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Kinetic and Isotherm studies on the removal of acid dye (NG) from aqueous solutions by adsorption onto activated carbon low cost agricultural waste

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Abstract : In this research five low cost carbon adsorbents, namely, Sorghum Vulgare Carbon (SVC), Zea Mays Carbon (ZMC), Sorghum Vulgare Varity Carbon (SVVC), Ceiba Peutandra Carbon (CPC), Projobis Juliflora Carbon (PJC) were prepared for the adsorption of Nigrosinedye(NG). Adsorption was studied as a function of pH (2-12), adsorbent dose (0.2-1.6g), contact time (5-40mints), initial MG concentration (50-100mg/L); agitation seed (120-180rpm) and characterization of FT-IR, XRD, EDAX, and SEM. From the results obtained it was observed that with the increase in the pH value, the percentage NG removal increases from 48.62,52.33,38.74,46.68, and 55.03% to 94.48,95.15 , 95.45,94.5,and 94.84% for SVC,ZMC,SVVC,CPC, and PJC adsorbents, respectively. Additionally the percentage NG removal increased from 45.86, 43.12, 56.71, 47.78, and 39.81% for SVC, ZMC, SVVC, CPC, and PJC adsorbents ,respectively, by increasing, adsorbent dose from 0.2g to 1.6g.Hence optimize adsorbent dose for SVC, ZMC, SVVC, CPC, and PJC adsorbents 0.8,1.0,1.2,1.4, and 1.6g, respectively. The experimental data were analyzed by the Langmuir, Freundlich, Temkin, Redlich-Peterson,Dubinin- Radushkevich and BET-isotherm constants. Results showed that the maximum monolayer adsorption capacity of SVC, ZMC, SVVC, CPC, and PJC adsorbents for the adsorption of NG was 20.99, 21.64, 21.51, 21.58 and 20.9mg/g respectively. The kinetic data were fitted to the pseudo-first-order, pseudo-second-order, intraparticle diffusion models, Elovich, Natrajan and Khalaf, Bhattacharaya and Venkobachar models. Adsorbents tracked Langmuir adsorption isotherm models and pseudo-second-order kinetics. Kinetics parameters were evaluated to predict the nature of adsorption. In this paper indicate the endothermic and spontaneous nature of the adsorption process.

Keywords : Agricultural waste, lowcost carbon, Nigrosine dye, optimization, Batch adsorption, Kinetics.

1. Introduction

Nigrosine is the anionic azo dye. It is often used for dying textiles and leather. Generally, the acute toxicity of azo dyes is low and may cause skin and eye irritation, weakness and dizziness. The use of variety of dyes and chemicals in the dyeing processes causes considerable variation in the waste water characteristics like pH, colour and chemical oxygen demand (COD). It is an urgent need to treat the industrial effluent to remove the dyes from the effluent before discharging it into water. Different methods have been adopted to remove the dyes from solutions before discharging into the natural stream. Some of the methods used to remove dyes from waste water are reverse osmosis [1, 2]. Ultrafiltration [3], electro-Fenton process [4],photo catalytic decolourization [5] and adsorption [6]. Adsorption process is easy to operate, require less expensive and possess high efficiency. It is the most widely employed water and waste water treatment. Adsorption principle is successfully used in the removal ofdyes such as crystal violet, Rhoda mine B [7], Acid Violet [8], acid yellow RR [9], erythrocin B [10], methylene blue [11-12], acid blue [13], alizarin yellow [14] malachite green [15], methyl orange [16], orange G [17], reactive red [18], basic violet [19] etc. Activated carbon is the most effective adsorbent widely employed to tread waste water containing different types of dyes chemical and metal ions. The cost for the production the activated carbon is high because of chemical and physical treatments used in its synthesis, its low yields and high energy consumption. The researchers try to obtain new raw materials for the production of activated carbon and they keep in mind not only to lessen its cost of production, also to decrease environmental impact of agricultural and industrial wastes.

Recently the numbers of adsorbents prepared from agricultural wastes are tent to be increased. Some of them are peanut shells[20], locust bean tree bark[21],husk ofBhagar seeds[22], sunflower seed hull[23],melon seed shell, areca nut pod, yarmpeels,flamboyant pod back, milk kernal shell, Diospyrousmelanoxyl on leaf waste, redseaweed Laurencia papillosa, Bidi, Achyranthes aspera linn, jackfruit seed, cotton plant wastes , Barely starw, Oak saw dust, bottlegourd, Syzygium cuminis eed, amla seed, coconut oil cake, Caussia auricultaa bark and Emblica officinalis bark etc.

Plentiful agricultural and wood-products give an inexpensive and renewable additional source of adsorbents. Some of the adsorbents developed from agricultural wastes were palm kernel shell,beet pulp, rice husk,date stones, as leaf,wood apple outer shell[24],sugar cane stalks[25] thespesiapapulnes pods [26], Azadirachta indica bark [27], grounded rice hull [28], palm flower [29], Terminate Catappa Linn [30], nilgiri(eucalyptus globulus) leaves [33], Phaseolus trilobus, leucensleucocepala and Casuarina[34],Miswak leaves[35],Cocoa(Theobroma cacao),Dhel[36],Bamboo[37],Corncob[38],Shells of bittim[39],Coconut husk[40],banana pith[41],groundnut shell[42],polar wood[43],neem leaves[44],mango seed shell[45], mosambi peel[46],apricot stone[47] and mango leaf powder[48]etc.

Many researched showed great interest on dye removed and prepared more numbers of adsorbents. Some of them are oil palm shell[49],palm ash[50],pathernium[51],wheat bran[52],coconut tree flower and jute fibre[53],cereal chaf[54], Thevetia penuviana[55],seeds of Martynia annua L and Xanthiyum strumarium plant[56],ground nut[57],mustard straw[58],teak tree bark[59],Euphorbia Tircali L wood[60],fruids of mimusopselengi[61],efuwa shells, marula fruits stones, jackalberry seeds, eembe seeds and embu seeds[62],cashewnut shell[63],Tapioca peel[64], Punci agranatum(Pomegranate rind)[65],Poly gonumorientale Linn[66],Jatropha husk[67],plum kernel and jacaranda[68]etc.This research is an attempt to remove hazardous dye Nigrosine dye (basic dye) by using Sorghum Vulgare Carbon (SVC), Zea Mays Carbon (ZMC), Sorghum Vulgare Varity Carbon (SVVC), Ceiba Peutandra Carbon (CPC) and Projobis Juliflora Carbon (PJC) as adsorbents. The aim of the chapter is as follows;To study the effect of various process parameters on the extent of removal of NG.

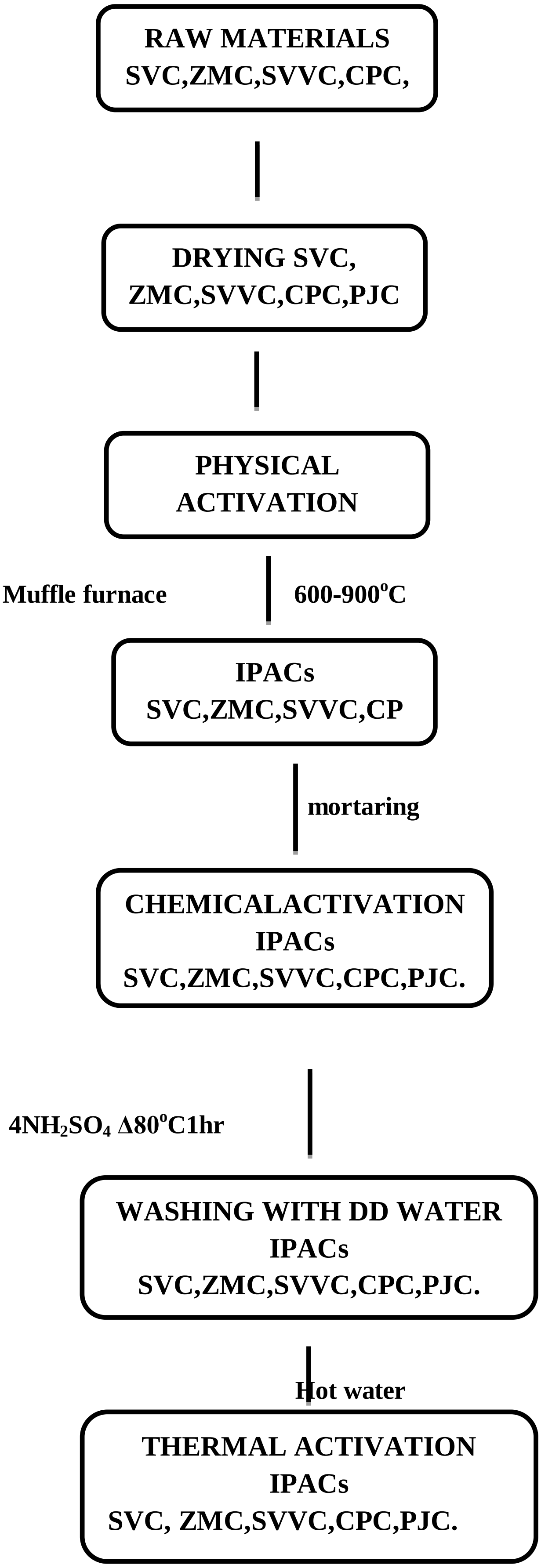
- To optimize the process parameters.
- To apply various adsorption isotherm to the adsorption data.
- To study kinetic and dynamics of adsorption.

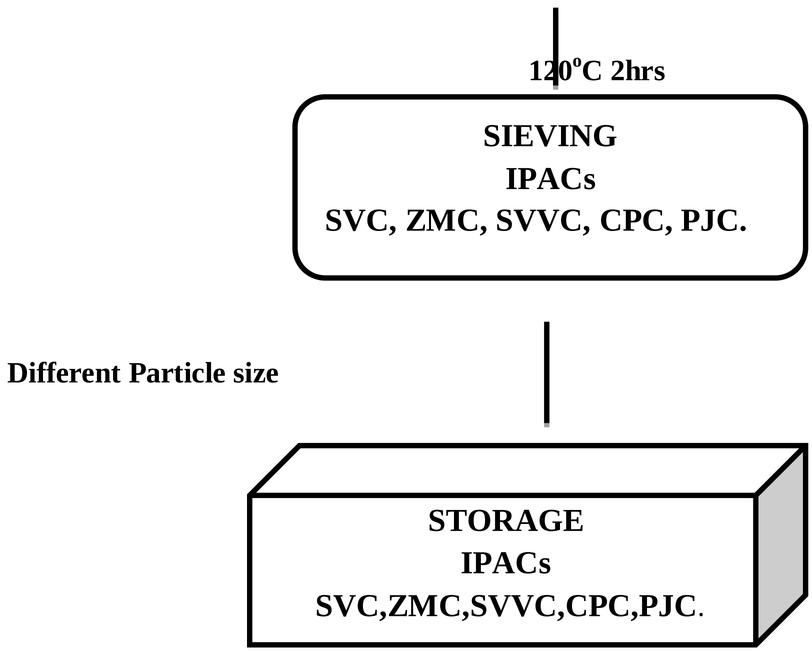
The adsorption experiments were carried out at different experimental conditions, and result obtained is discussed.

2. Experimental Procedure

2.1. Preparation of activated carbon.

The collected plants material was washed and air dried two or months. The preparation of carbon material was made according to the literature method [69].Scheme 2.1 the represents the illustrations of the IPACspreparation and activation. The raw materials were locally collected, cut in to small spices, washed with water dried and carbonized at the temperature range of 300-800^{o}C in a 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 at80^{o} C for 60 min. then, these ACs were thoroughly washed with double distilled water until washings were free from acids and other ions (tested with Eriochrome Black –T indicator). After the activation the adsorbents materials were then subjected to thermal activation by heating them at 120°C for 2h in on air-oven and cooled, stored in separates brown bottles. The activated carbon 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 particles size(90-250µ) collected and stored separately.





Scheme-2.1. Illustration of the preparation IPACs

2.2. Adsorbate

For adsorption studies NG (color index number: 50420) molecular formula $C_{22}H_{14}N_6Na_2O_9S_2$-; a commercial acid dye, purchased from Sigma-Aldrich was Experimental dye solution of different concentrations was prepared by reducing the stock solution with appropriate volume of double-distilled water. Nigrosine-WS (CI-50420, Acid black 2). In biology, nigrosine is used for negative staining of bacteria. as well as the capsule containing fungus, Cryptococcus neoformans. The shapes and sizes of the organisms are seen as colourfree outlines against the dark background. An advantage of using this method, rather than regular positive stains like methylene blue or carbolfuchsin, is that prior fixation by heat or alcohol is not needed, so the organisms are seen in more lifelike shapes. Furthermore, negative staining with nigrosine can reveal some microorganisms that cannot be stained by regular methods. Nigrosin WS is used in tests for viability; living cells exclude the dye, but it enters dead cells. Nigrosine is a dark black pigment (or dye), obtained primarily from aniline.

2.2.1. Batch Adsorption Experiments

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 ± 1^0C) under batch mode.

2.2.2. Experiments for removal of NG-dye

The 25mL of 10 mg/L of NG solution with 100mg of particle size 150 to 355 μ 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 11. The solutions were withdrawn at different time intervals and the adsorbent was removed from the solution by centrifugation using centrifuge machine (Kemi 1ml) [70]. 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.

$$q_e = (C_i - C_e) V / W \quad \text{------------------------} \quad 1$$

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

Percentage removal = $(C_i - C_e) / C_i \times 100$ ------------------2

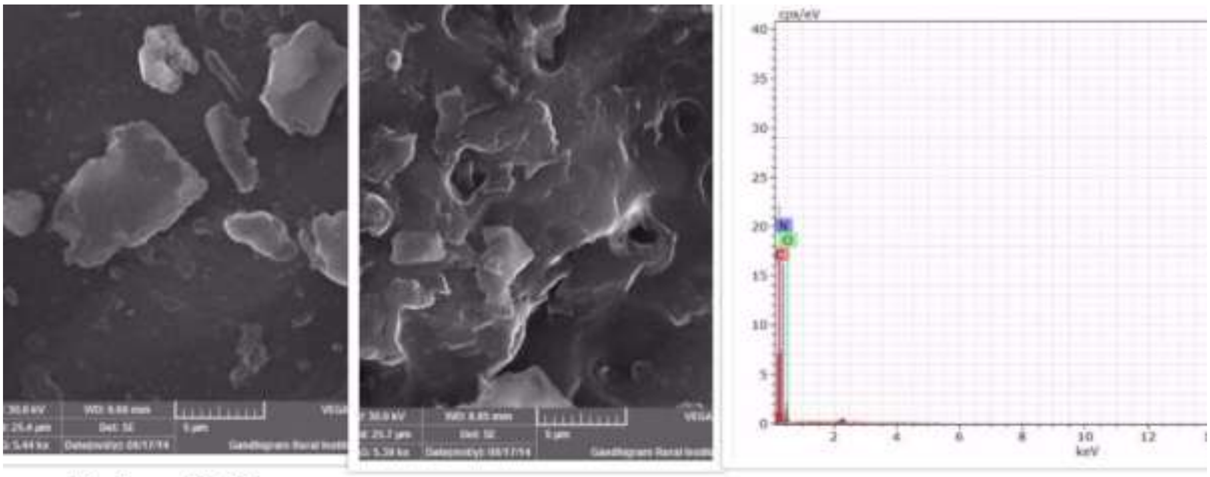
Where, Ci and Ce are initial and final absorbance of NG solutions before and after adsorption. The consequences of different parameters such as effect of pH, adsorbent dose and agitation time were studied. The obtained kinetic data were applied to various kinetics models: pseudo –first- order, pseudo-second-order,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

3. Characterization of spectra

3.1. Textural Studies using SEM

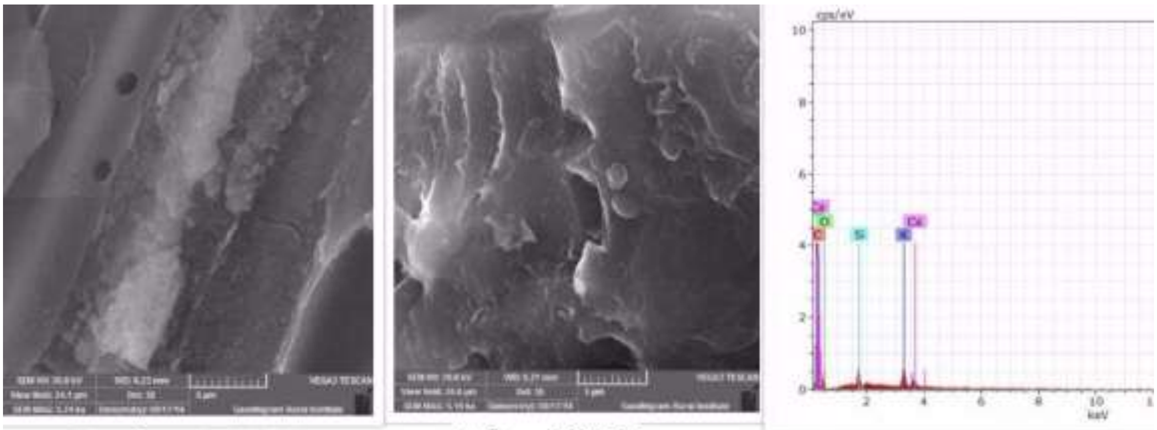
The textural / morphological characteristics of the surface of the adsorbents are studied by Scanning Electron Microscope (SEM) [71-73]. The scanning electron micrographs (SEMs) of the AC samples Edax studies and after SEM adsorption of dyes are recorded. The typical SEM photographs of AC samples, Edax studies and after SEM adsorption of dyes are shown in Figure 3.1 - 3.5.

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 [71]. 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 [73].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- which are indigenously prepared from agricultural wastes/by products.



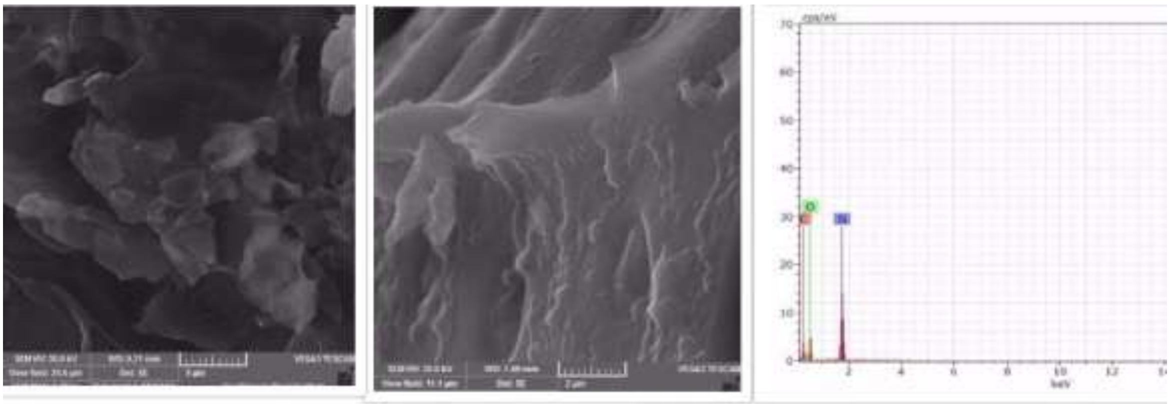
Before SVC After SVC EDAX - SVC

Figure 3.1 SEM and EDAX of SVC



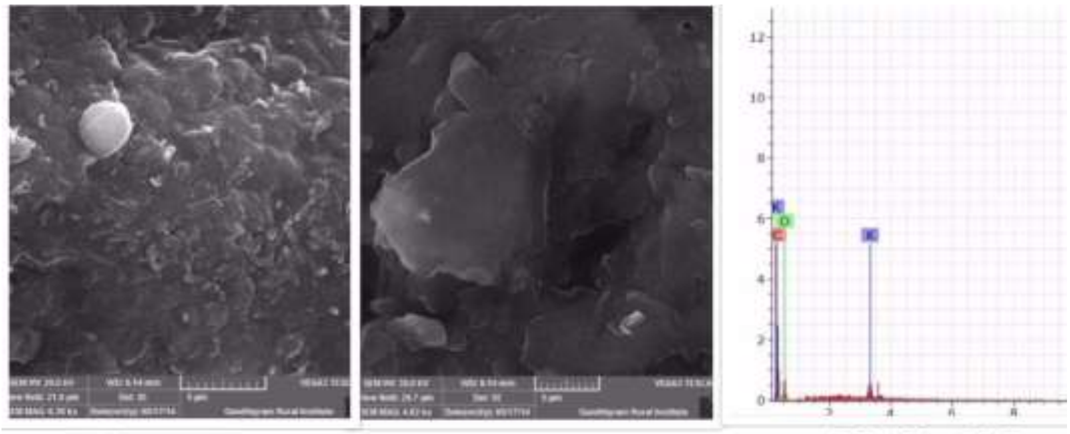
Before ZMC After ZMC EDAX - ZMC

Figure 3.2 SEM and EDAX of ZMC



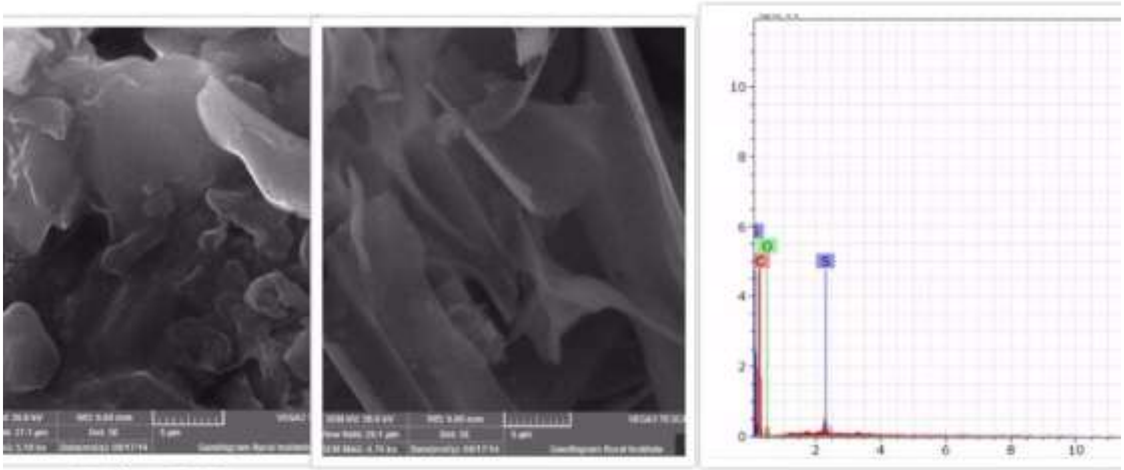
Before SVVC After SVVC EDAX - SVVC

Figure 3.3 SEM and EDAX of SVVC



Before CPC After CPC EDAX - CPC

Figure 3.4 SEM and EDAX of CPC

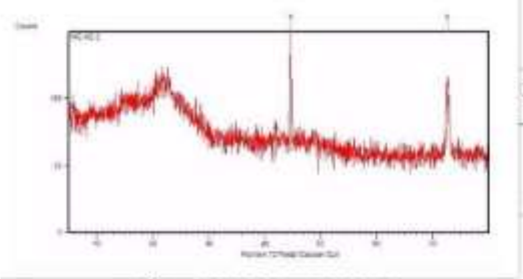


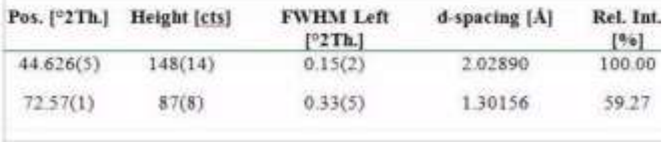
Before PJC After PJC EDAX - PJC

Figure 3.5 SEM and EDAX of PJC

3.2. XRD

X-ray diffraction (XRD) analyses of prepared magnetic activated carbon sample were carried out with X-ray. Madurai Kamarajar University Diffractometer model (Diffractometer system=XPERT-PRO). XRD patterns are given inFig 3.3, 3.4, 3.5, 3.6 and 3.7 respectively. The XRD pattern shows a crystalline structure and indicates the amorphous character of the carbon matrix in which powder particles is impregnated. The X-ray diffraction patterns for IPACs show a number of sharp peaks which are compatible with the presence of high peak. Ion measurement was used to determine the crystal structure of the adsorbents. Upper peaks and broadness be there observed in acid activated samples than the non-acid activated samples. Also, the occurrence of high diffraction peaks and broadness are sign of good crystallinity of the prepared powdered samples. The intensities for each samples as presented in Figure 3.6-3.10 and 3.6 are in the range of 10-79^{o}= 2ϴ.Thus, this indicates that other low intensity peaks corresponding to other crystalline phases of carbon have also been observed.

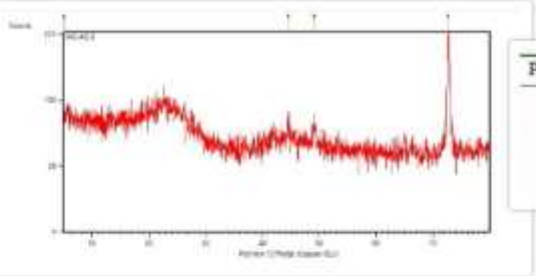


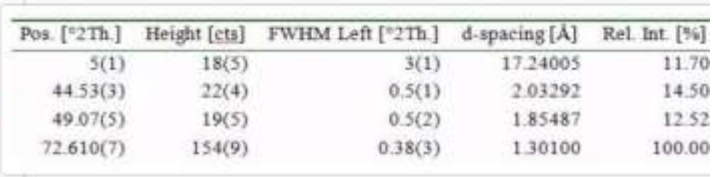


Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
44.626(5)	148(14)	0.15(2)	2.02890	100.00
72.57(1)	87(8)	0.33(5)	1.30156	59.27

After XRD - SVC

Figure 3.6 XRD of SVC

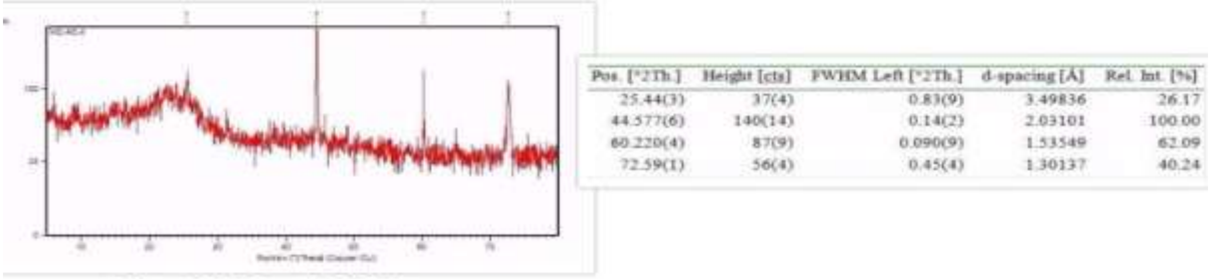




Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
5(1)	18(5)	3(1)	17.24005	11.70
44.53(3)	22(4)	0.5(1)	2.03292	14.50
49.07(5)	19(5)	0.5(2)	1.85487	12.52
72.610(7)	154(9)	0.38(3)	1.30100	100.00

After XRD - ZMC

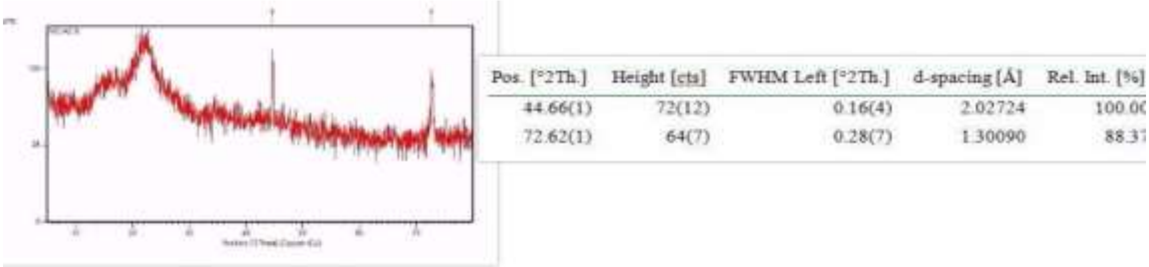
Figure 3.7 XRD of ZMC



Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
25.44(3)	37(4)	0.83(9)	3.49836	26.17
44.577(6)	140(14)	0.14(2)	2.03101	100.00
60.220(4)	87(9)	0.090(9)	1.53549	62.09
72.59(1)	56(4)	0.45(4)	1.30137	40.24

After XRD - SVVC

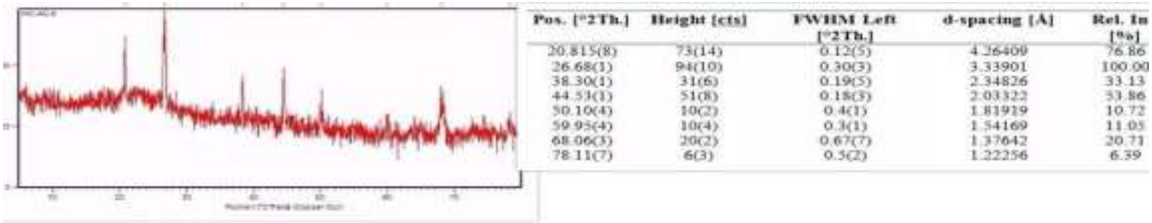
Figure 3.8 XRD of SVVC



Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
44.66(1)	72(12)	0.16(4)	2.02724	100.0
72.62(1)	64(7)	0.28(7)	1.30090	88.3

After XRD - CPC

Figure 3.9 XRD of CPC



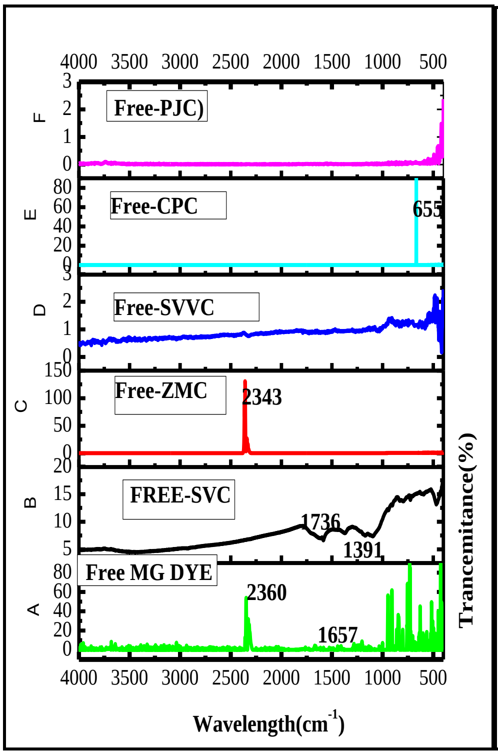
Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. In [%]
20.815(8)	73(14)	0.12(5)	4.26409	76.86
26.68(1)	94(10)	0.30(3)	3.33901	100.00
38.30(1)	31(6)	0.19(5)	2.34826	33.13
44.53(1)	51(8)	0.18(3)	2.03322	53.86
50.10(4)	10(2)	0.4(1)	1.81919	10.72
59.95(4)	10(4)	0.3(1)	1.54169	11.05
68.06(3)	20(2)	0.67(7)	1.37642	20.71
78.11(7)	6(3)	0.5(2)	1.22256	6.39

After XRD - PJC

Figure 3.10 XRD of PJC

3.3. FT-IR Studies

Fourier-transform infrared (FT-IR) spectra were recorded using SHIMADZU – 1800 FT-IR spectrophotometer in the wave number range 400-4000 cm^{-1}.After equilibrium the dye loaded IPACs was filtered through filter paper. The dye loaded and pure IPACs were dried at 50 °C in a heating oven. The samples were grounded in an agate pestle and mortar with KBr. The background obtained from KBr disc was automatically subtracted from the sample discs spectra prepared with KBr. Totally spectra were plotted using the similar scale on the transmittance axis. FT-IR spectrophotometer was collected using a SHIMADZU– 1800 Mdura college Chemistry laboratory Madurai-14. This instrument was used for the adsorbent surface analysis both before and after MG-dye treatments.



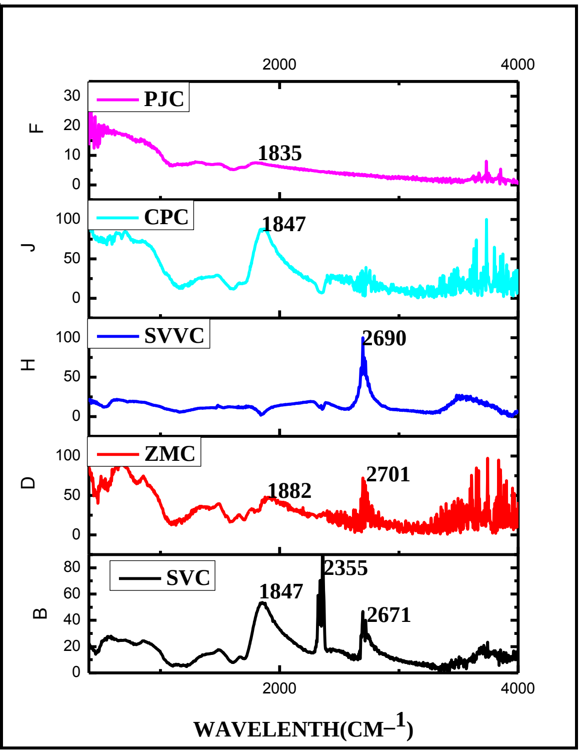


Figure 3.11.a Free IPACs FT-IR **Figure 3.11.b Loaded IPACs FT-IR**

4. Effect of initial concentration

The effect of initial concentration on the extent of removal of dye Nigrosine (NG) in terms of percentage removal and amount adsorbed q) on various adsorbents were studied[Table 4.1.] and Figure 4.1.The percentage removal is found to be decreases exponentially, while the amount of dye adsorbed increases exponentially with the increase in initial concentration of Nigrosine(NG).This may be due to lack of available actives sides required for the higher initial concentration of NG. At lower concentrations of substantial amount of NG got adsorbed leaving behind more number of active sides on the adsorbents and at higher concentrations lesser number of actives is available. Similar numbers of results have been reported in literature for the removal of dyes[74-76].

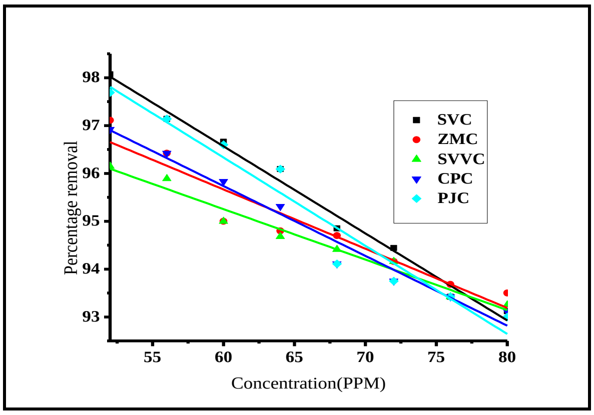


Figure 4.1Effect of initial concentration for the removal of MG on IPACs

Table 4.1 Effect of experimental parameters on the extent of removal of Nigrosine (NG) by IPACs

Experimental parameters	Range					
		SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
Concentration PPM	%R	52- 80	52- 80	52- 80	52- 80	52- 80
		98.07-93.2	97.11-93.50	96.15-93.25	96.92-93.12	97.69-93
Contact time(min)		5-40	5-40	5-40	5-40	5-40
	%R	90.19-98.87	92-98.16	90.83-98.66	91.66-98.33	91.66-98.5
DosegL^{-1}		0.2-1.6	0.2-1.6	0.2-1.6	0.2-1.6	0.2-1.6
	%R	90.19- 98.87	89.80-98.57	90.19-98.37	88.33-97.5	89.80-98.50
Initial pH		2-12	2-12	2-12	2-12	2-12
	%R	96.33-88.33	97.83-93	98.50-93.16	98.83-93.66	98.16-91.50
Particle size		90-182	90-182	90-182	90-182	90-182
	%R	96-89.2	95.3-91.03	95-92.6	94-91.5	94.1-92
Temperature		30-60	30-60	30-60	30-60	30-60
	%R	94.1-96.2	96.3-98.1	93.5-96.4	90.3-93.16	91-94.15

4.1 Adsorption Isotherms

The adsorption isotherms explain the distribution of adsorption molecules between liquid phase and solid phase equilibrium state. The purpose of the adsorption isotherms is to relate the Adsorbate concentration in the bulk and adsorbed amount of at the interface[77]. The suitable model that can be used as for design purpose[78], is evaluated by fitting isotherm data to different isotherm models such as Freundlich, Langmuir[79],Tempkin[80],Redlich-Peterson[81-82], and DubininRadushkevich**[**80**],** BETadsorption isotherm is critical in optimizing the use of adsorbents and describe the interactions of solutes with adsorbents.At low concentrations, the equilibrium adsorptions isotherms of Nigrosine [NG] on the prepared activated carbon show a step increases which indicates the high affinity of towards the solute. The linearized form of Freundlich and Langmuir isotherms were used to analyze data. The data are given table 4.1. The Freundlich isotherm is the earliest known relationship describing the sorption equation[83]. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules and a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [84]. The presentation of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorptionalcentres of an adsorbent. This isotherm is an empirical equation working to describe heterogeneous systems and is expressed by the following equation:

Freundlich isotherm: $\log q_e = \log K + (1/n)\log C_e$ --- (4.1)

By plotting log q_e versus log C_e enables to determine the constants K and 1/n (Figure 4.2).

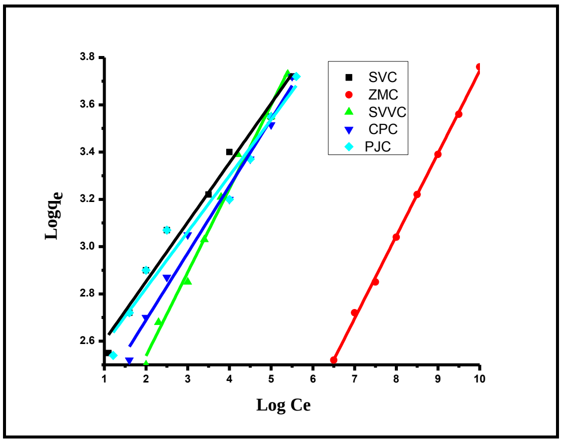


Figure 4.2Freundlich isotherms for the removal of NG on IPACs

The Langmuir sorption isotherm is most widely used for the sorption of a pollutant from a liquid solution. The model is based on several basic assumptions [85].

i. The sorption takes place at specific homogeneous sites within the adsorbent
ii. Once a dye molecule occupies a site
iii. The adsorbent has a finite capacity for the adsorbate (at equilibrium, a saturation point is reached where no further adsorption can occur)
iv. All sites are identical and energetically equivalent (the adsorbent is structurally homogeneous)

The equation of Langmuir is represented as follows:

Longmuir isotherm: $(C_e/q_e) = (1/Q_o b) + (C_e/Q_o)$ **---- (4.2)**

Langmuir parameters have been obtained from the linear correlation between the values of $C_e/q_e$and C_e (Figure 4.3).

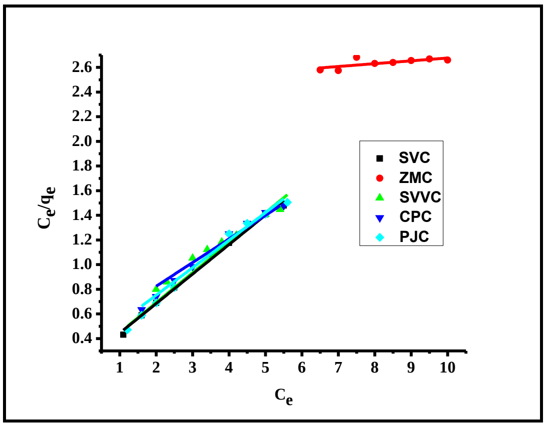


Figure 4.3Langmuir Isotherm for the removal of NG on IPACs

Isotherm	Parameters	Adsorbents				
		SVC	ZMC	SVVC	CPC	PJC
Freundlich	Slope(1/n)	0.354	0.283	0.237	0.250	0.349
	Intercept(log k)	1.829	2.123	2.348	2.350	0.248
	r-value	0.987	0.983	0.954	0.977	0.998
Langmuir	Slope(1/n)	0.243	0.239	0.022	0.191	0.223
	Intercept(log k)	0.2054	0.2052	02.446	0.441	0.305
	r-value	0.988	0.993	0.920	0.986	0.988
	$Q_0(mgg^{-1})$	21.18	17.37	11.40	8.39	7.99

	b(gL^{-1})	0.225	0.055	0.053	0.089	0.091
	R_L=1/(1+C_0b)	0.035	0.602	0.652	0.558	0.543
Tempkin	A(Lg^{-1})	2.421	2.827	1.61	1.98	2.40
	B	2.708	2.8	1.21	0.94	0.69
	r-value	0.978	0.992	0.976	0.949	0.949
Redlich-Peterson	K_R	4.765	0.9553	0.6042	0.7467	0.7270
	αR	-0.0221	0.1961	0.1712	0.4692	0.5161
	β	0.9160	3.930	0.6663	-0.0228	-0.0485
	r-value	0.9865	0.3816	0.9118	-0.1533	-0.0893
DubininRadushkevich	X’$_m$(mgg^{-1})	0.4616	-0.0676	0.4021	0.429	0.456
	E(kjmol^{-1})	0.4463	0.8918	0.5709	0.5053	0.4418
	K’(mol^{2}KJ^{-2})10^{-6}	-0.0996	-0.3977	-0.163	-0.1277	-0.0976
	r-value	0.988	0.998	0.972	0.982	0.961
BET Isotherm	Slope	2.042	1.88	1.89	2.29	1.69
	Intercept	4.85	4.50	4.58	5.64	4.35
	r-Value	0.78618	0.65842	0.5869	0.60851	0.74017

Temkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This relates the heat of adsorption and surface coverage of the dye molecules on the adsorbent [86]. This isotherm assumes that

i. The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate interactions
ii. Adsorption is considered by uniform distribution of binding energies, up to some maximum binding energy [87].

$$q_e = B \ In\ A + B \ In\ C_e \qquad \text{----- (4.3)}$$

By plotting q_e versus C_e enables to determine the constants A and B (Fig 4.4). Where A is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy and constant B is related to the heat of adsorption. The values of the parameters are given in

Table 4.2.

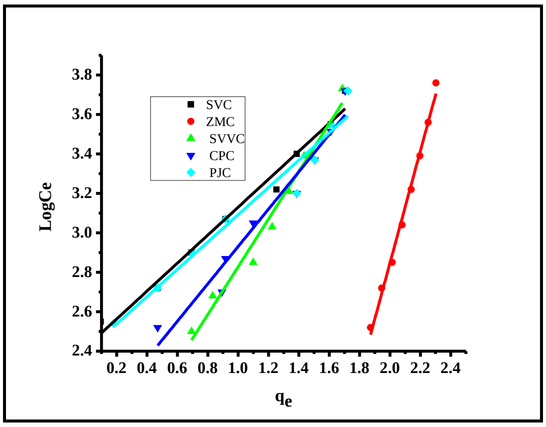


Figure 4.4Temkin Isotherm for the removal of NG on IPACs

The Redlich Peterson isotherm can be used to describe adsorption on both homogeneous and heterogeneous surfaces [88].

$$\text{Log}\ [(K_R C_e/q_e)-1] = \beta \log C_e + \log(\alpha R) \qquad \text{---- (4.4)}$$

by plotting the values of log [(K_RC_e/q_e)-1] against β log C_e , the values of (αR) and β can be determined from the intercept log (αR) and the slope (β), respectively (Figure 4.5).

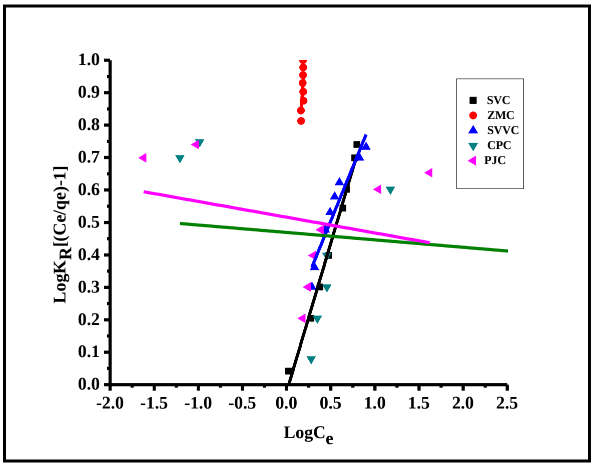


Figure 4.5Redlich Peterson Isotherm for the removal of MG on IPACs

The Dubinin-Radushkevich isotherm model was also applied to estimate the porosity apparent free energy and the characteristic of adsorption [89, 90, 91]. The D-R isotherm does not assume a homogeneous surface or constant adsorption potential.

$$\mathbf{In\ q = In\ X'_m - K'\ E^2} \qquad \text{----- (4.5)}$$

by plotting In q against E^2, give the parameters X'_m and K′ from the values of intercept and slope (Figure 4.6).

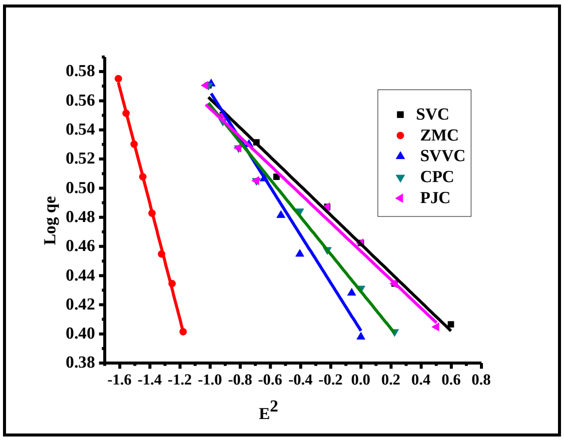


Figure 4.6 Dubinin-Radushkevich Isotherm for the removal of NG on IPACs

The mean energy of adsorption (E, in kJ mole $^{-1}$), can be calculated from the k' value using the following equation:

$$\mathbf{E= (-2K')^{-0.5}} \qquad \text{----- (4.6)}$$

Here, the magnitude of E is useful for estimating the mechanism of the adsorption reaction. In the case of E < 8 kJ/mole, physical forces may affect the adsorption. If E is in the range of 8-16 kJ/mole, adsorption is governed by ion-exchange mechanism, while for the values of E<19 kJ/mole, adsorption may be dominated by particle diffusion[92]. From the experimental values (Table 4.2) it is confirmed that these processes are carried out through particle diffusion. The BET equation is an extension of the Langmuir relationship that accounts for multilayer coverage (Figure 4.7).

$$\mathbf{C_e/X(C_o-C_e) = 1/X_mK + (k-1)\ C_e/X_mkC_o} \qquad \text{------- (4.7)}$$

Where, C_o and C_e are the initial and equilibrium concentrations, k is a constant related to the energy (enthalpy) of adsorption.

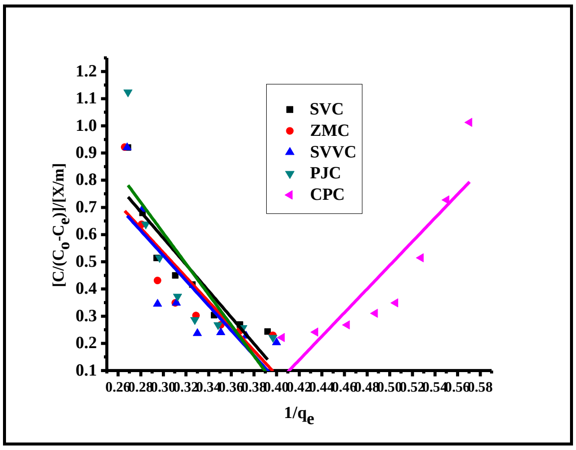


Figure 4.7BET Isotherm for the removal of NG on and IPACs.

The non-linearity in the BET isotherm plot is evidenced by very low values (0.335-0.437) which clearly indicate the absence of multilayer adsorption of NG on the adsorbents surface. The high values of ‘r’ obtained for the plot of C_e/q_e versus C_e reveal that the adsorption of NG over SVC, ZMC, SVVC, CPC and PJC follows Langmuir isotherm model. The Langmuir theory assumes that adsorption is localized in a monolayer and no interaction between adsorbate molecules taken place.According to this theory, once dye molecule occupies a site, no further adsorption taken place at that site. Therefore, no further adsorption can take place once a saturated value is reached. The Langmuir isotherm also gives the value of monolayer adsorption capacity (Q_o, in mg g^{-1}). The value of $Q_o$indicates that all the IPACs are found to be suitable for dye removal. Among the IPACs, SVVC, ZMC, SVC, CPC and PJC has high value of monolayer adsorption capacity for the removal of NG.Based on the correlation coefficient (r) the adsorption isotherm with SVVC, ZMC, SVC, CPC, and PJC can be better described by Langmuir equation. The applicability of the Langmuir isotherm suggests the mono layer coverage of the NG dye on the surface of the adsorbents. The mono layer adsorption capacities of the adsorbents are found to be of the order given below:

SVC < ZMC < SVVC<CPC<PJC

The important features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (R_L, also called equilibrium parameter) which is defined by the following equation [93, 94].

RL = [1/ (1+bC_i)] ------- (4.8)

Where, Ci = optimum initial concentration of NG (mg L^{-1}), b = Langmuir constant (L mg^{-1}).The values of separation factor, R_L indicate the nature of the adsorption process as given here [93],

R_L Values	**Nature of adsorption process**
$R_L>1$	Unfavourable
$R_L = 1$	Linear
$0<R_L<1$	Favourable
$R_L = 0$	Irreversible

In the present study, the values of R_L (Table) are observed to be fraction *i.e.*, in the range of zero to one (0.001-0.121). The fractional value of R_L indicates that the favourable nature of the adsorption process. Therefore the adsorption process is favourable for all these adsorbents.

The values of R_L (Table 4.2) are observed to be fraction i.e., in the range of zero to one (0.035-0.652) which indicate that the adsorption process is favorable for all these adsorbents. For activated carbonsother than

SVC, SVVC is found to have higher value of adsorption capacity (Q_0) carbons. The concentration coefficient (r-value) is found to be almost equal to unity for all the isotherms.

5. 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 relevant data are given in table 5.1. The extert of removal of Nigrosine by these adsorbents is found to increases exponentially and reach a maximum value with increase in contact time Figure5.1. The relative increases in the extert of value removal of dye after 30 min.,of contact time is not significant and henceit's fixed as the optimum contact time.Similar results have been reported in literature for the removal of dyes [94,95],metal ions [96], and carboxylic acids [97].

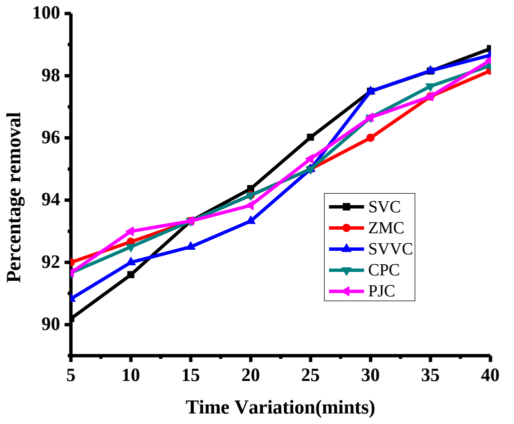


Figure 5.1Effect of contact time for the extent removal of NG on IPACs

5.1 Kinetics of Adsorbents

The Kinetics and dynamics of adsorption of Nigrisine(NG) on various adsorbents have been studied by applying the various kinetics equations[98].the values of (i)$1/q_t$(ii)log (Ci/Ct),(iii)[1-U(T)],(iv) Log(q_e-q_t), (v) $t/g_t$with linearedcorrelated with time(t). The values of first order constant and correlation co-efficient (r-values) are given table 7.3.all the linear correlations were found to be statistically significant, indicating the applicability of these equations and the pseudo second order nature of adsorption process Nigrosine on the low cost adsorbents.

The results of kinetics studies are presented Table 7.4. The straight lines for at the initial concentrations with extremely high correlation co efficients for pseudo second order model compared to those for the all first order kinetic models for the adsorption of nigrosine dye onto IPACs 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 valence forces through sharing or exchange of electrons between the active sites of carbons and polar dye ions.The calculated values q_e found from pseudo first order kinetic model give less reasonable values for all the adsorbents, IPACs than those from the pseudo second order kinetic model. For all the adsorbents, $q_e$calculated agreed well with experimental q_e in the pseudo second order kinetics.The kinetics and dynamics of adsorption of NG on various adsorbents have been studied by applying various kinetic equations of Natarajan and Khalaf[99], Lagergren[100], Bhattacharya-Venkobachar[101]and modified Elovich[102] equations.

Natarajan and Khalaf equation:

$\log (C_i/C_t) = k(k/2.303)t$ ----- (5.1)

Lagergren equation (First Order):

$\log (q_e-q_t) = \log q_e - [k_{ad} / 2.303]t$ ----- (5.2)

Lagergren equation (Pseudo Second Order):

$t/q_t = 1/k_2\, q_e^2 + t/q_e$ ----- (5.3)

Bhattacharya and Venkobachar equation:

$\log [1-U(t)] = -(k_{ad} / 2.303)t$ ----- (5.4)

Modified Elovich equation:

$(Ci-Ct) = (1\beta) \text{In} (\alpha/\beta) + (1/\beta) \text{Int}$ ----- (5.5)

Where,C_i and C_t = Concentration of NG at time zero and time t respectively (mg L^{-1});q_e and q_t = Amount of NG adsorbed at equilibrium time and time t respectively;(mg g^{-1})U (T) = $[(C_i-C_t) / C_i-C_e)]$; C_e = equilibrium concentration NG (mg L^{-1});k = first order adsorption rate constant (min^{-1}).The values of i)$1/q_t$, ii) log (C_i/C_t), iii)log [1-U(T)], iv)log (q_e-q_t), v)t/q_t were linearly correlated with contact time (t) and the values of first order rate constant, Δq (%) and correlation co-efficient (r values) are given in Table 5.1 and Figures 5.1-5.5.The Elovich parameter β was obtained from the negative inverse of the slope of the linear plot of values of Ct against in t and α value can be obtained from the intercept [(1/β) In (α/β)-C] of the plot by substituting the values of Ci and Ct.

Table 5.1 Kinetics and dynamics of adsorption of Nigrosine dye on SVC, ZMC, SVVC, CPC and PJC.

Kinetic Equation	**Parameters**	**Adsorbents**				
		SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
First order	K (min^{-1})	0.354	2.29	2.41	2.33	3.10
	r- value	0.902	0.848	0.850	0.865	0.862
Natarajan and Khalaf	K (min^{-1})	0.152	0.075	0.059	0.057	0.056
	r- value	0.954	0.983	0.983	0.983	0.983
	102K(min^{-1})	37.57	21.218	18.413	15.417	13.147
	Δq (%)	0.686	0.434	0.356	0.323	0.229
Bhattacharya and Venkobachar equation	K (min^{-1})	0.229	0.113	0.093	0.092	0.083
	r- value	0.966	0.986	0.943	0.936	0.963
	102K(min^{-1})	11.702	9.107	7.978	10.275	11.978
	Δq (%)	25.48	22.47	19.495	16.174	15.16
Psudo first order	K (min^{-1})	0.229	0.110	0.094	0.093	0.071
	r- value	0.966	0.963	0.962	0.962	0.963
Psudo second order	K (min^{-1})	6.78	0.397	0.379	0.372	0.304
	r- value	0.999	0.995	0.994	0.996	0.992
Intra Particle diffusion	k_p	1.365	0.545	0.544	0.484	0.544
	intercept	104.46	4.31	4.01	4.14	2.81
	r- value	0.974	0.979	0.979	0.962	0.979
Modified Elovich equation	Correlation coefficient (r)	0.9347	0.9313	0.940	0.934	0.965
	A	185.22	254.45	87.27	88.56	145.2
	B	0.175	0.048	0.178	0.085	0.345
	Δq (%)	82.76	41.27	25.21	34.25	15.07

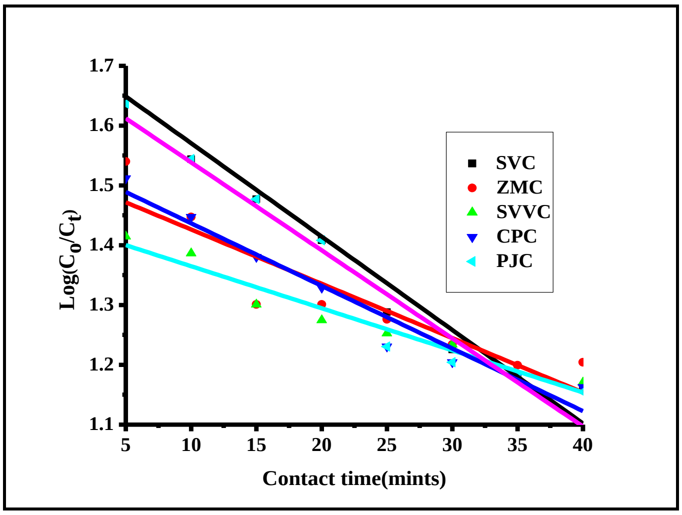


Figure 5.1 Natarajan and Khalaf kinetic plot for the removal of NG on IPACs

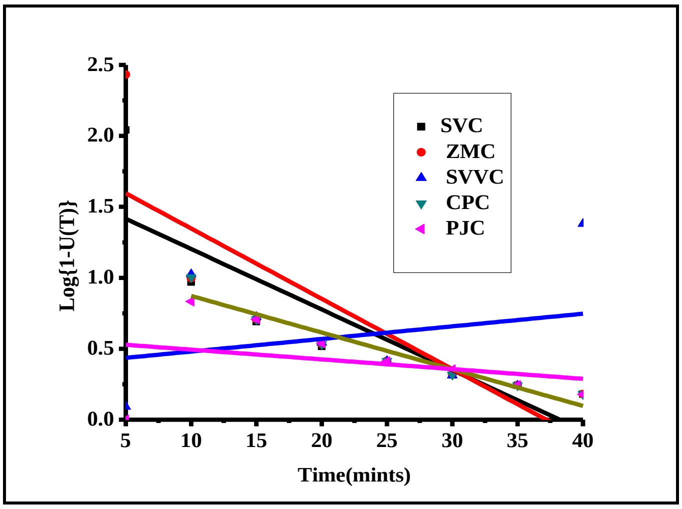


Figure 5.2 Bhattacharya and Venkobachar kinetic plot for the removal of NG on IPACs

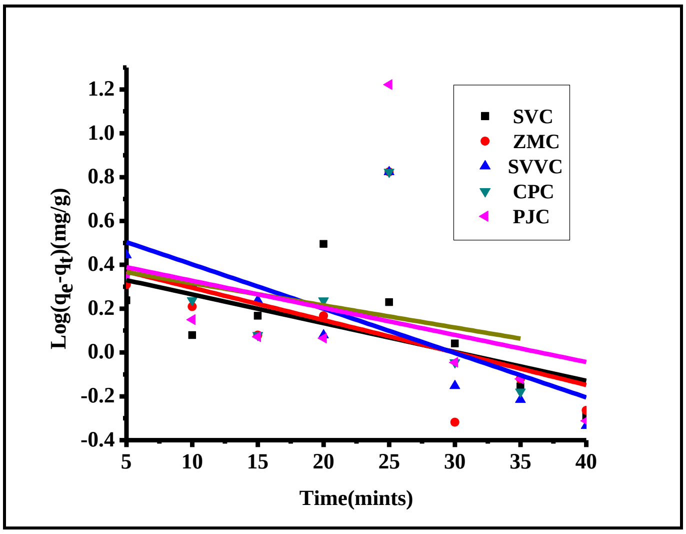


Figure 5.3Pseudo first order kinetic plot for the removal of NG on IPACs

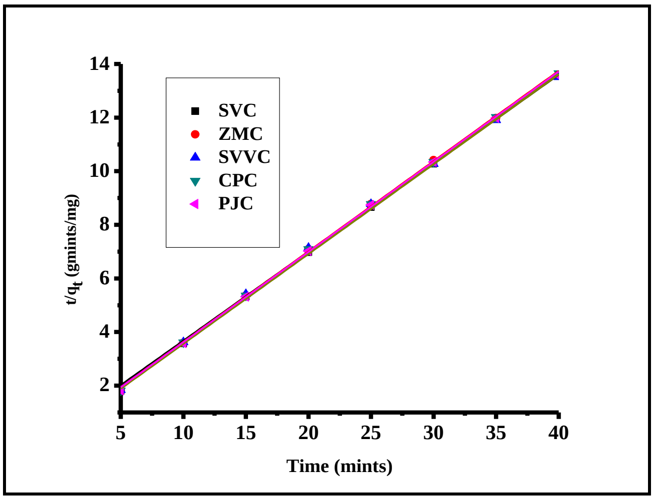


Figure 5.4 Pseudo second order kinetic plot for the removal of NG on IPACs

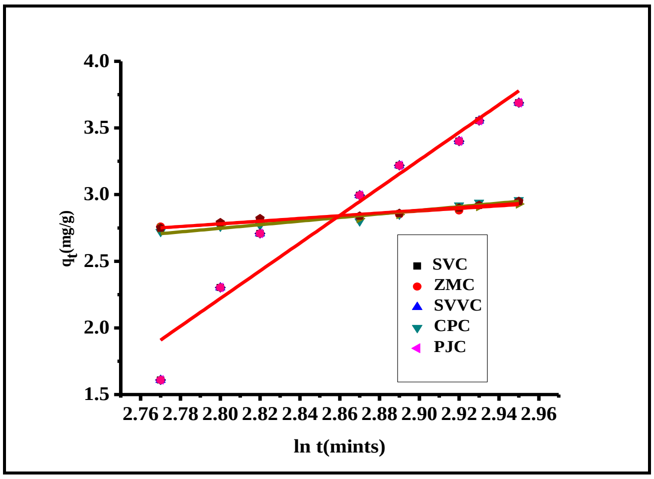


Figure 5.5Modified Elovich kinetic plot for the removal of NG on IPACs

Table 5.2.Comparison of calculated and experimental qe values and Δq values of Nigrosine dye with IPACs

Kinetic Equation	**Parameters**	**Adsorbents**				
		SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
Psudo first order	qeexp (mgg^{-1})	114.1	10.5	8.2	8.1	7
	qecal (mgg^{-1})	59.62	3.96	3.97	3.97	4.70
	R^2 value	0.934	0.926	0.930	0.930	0.928
	Δq (%)	89.91	98.97	98.60	98.58	98.26
Psudo second order	qeexp (mgg^{-1})	114.1	8.5	8.2	7.6	7.0
	qecal (mgg^{-1})	114.01	8.24	7.90	7.57	6.74
	R^2 value	0.999	0.990	0.991	0.993	0.990
	Δq (%)	1.675	10.04	10.27	8.51	11.23

The high values of correlation co-efficient (r values) indicate the applicability of first order kinetic model for the adsorption of NG on to IPACs. The r-values and k-values (Table 5.2) obtained from Pseudo first order equation for all the adsorbents are found to be almost equal with the values obtained from Bhattacharya and Venkobachar equation. Hence, any one of these kinetic equations could be used to calculate the first order rate constant for adsorptions for dyes.

It is in inferred that each dye adsorption system using IPACs follows the pseudo 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.

$\Delta q(\%) = 100\ x\{([(q_t^{exp}-q_t^{cal})/q_t^{exp}]^2\ /(n-1)\}^{1/2}$………..5.6

Where the subscripts exp and cal, are the experimental and calculated values qt viz. the amount adsorbed different time's t and n is the numbers of observations. The Δq(%) values are also given table 5.2. Based on low values of Δq(%) it is concluded that the adsorption of Nigrosine dye can be best described by the pseudo second order model.

5.1 Intra particle diffusion model

Besides adsorptionat the outer source of the adsorbent there is also a possibility of intra particle diffusion of dyes from the bulk of the solution to the solid phase through the intra particle diffusion which is often the rate limiting step in many adsorption processes. The intra particle diffusion process in the present adsorption system is also tested by the applying the intra particle diffusion model[103].

$q_t=Kpt^{1/2} + C$……………………………………5.7
Where q_t = amount of CH adsorbed at time, t (mgg^{-1}).
C= intercept
Kp= intra –particle diffusion rate constant($mgg^{-1}\ min^{-1/2}$)

The values of $q_t$were found to be linearly correlated with values of $t^{1/2}$. The Kp values were calculated by using correlation analysis (7.3) intra-particle diffusion is an empirically found functional relationship, common to the most adsorption processes were uptake with varies almost proportionally with $t^{1/2}$ rather than the with contact time t and Kp is the intra particle diffusion rate constant ($mgg^{-1}\ min^{-1/2}$) that gives idea about the thickness of the boundary layer,i.e. larger the value of C the greater is the boundary layer effect[104-107]. If intra particle diffusion occurs, then qtversus $t^{1/2}$ will be linear and if the plot passes through the orgin, then the rate restrictive process is only due to the intra-particle diffusion. Otherwise, some other mechanism along with intra-particle diffusion is also involved[108].

Log (%removal) = C+ m log (time)…………….7.3.

Where C= intercept and m =slope.

The correlation of values of Log (%removal) and log (time)shows that the process of intraparticle diffusion is taking place in these adsorption system(Table.7.5.) the values of slope indicates the presence of intra particle diffusion process as one of the rate limiting steps, besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously [109].The r-value of found to be close to unity indicating the application of the model. The calculated the values of Kp($mgg^{-1}\ min^{-1/2}$) for the adsorbents are maximum for SVC(1.365) and minimum for PJC(0.543). This result indicates that the intra particle diffusion processes is fast in SVC and PJC.Thevalues of intercept table 5.6 given an idea about the boundary layer thickness i.e. the larger the values of C greater are the contribution of surface adsorption in the rate limiting step. The intercept (C) value of adsorbents maximum in SVC (1.92) minimum PJC(1.49) the indicating that the boundary layer effect is maximum in SVC and minimum in PJC.

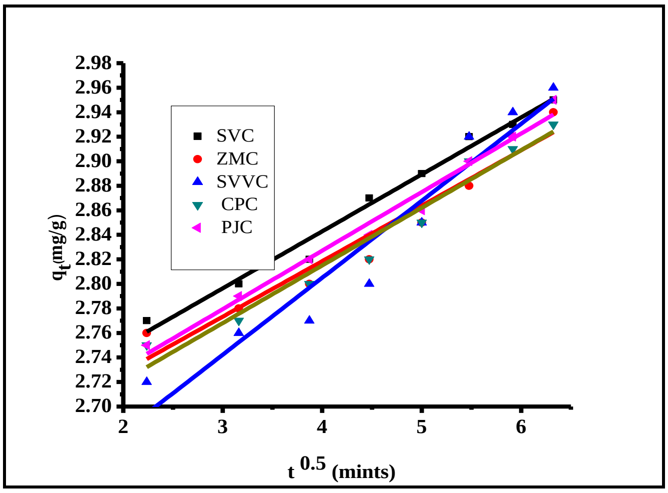


Figure 5.6Intra-Particle Diffusion of kinetic plot for the removal of NG on IPACs

Table 5.3 statistical results of intra-particle model for the adsorption of NG dye on IPACs

Kinetic model	**Parameters**	**Adsorbents**				
		SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
Intraparticle Diffusion	Kp	1.365	0.546	0.545	0.544	0.543
	Correlation co- efficient(r)	0.974	0.979	0.979	0.962	0.979
	Intercept(C)	104.46	4.31	4.14	4.01	2.81
	Δq(%)	0.45	2.69	2.75	3.19	3.37
Log(%removal) vs log (time)	slope	0.028	0.131	0.177	0.180	0.217
	Correlation co- efficient(r)	0.985	0.958	0.961	0.961	0.963
	Intercept(C)	1.92	1.69	1.58	1.57	1.49

6. Effect of dose of adsorbent

The effect of different dose of adsorbent for the removal of Nigrosine (NG) by adsorption on various indigenously prepared ACs. (viz., SVC,ZMC,SVVC,CPC and PJC) at the initial concentration(Ci) of dye. 30 min.,of Contact time and 90 microns particle size. At the solution pH itself were studied at 30± 1^{0}C. The adsorption data for removal of Nigrosine by various indigenously prepared ACs in presented in table.7.6. The exponential variation of the percentage removal of dye with the dose of adsorbent is depicted in table 6.1. The values of percentage removal of dye by adsorption onto various ACs are found to increases exponential with the increase in dose of the adsorbents and then level of at higher dose of adsorbents(ACs). The amount of dye adsorbed per unit mass of the adsorbent (q) decreases exponentially with the increase in dose of adsorbent. As the dose of adsorbent(AC) increases, the surface area proportionally increases (as the particle size of ACremains almost constant; 90microns), which has resulted in an increases in percentage removal of dyes, greater availability of surface active dyes. The results are found to be in harmony with the results in literature on the such on the effect of dose of various adsorbents on the removal of dyes by adsorption ACs[110].Similartrend on the effect of dose of adsorbents is also available in the literature based on the studies on the removal of dye [111-113]pesticides [114] other organic substances the phenol, toluene, xylene etc.,[115-117] and metal ions [118,119] by various adsorbents. The optimum dose is fixed as 1gL^{-1} for various indigenously prepared ACs.

Table 6.1 Effect of dose of adsorbent on the extent of removal of NG by ACs at 30±1^{0}C

Dose of Adsorbents	**% Removal (Amount adsorbed in mgg^{-1})**				
	SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
0.2	90.19(2.34)	89.80(2.33)	90.19(2.34)	88.33(2.65)	89.80(2.33)
0.4	91.60(2.56)	91.07(2.55)	91.96(2.57)	90.83(2.72)	91.60(2.56)
0.6	93.33(2.80)	92.66(2.78)	93(2.79)	91.33(2.74)	93.33(2.80)
0.8	94.37(3.02)	93.75(3)	94.53(3.02)	93.33(2.80)	94.53(3.02)
1	96.02(3.26)	94.85(3.22)	95.88(3.26)	94.16(2.82)	95.58(3.25)
1.2	97.5(3.51)	95.83(3.45)	96.52(3.47)	96.66(2.89)	97.50(3.51)

1.4	98.15(3.73)	97.36(3.7)	97.36(3.70)	97.16(2.91)	98.15(3.73)
1.6	98.87(3.95)	98.57(3.93)	98.37(3.93)	97.5(2.93)	98.50(3.94)

The values of amount of dye adsorbed are found to vary exponentially with the natural power term of the dose of adsorbents [120] according to the following model:

$qe = [dose]^{-1} + C$ ------ (6.1)

On taking logarithm, the above equation becomes equation.

$Logq_e = -n \log [dose] + C$ ----(6.2)

Where, q_e = amount of dye adsorbed (in mgg^{-1}) at equilibrium contact time, 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 6.1 and 6.2respectively. The values of log qe are linearly correlated with log [dose] for the various dye AC systems. The results of the linear regression analysis of log q_e withlog [dose] are listed in Table 6.2.

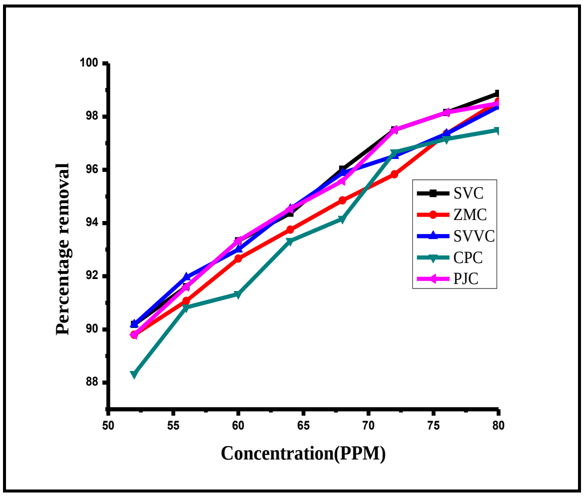


Figure 6.1Adsorption of Dose of the removal of NG on IPACs

Table 6.2 Results of the linear regression analysis of log amount adsorbed with Log dose for the removal of NG by adsorption on ACs.

Parameter	**SVC**	**ZMC**	**SVVC**	**CPC**	**PJC**
Slope (n)	0.114	1.601	1.557	1.474	1.426
Correlation Co efficient (r)	0.982	0.988	0.951	0.951	0.967
Intercept (c)	0.511	-3.406	-3.665	-3.780	-3.841

8. Effect of Initial pH

The effects of initial pH on adsorption process for dye Nigrosine (NG) on ACs were studied at different pH values range from 2-12. The experimental conditionals like optimum initial concentration of dye NG, 30 min. of contact time, dose of adsorbent $2g/L^{-1}$ and 90 microns particle size were maintained. The results are presented in Table 8.1 and Figure 8.1.pH is an important factor that controls the sorption of dyes from aqueous solutions on to solids. Therefore, the pH effect on the sorption of Nigrosine dye on cotton was studied in the pH range of 2-12. The change of pH decides the dye-binding capacity of each sorbent. 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 COOH groups [121], which may take part in binding mechanism. Therefore, the interaction between dye molecules and sorbent is basically a combined result of charges on dye molecules and the surface of sorbent.

Table 8.1 Effect of pH on the extent of removal of NG by IPACs at 30 ± 1^{0}C

Dye pH	% Removal (Amount adsorbed in mgg^{-1})				
	SVC	ZMC	SVVC	CPC	PJC
2	96.33(2.89)	97.83(2.93)	98.50(2.95)	98.83(2.96)	98.16(2.94)
4	95.66(2.87)	97(2.91)	98(2.93)	96.33(2.94)	96.50(2.89)
6	94.16(2.82)	95.66(2.87)	96.66(2.90)	97.5(2.92)	95.83(2.87)
8	90.66(2.72)	94.50(2.83)	95.66(2.87)	96.33(2.89)	94.16(2.82)
10	89.16(2.67)	93.83(2.81)	94.16(2.82)	94.33(2.84)	93.33(2.80)
12	88.33(2.65)	93(2.78)	93.16(2.79)	93.66(2.81)	91.5(2.74)

At low pH, the surfaces of activated carbons may become positively changed due to access of H^* ions in solution. The electrostatic attraction between NG and surfaces of adsorbents increases the amount of NG adsorbed. At high pH, the surfaces of activated carbons may become negatively charged due to excess of OH^- ions in solution. Consequently electrostatic repulsion between anionic dye and anionic surfaces of activated carbons decreases the amount of NG adsorbed. Thus pH affects the surface change on the adsorbents and acidic or basic nature of dyes. The acidic pH is noted to be highly favorable for the removal of NG by adsorbents. The maximum percentage removal of NG occurs at pH 2-10, Similar results havebeen reported from the literature study [122-125].

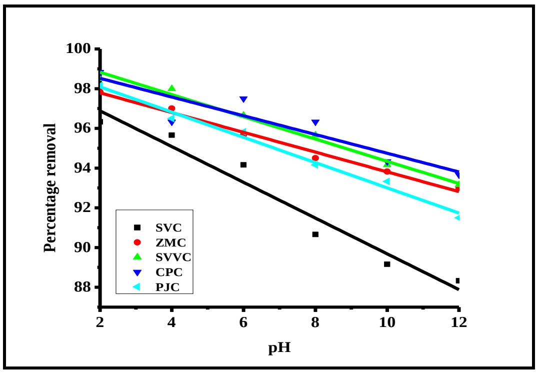


Figure 8.1Adsorption pH of the removal of NG on IPACs

9. Effect of particle size

The effect of particle size in adsorption process for Nigrosine dye on SVC, ZMC, SVVC, CPC and PJC carbons were studied by varying particle sizes. The experimental conditions like optimum initial concentration of dye NG, 30 min of contact time dose adsorbent 2g/L^{-1} and initial pH are shown in Table 8.1. The experimental results are presented in Table 9.1The adsorption capacity for dye increased with decrease in the particle size of adsorbents.For the particle size range from 90-212 µm, the amount of dye adsorbed linearly increases with the decreases in particle size of the adsorbent. The decrease in particle size leads to increase in surface area and increase the chances 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 [126, 127].

Table 9.1 Results of the linear regression analysis of particle size variation with % removal of NG by adsorption on ACs.

Parameter	SVC	ZMC	SVVC	CPC	PJC
Slope (n)	-0.133	-0.130	-0.125	-0.106	-0.04
Correlation Co efficient (r)	0.982	0.957	0.946	0.974	0.973
Intercept (c)	57.80	51.59	49.30	41.15	39.03

10. Effect of Temperature

The effect of temperature on the adsorption of Nigrosine dye bye SVC, ZMC, SVVC, CPC and PJC carbons were studied at temperature 30^0C, 40^0C, 50^0C and 60^0C. The adsorption of Nigrosine dye increased with increase of temperature upto 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 and in the total pore volume of the adsorbent. The improvement in adsorption could be also due to the decreases in the thickness of the boundary layer surrounding thesusbtend 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 increases 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 Nigrosine on the six sorbents is an endothermic process and NG dye sorption may involve not only physical but also chemical sorption [128].

10.1 Thermodynamic Parameters

The thermodynamic parameters such as ΔH^0 and ΔS^0 could be obtained from the waltz Hoff plots viz., the plots of log K_{eqm} vs 1/T, respectively from the slope and intercept values. The as ΔH^0 and ΔS^0 (Calculated by least-squares methods) are reported in Table 10.1

Table 10.1 Thermodynamic parameters for the adsorption of NG with IPACs.

Parameter	**Adsorbents**				
	SVC	**ZMC**	**SVVC**	**CPC**	**PJC**
ΔG^0 KJmole^{-1}	-12.34	-0.98	-0.83	-0.81	-0.56
ΔH^0 KJmole^{-1}	10.65	5.66	4.42	4.21	3.80
ΔS^0 KJmole^{-1}	12.40	4.20	3.16	2.35	0.72

The increase in temperature mostly alters the equilibrium solute (dye) concentration with negligible effect on the pore volume fillings. Hence, the overall enthalpy change (ΔH^0) for the adsorption process will be low and will decrease with the increase in the temperature. The energy of physical adsorption, which is due to the Vander Waals forces is typically around 5-20 kJmol^{-1}, which could not efficiently perturb the bonding structure of the adsorbate, before and after the adsorption. The observed values of ΔH^0 (range: 3.45-10.65 kJmol^{-1}) lie within the range of Vander Waals interaction energy and hence it is concluded that ‘Physisorption’ is also taking place in addition to Chemisorption.The negative values of ΔG^0 (6.47 to 12.34KJmol^{-1}).The negative valueof ΔG^oC(-0.47 to 12.34KJmol^{-1}) indicatedesolubility acid and spontaneity of adsorption process. The positive value of the ΔS^0C 0.55 to 12.40Jmole^{-1}K^{-1}.Suggests that randomnessor disorder increases of the solid/solution inter space with some structural changes in the adsorbates and the adsorbent and anaffinity of the adsorbent. thermodynamic parameters indicates that the adsorption process is spontaneous endothermic physisorptive in nature. These observations are also in harmony with the results obtained in many chemical reactions [129,130].

11. Desorption

The Nigrosine dye loaded adsorbents are diluted with DD water as eluents HCl, HNO_3, H_2SO_4, CH_3COOH, and NaOH. The values of percentage of desorption with DD water and eluents (0.5N) reported in Table 11.1. Among these acidic acid is found to be an effective eluent. The extent of desorption increases exponentially with the increases in concentration of HNO_3, and becomes constant. The optimum concentration of HNO_3, for effective desorption of Nigrosine from loaded adsorbent is fixed as 0.5N. The adsorption capacity of redeveloped adsorbents is checked for these cycles and found to be less compared to the original samples but it is also suitable for the removal of Nigrosine from dilute solutions. This will again definitely lower the cost of removal of eluent treatment process. SVC andPJC could be used as low cost adsorbents as for the removal of dyes in general Nigrosine in particular.

Table 11.1 Extent of desorption of adsorbed NG using various eluents

Parameter	Adsorbents located with AV				
	SVC	ZMC	SVVC	CPC	PJC
DD water	61.1	60.1	59.3	54.4	48.1
HCl	72.1	65.8	64.1	62.7	56.7
HNO_3	83.3	75.9	74.3	72.4	63.3
H_2SO4	73.1	67.8	66.8	64.1	57.1
CH_3COOH	70.2	63.8	62.7	60.2	52.8
NaoH	66.4	62.3	61.3	58.1	50.1

11.1 Relative adsorption capacity

The increasing order of relative adsorption capacity of various isotherms compared to (Calculated from Qo values) under optimum experimental conditions as given below:

SVC < ZMC < SVVC < CPC << PJC

Among the adsorbents other than CPC, PJC has the maximum adsorption capacity, whereas SVC has the minimum adsorption capacity. The relative adsorption capacity (in terms of Q_o) values of various adsorbents for NG are shown in the Table 11.1. Cost wise these low cost adsorbents, especially CPC and SVVC are very much cheaper than the PJC and also easily available in India (especially in Tamil Nadu) as agricultural waste materials.

12. Conclusion

The following are the conclusions arrived at from the present study.Nigrosine (NG) dye is adsorbed on the surface of CPC and PJC.The percentage removal of Nigrosine dye increases with decrease in the initial concentration of the dye, particle size of adsorbents, initial pH and increases with increase in the contact time and dose of adsorbents.

Adsorption data are fitted with the Freundlich, Temkin, Langmuir, Redlich-Peterson and Dubinin-Radushkevich adsorption isotherms.

The adsorption data are fitted with kinetic equations such as Natarajan and Khalaf, Bhattacharya and Venkobachar, first order, pseudo first order, pseudo second order and modified Elovichto study the kinetic and dynamics of adsorption of acid violet on adsorbents. The adsorption of acid violet dye onto CPC and PJC 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 behavior is described by a mono-layer Langmuir type isotherm. The adsorption process is found to be first order with intra-particle diffusion, as one of the rate determining steps.The negative values of ΔG^0 and 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 SVVC, CPC and PJC could be employed as low cost adsorbents as for the removal of NG.

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