiently peturb the bonding structure of the adsorbate, before and after the adsorption. The observed values of ΔH^0 (range 11.25- 18.85 KJmol^{-1}) lie within the range of vander waals interaction energy. At hence, it is concluded that ‘physisorption’ is also taking place in addition to adsorption. Strong bonding occurs without affecting the bonding structure of the sorbate (dye) molecules. Thermodynamic parameters indicate that the adsorption process is spontaneous, endothermic and physisorptive in nature.

A. Desorption

The Azure A dye loaded adsorbents are desorbed with DD water and eluents like HCl, HNO_3, H_2SO_4, CH_3COOH and NaOH. The values of percentage of desorption with DD water and eluents (0.5N) are reported in Table 12. Among these, nitric acid is found to be an effective eluent. The extent of desorption increases exponentially with the increase in concentration of HNO_3 and becomes constant. The optimum concentration of HNO_3 for effective desorption of Azure A from loaded adsorbents is fixed as 0.5N.

The adsorption capacity of regenerated adsorbents is checked for three cycles and found to be less compared to the original samples but it also suitable for removal of Azure A from dilute solutions. This will again definitely lower the cost of removal of effluent treatment process. SVC and ZMC could be used as low cost adsorbents as for the removal of dyes in general, Azure -A in particular.

TABLE XII EXTENT OF DESORPTION OF ADSORBED AA USING VARIOUS ELUENTS

Parameters	Adsorbents				
	SVC	ZMC	SVVC	CPC	PJC
DD water	71.1	68.4	65.6	60.2	58.9
HCl	76.9	75.1	73.8	67.8	65.4
HNO_3	87.8	86.2	84.3	75.2	73.4
H_2SO_4	78.9	77.9	75.2	68.8	66.2
CH_3COOH	74.9	74.8	71.3	63.9	60.4
NaOH	73	72.5	70.1	61.2	59.9

B. Relative adsorbents of Increasing Order

The increasing order of relative adsorption capacity of values adsorbents compared to that of SVC (Calculated from qe values) under optimum adsorbents condition is as given below:

PJC < CPC < SVVC < ZMC < SVC

Among the adsorbents other than SVC has the maximum adsorption capacity, whereas PJC has the maximum adsorption capacity. The relative adsorption capacity (in term of qe) values of various adsorbents for AA are shown in Table 12. Cost wise these low cost adsorbents, especially SVC and ZMC are may easily available in India (especially in Tamilnadu) as agriculture waste materials.

VI. CONCLUSION

Azure- A (AA) dye is strongly adsorbed on the surface of SVC and ZMC. The percentage removal of Azure A dye increases with decrease in the initial concentration of the dye, particle size of adsorbents and increases with decrease in the initial concentration of the dye, particle size of adsorbents and increases with decrease of the contact time, initial pH and dose of adsorbents.

Adsorption data are fitted with the Freundlich, Temkin, Langmuir, Peterson and Dubinin-Radushkevich adsorption isotherms. The experimental data are fitted with kinetic equations such as Natarajan and Khalf, Bhattacharya and Venkobachar, first order, pseudo first order and pseudo second order to study the kinetic and dynamics of adsorption of Azure A on adsorbents. The adsorption of Azure A dye onto SVC and ACs strongly suggest that all the adsorption systems are of pseudo second order model.

The results suggest that pore diffusion i.e. intra particle diffusion is more important. Adsorption performance is described by a mono-layer Langmuir category isotherm. The adsorption process is create to be first order with intra particle diffusion as one of the rate defining steps. The negative values of ΔG^0, positive values of ΔS^0 and positive values of ΔH^0 indicate that the adsorption process is spontaneous, randomness or disorder increases at the solid solution interface and endothermic in nature. The present study concludes that SVC, ZMC and SVVC could be employed at low cost adsorbents as for the removal of AA.

ACKNOWLEDGMENT

Authors would like to acknowledge the technical and instrumentation support of Madurai Kama ajar University of The Madura Arts and Sciences College and Laboratory’s experts. The authors thank Mr. MuthuramanPandi, The Principal,The Madura Arts and Sciences Tamilnadu, India. College, Madurai and The Board members of College Education, Madurai for carrying out this research work successfully

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