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Removal Of Fluoride From Water Using Zirconium And Sodium Hydroxide Impregnated Activated Carbon

C. Vellathurai[1],P Sri Renganathan[2*], V Selvaraj[3], S. Selvaraj[1], and Kumar T. Anantha[4]

[1]PG & Research Department of Chemistry, Sri Paramakalyani College, Alwarkurichi, Affiliated to ManonmaniamSundaranar University, Abishekapatti, Tirunelveli – 627012, TamilNadu, India.
[1] PG & Research Department of Chemistry, Sri Paramakalyani College, Alwarkurichi, Affiliated to ManonmaniamSundaranar University, Abishekapatti, Tirunelveli – 627012, TamilNadu, India.
[2]*Department of Chemistry, Rani Anna Govt. College for Women, Tirunelveli, Affiliated to ManonmaniamSundaranar University, Abishekapatti, Tirunelveli – 627012, TamilNadu, India.
[3]Department of Chemistry, Morning Star Polytechnic College, Nagercoil – 629003.
[4]Department of Chemistry, Merit Arts and Science College, Idaikal, Ambasamudram, Affiliated to ManonmaniamSundaranar University, Abishekapatti, Tirunelveli – 627012, TamilNadu, India.

ABSTRACT

This study deals with the application of Zirconium and Sodium hydroxide impregnated activated carbon using *Vitexnigundo* for fluoride toxicity. The batch adsorption technique was followed at neutral pH as a function of pH, adsorbent dose, contact time, adsorbate concentration and temperature. The experimental parameters were adsorbent dosage, contact time, initial concentration and temperature. The results indicated that increase in adsorption with the increase of contact time and adsorbent dosage. The equilibrium time was found to be around 3 hours. Initial solution pH was maintained as 7 because acidic and alkaline solutions reduce the F^{-} ion concentration in the solution.The present system followed the Freundlich isotherm as well as the Langmuir adsorption isotherm model. The adsorption kinetics was investigated and best kinetic model describing each adsorbate – adsorbent system was determined by the statistical tool 'Mean of Sum of Squared Error' which indicated that both the adsorbent – adsorbate system followed pseudo first-order reaction kinetics.Thermodynamic parameter values such as enthalpy change, entropy change and Gibbs free energy change determined indicated that studied adsorption processes were spontaneous, endothermic with increased randomness at the solid – liquid inter phase. Field studies were carried out with the fluoride containing water sample collected from a fluoride-endemic area in order to test the suitability of the sorbent at field conditions and obtained good success rate.

KEYWORDS: Zirconium, Sodium Hydrdoxide, Adsorbent, Fluoride, Adsorption

***Corresponding author**

P Sri Renganathan

Department of Chemistry,

Merit Arts and Science College, Idaikal, Ambasamudram,

Affiliated to ManonmaniamSundaranar University, Abishekapatti,

Tirunelveli – 627012, TamilNadu, India.

Email :ananthspkc@gmail.com

INTRODUCTION

Fluoride pollution of water can occur due to anthropogenic activities or geochemical processes[1]. The removal of fluoride from water is one of the most important issues due to the effect on human health and environment. Fluoride in drinking water may be beneficial or detrimental depending on its concentration.Though fluoride in minute amounts is an essential component for bones and for the formation of dental enamel in animals and humans[2-6], its high concentration cause irreversible demineralization of bones and tooth tissues which is known as dental and skeletal fluorosis, damageto the brain, liver, and kidney, headache, skin rashes, bone cancer, and even death in extreme cases[7-17].

The optimum fluoride level in drinking water for general good healthset by World Health Organization is 1.5 mg/L[18]. Drinking water is a major source of fluoride intake. There is no treatment for fluorosis but it can be easily prevented. One such preventive measure is defluoridation of water. Available techniques for the removal of fluoride belong to the following three major categories viz., adsorption[19-20], chemical precipitation[21] and ion exchange[22]. Membrane processes such as reverse osmosis[23], nano filtration[24], electro dialysis[25] and Donnan dialysis[26] were investigated to reduce fluoride concentration from water. Among the methods, adsorption technology is economical and efficient method for producing high quality of water. In recent years, a variety of adsorbents like metal loaded adsorbents[1], activated alumina[19], chitosan beads[27], composites[28], activated carbon[29], clay[30], hydroxyapatite[31], etc., have been identified as the promising defluoridatingagents. Hence, In this work, we searched for active carbons derived from plant materials belonging to different classes of plant kingdom. Our primary investigation indicated that there is strong affinity between fluoride and zirconium impregnated active carbon derived from leafs of *Vitexnegundo* plant.

MATERIALS & METHODS:

RAW MATERIAL COLLECTION AND PRETREATMENT

The *VitexNigundo* leaves used in this research ware collected from ‘Tirunelveli’ and washed with deionized water to remove dirt and impurities (fig.1). Afterdriedin an oven at 373 K for 2 hours to reduce moisture content, they were crushed and sieved mechanically to get a uniform sizedistribution. The dried leaf powder was then stored in air tight plastic bags for further experiments.

Figure 1.*VitexNigundo***leaf**

PRODUCTION OF ACTIVATED CARBONS

PRODUCTION OF ZIRCONIUM IMPREGNATED ACTIVATED CARBON

The leaf powder said above was pyrolysed in a muffle furnace at 673K for 2 hours. The charcoal obtained was immersed in 5% $ZrOCl_{2.}8H_2O$ solution in the ratio of 1:1 by weight. The mixture was stirred for 2 days at room temperature and then filtered. The samples were then driedin an oven for 2 hrs at 105^0C to remove water. The charcoal was further carbonized at 600°C in a muffle furnace for 2 hours. Then the product was stored in a desiccator for a certain time and then it was continuously washed using distilled water till the washings attain a neutral pH.Thereafter the carbon was dried in an ovenat 383 K, sieved to get the required particle size and stored in air tight plastic bags. This carbon was designated as zirconium impregnated *VitexNigundo* leaves Activated Carbon (ZVAC) [32].

PRODUCTION OF SODIUM HYDROXIDE IMPREGNATED ACTIVATED CARBON

The leaf powder was pyrolysed in a muffle furnace at 673K for 2 hours. The char coal obtained was immersed in 5% NaOH solution in the ratio of 1:1(wt/wt). The mixture was stirred for 2 days at room temperature then filtered. The samples were then dried in aoven for 2 hrs at 105^0C to remove water. The charcoal was further carbonized at 600°C in a muffle furnace for 2 hours.,Then the product was stored in a desiccator for a certain time and then continuously washed using 1M sulfuricacid so as to remove the activating agents and impurities. Subsequently, the activated carbon waswashed using distilled water to remove the sulfuric acid tillthe washings attain a neutral pH. Thereafter the carbon was dried in an oven, sieved to get the required particle size and stored in air tight plastic bags. This carbon was designated as Sodium impregnated *VitexNigundo* leaves Activated Carbon (SVAC) [33].

SORPTION EXPERIMENTS

Defluoridation experiments were carried out by batch equilibrationmethod in duplicate. In a typical case, 1 g of thesorbent was added to 50 ml of NaF solution of initial concentration3 mg/L. The contents were shaken thoroughly using athermostated shaker rotating at a speed of 200 rpm. The solutionwas then filtered and the residual fluoride concentrationwas measured. Kinetic studies were carried out in a temperaturecontrolled water bath shaker. The effect of initial fluoride concentrationwith different temperatures at 303, 313 and 323 K onsorption rate was studied at the following initial fluoride concentrationsviz., 2, 4, 6, 8 and 10 mg/L by keeping the mass ofsorbent as 1 g and volume of fluoride solution as 50 ml at pH7.

RESULTS & DISCUSSION:

EFFECT OF PARAMETERS ON REMOVAL OF FLUORIDE

EFFECT OF PH

pH is one of the important parameter that affect adsorption process. Acidic condition always favors the adsorption of anion onto the surface of the solid adsorbent because at acidic condition, the solid adsorbent have positive charge on its surface due to adsorption of excess H^+ ions which would exert columbic attraction towards anions. But in the case fluoride adsorption, it is different due to speciation of fluoride in acidic pH. At pH at less than 3, fluoride ion exist as neutral Hydrofluoride[34]. Hydrofluoride molecules will have low affinity for the positively charged adsorbent surface at acidic solution pH. When the solution pH is increased, the concentration of HF would decrease due to the decrease of H^+ ions in the solution and hence the fluoride ion concentration would increase. Inorder to understand the influence pH on the speciation of fluoride ion, concentration of fluoride ion solution (10 mg/L) under different solution pH ranging from 2 to 12 was determined using ‘Labman pH ion meter’. Obtained results are shown in the fig.2& 3.It is observed that maximum concentration (10 mg/L) is observed at pH 7.It infers that fluoride exist as F^- ion at pH 7 and acidic and alkaline solution lower the existence of F^- ion in the solution.It also revealed that all the fluoride ions might be converted as HF molecule below pH 5. Hence it is more appropriate to conduct the adsorption study in neutral medium. Further at alkaline solution, there will be competition between fluoride ion and hydroxide ion towards the adsorption site. Therefore present adsorption study was carried out at neutral pH. Optimum pH maintained for fluoride removal by various researchers.

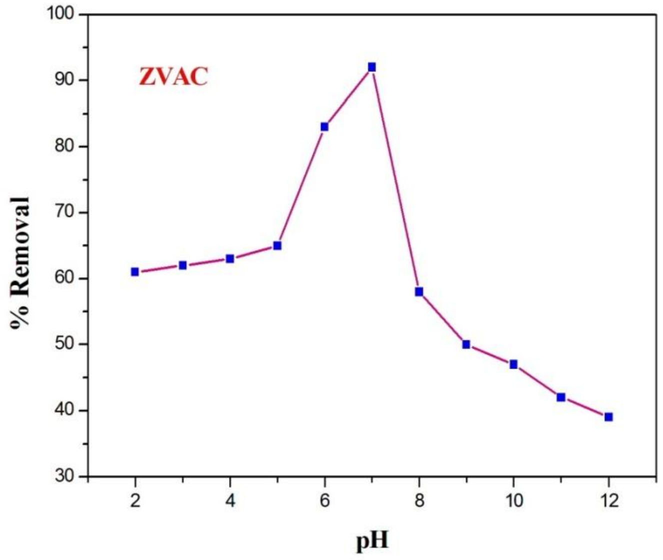

Figure 2. Effect of pH on ZVAC

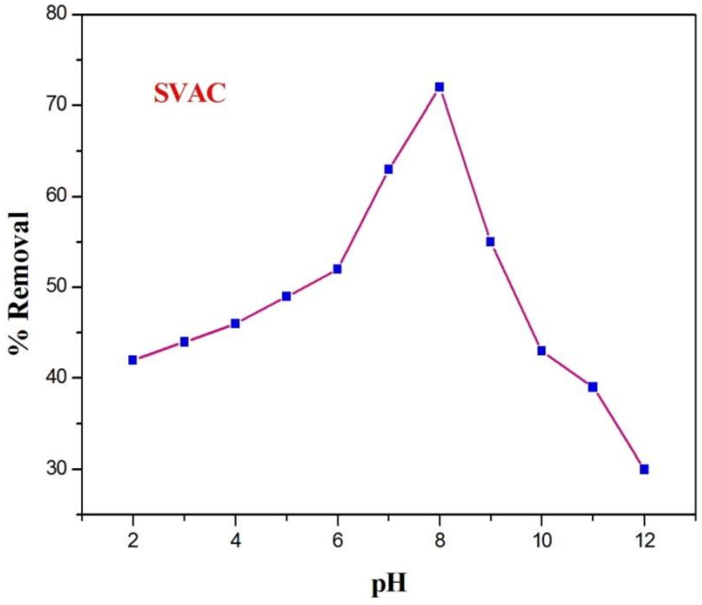

Figure 3. Effect of pH on SVAC

EFFECT OF ADSORBENT DOSAGE

Adsorption efficiency of adsorbents was analyzed using 10 mg/L fluoride solution. Dose of adsorbents varied from 10 – 100 mg /50 mL having agitation time 3 hrs. at 305K temperature. The effect of adsorbent dose on percentage of removal was shown in Table: 1 and in fig. 4. Different doses of adsorbents ranging from 10 mg – 100 mg per 50 mL were studied and other process parameters were maintained constant. It is evident that the percentage of fluoride removal increased with the increase of the sorbent concentration which is due to the fact that a greater amount of sorbent implies a greater amount available binding sites. The percentage removal increased with the increase of adsorbent dose.80 mg/50 mL was chosen for further studies[35]. This is due to the enhanced active sites with an increase in the amount of adsorbent. Similar studies are also reported by sundaram et al [36].

Table: 1 Effect of dose on percentage of removal

(Ci : 10 mg/l Contact time : 3hrs)

Dose in mg/50 mL	**% of Removal**	
	ZVAC	**SVAC**
10	31.60	18.6
20	43.20	27.3
30	52.10	34.9
40	55.70	42.6
50	59.30	44.8
60	62.50	48.7
70	65.10	52.1
80	67.50	53.8
90	69.80	55.9
100	72.30	57.4

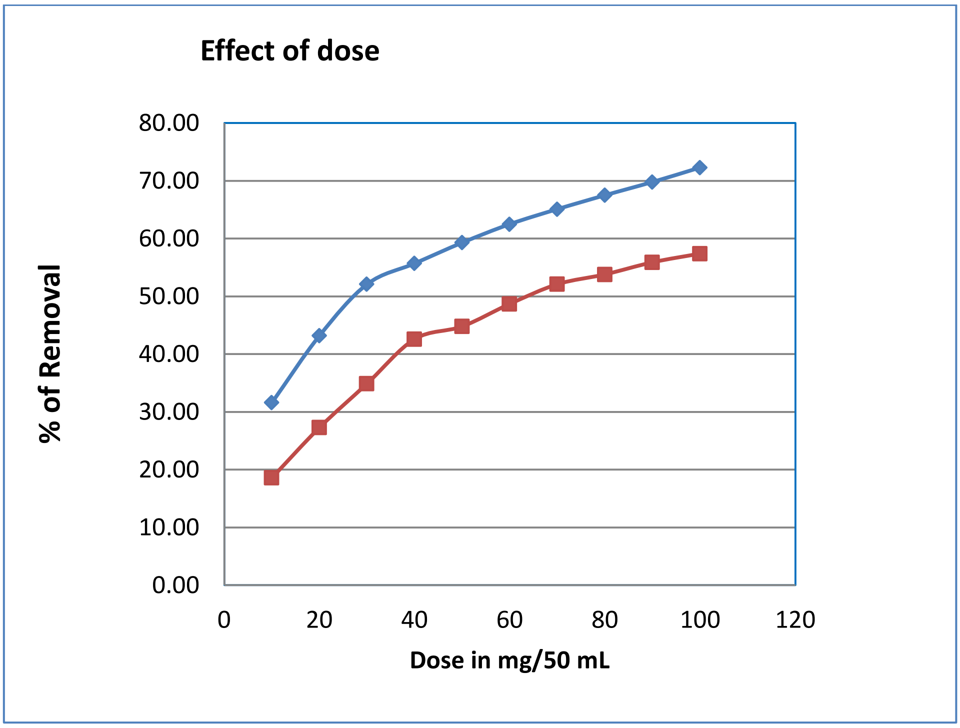

Figure 4. Effect of Dose

EFFECT OF CONTACT TIME

The equilibrium time for the sorption isotherm needs to be identified before any other experiments are conducted. The influence of contact time on removal of fluoride was conducted by using synthetic test solution and the extent of removal of the fluoride ion was also known by varying the contact time from 5 to 210 min, with 6,8.10,12 and 14 mg/L of fluoride ion concentration. Contact time was found to have an effect on the percentage removal of fluoride from aqueous solution.Initially as contact time increases, the percentage removal of the fluoride ion was increased gradually and after a certain time it became almost constant indicating an attainment of equilibrium condition. The equilibrium was reached at 180-190 minutes. The rate of removal of the fluoride ion with time was higher at initial stages because in the beginning, all adsorbent sites were vacant and the solute concentration gradient was high. Later, the fluoride uptake by adsorbent decreased significantly, due to the decrease in the number of adsorption sites[37]. The results obtained were plotted as percentage removal of the fluoride ion versus contact time (min) as shown in fig. 5 and 6. Percentage of removal was found to high for ZVAC when compared to SVAC at same experimental conditions. Thus changing the activation method influenced percentage removal of fluoride. This may be due to change in the total pore volume and surface area. Therefore 180 min in fixed as optimum contact time for maximum defluoridation of the sorbents. Based on these findings, the contact time of 180 min was fixed for further experiments.

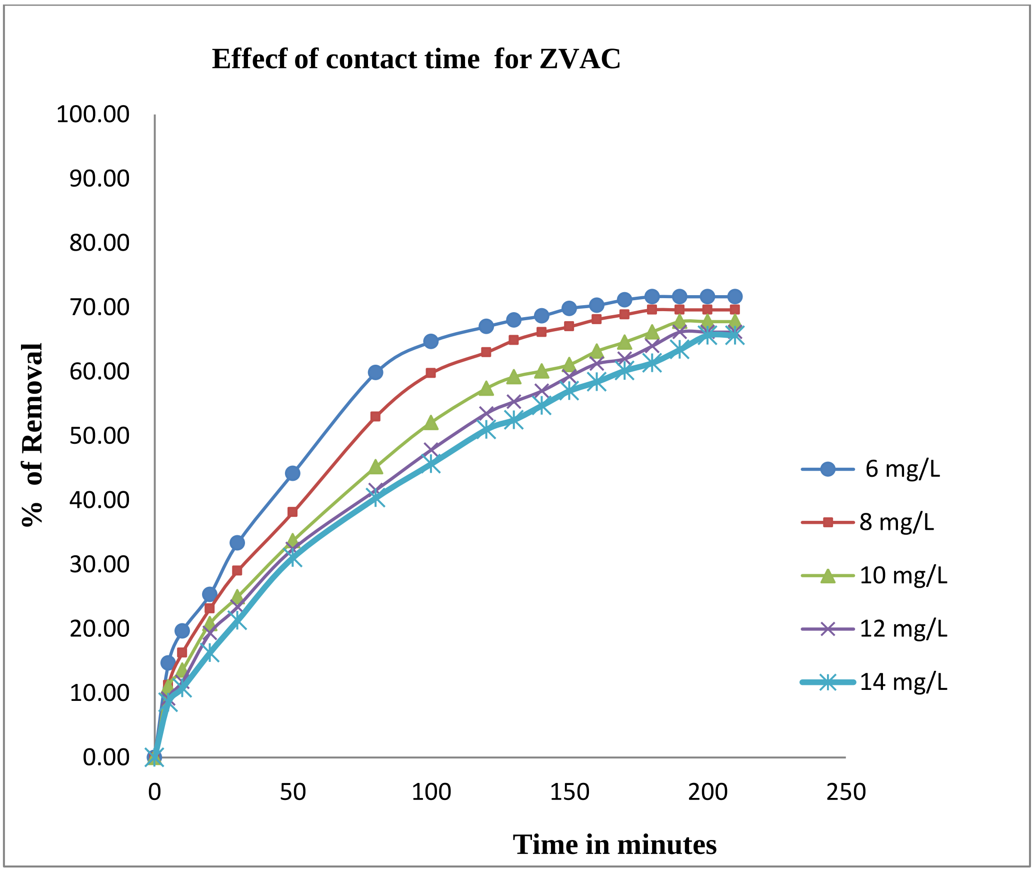

Figure 5. Effect of Contact time for ZVAC

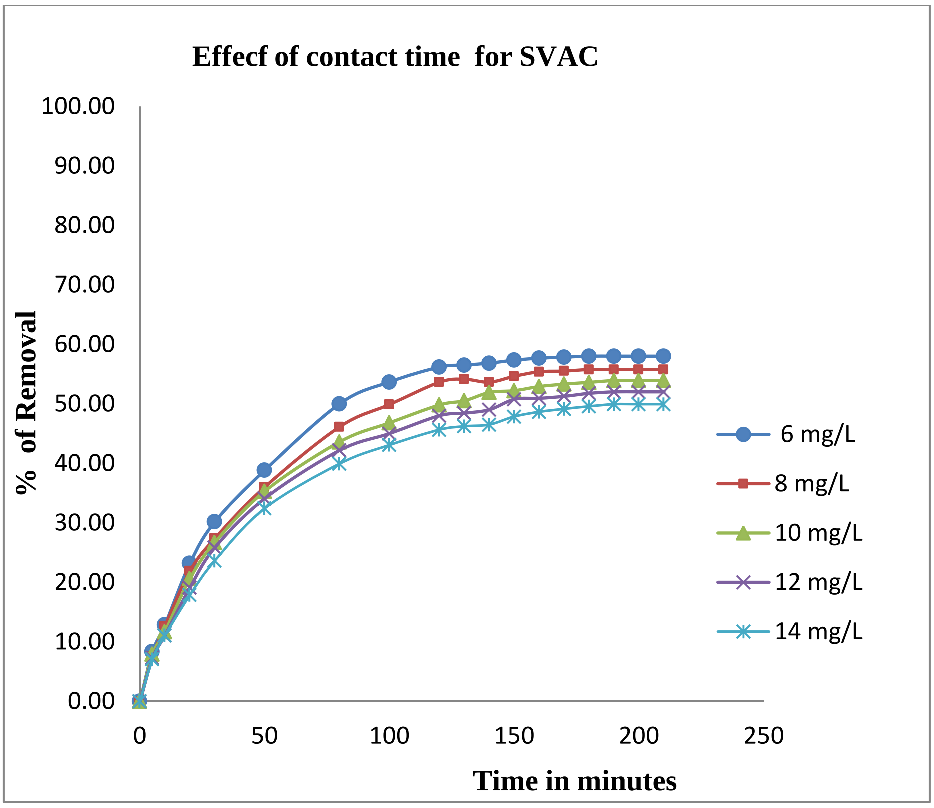

Figure 6. Effect of Contact time for SVAC

EFFECT OF INITIAL CONCENTRATION AND TEMPERATURE

The percentage of removal of fluoride ion from aqueous solution at equilibrium found to decrease with the increase of initial concentration of adsorbate and the percentage of removal of fluoride ion from aqueous solution at equilibrium found to increase with the increase of temperature as shown in Table: 2, fig. 7 and fig. 8. It means that the fraction of adsorbate transferred from liquid phase to solid phase decreased with the increase of solution concentration. This is because, the ratio of available adsorption sites on the adsorbent surface to amount of solutes in the liquid phase decrease with the increase of initial concentration of the adsorbatesolution[38].But the actual amount of fluoride adsorbed per unit mass of adsorbent increased with increase in the initial concentration of adsorbate solution (fig. 9 & 10). This shows that the adsorption is highly dependent on the initial concentration of the solution[38]. This is because, though the fraction of solutes transferred from the solution to adsorbent decreased with the increase of concentration of adsorbate solution, the amount of solutes in each fraction of the solution is proportional to concentration of the solution.The adsorption capacity was found to be high for ZVAC when compared to SVAC.

Table: 2 Effect of initial concentration and temperature

Dose: 80 mg/50 mL pH :7 Time :210 mins

TEMP(K)	C_i	%R		q_e	
		ZVAC	SVAC	ZVAC	SVAC
305	6	71.67	58.00	2.69	2.18
	8	69.63	55.75	3.48	2.79
	10	67.80	53.90	4.24	3.37
	12	66.17	52.00	4.96	3.90
	14	65.64	49.93	5.74	4.37
315	6	76.00	61.33	2.85	2.30
	8	74.63	58.63	3.73	2.93
	10	72.70	56.90	4.54	3.56
	12	71.75	55.33	5.38	4.15
	14	70.64	53.43	6.18	4.68
325	6	80.83	66.33	3.03	2.49
	8	78.38	64.00	3.92	3.20
	10	76.70	62.20	4.79	3.89
	12	76.25	61.08	5.72	4.58
	14	75.57	58.14	6.61	5.09
335	6	83.17	72.00	3.12	2.70
	8	81.63	69.38	4.08	3.47
	10	80.60	67.40	5.04	4.21
	12	79.92	66.17	5.99	4.96
	14	78.86	64.21	6.90	5.26

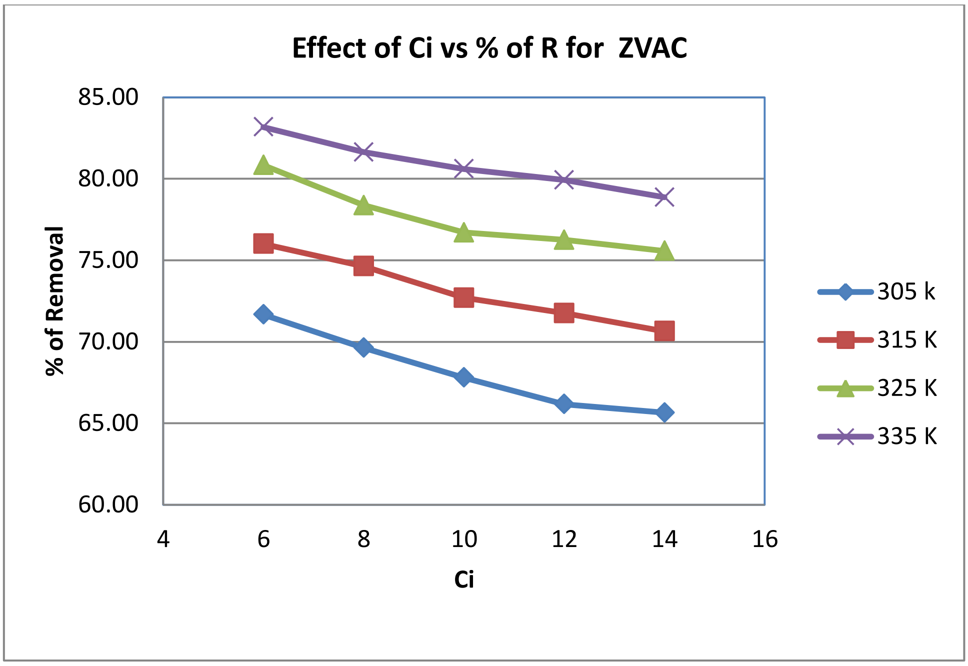

Figure 7. Effect of Civs of R for ZVAC

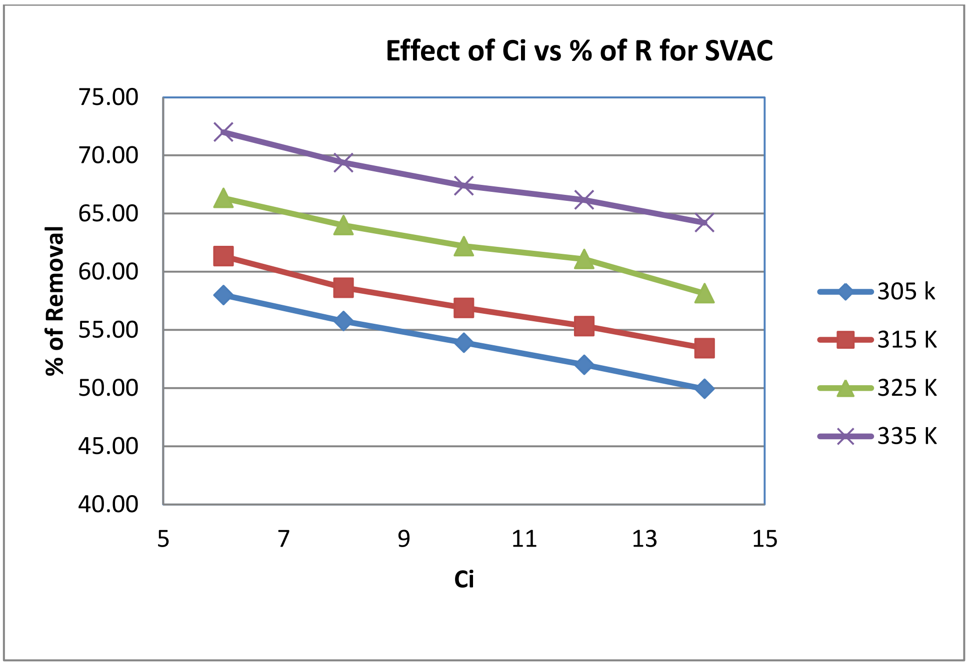

Figure 8. Effect of Civs of R for SVAC

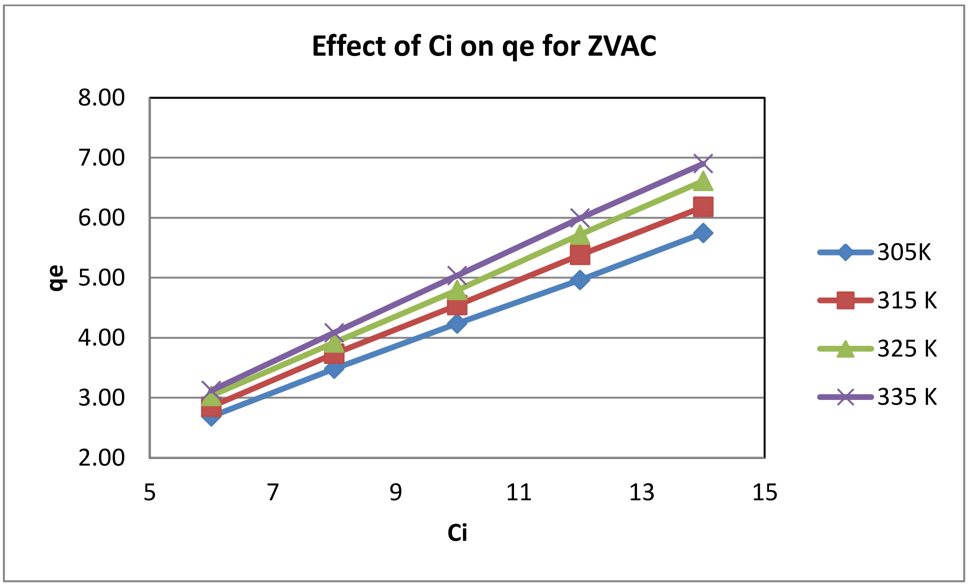

Figure 9. Effect of Ci on qe for ZVAC

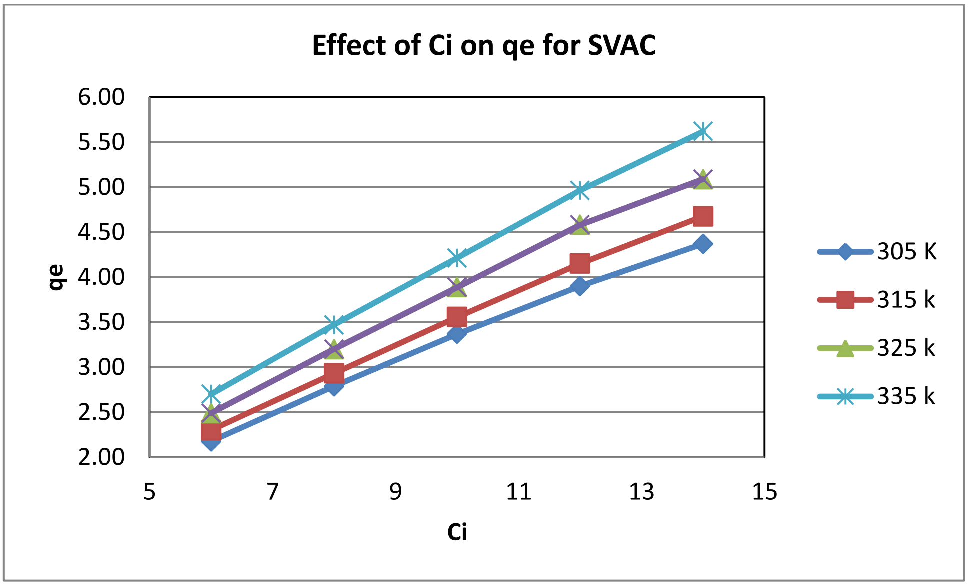

Figure 10.Effect of Ci on qe for SVAC

ADSORPTION ISOTHERM MODELS

Adsorption isotherm is mathematical model relating the amount of adsorbate adsorbed onto the adsorbent and the equilibrium concentration of the adsorbate in solution at a given constant temperature[39].

The adsorption isotherm is the most widely used method for representing the equilibrium states of an adsorption system. The objective of an adsorption isotherm is to relate the adsorbate concentration in the bulk solution to the amount adsorbed at the solid surface. These isotherms relate solute uptake per unit mass of adsorbent (q_e) to the equilibrium adsorbate concentration in the bulk fluid phase (C_e). Adsorption isotherm helps in determining the feasibility of adsorption process. The variation of extent of adsorption with concentration of solute is correlated by linear, form of Freundlich, Langmuir, Temkin and DubininRadushkevich isotherms.

FREUNDLICH ISOTHERM MODEL

Freundlich isotherm is the widely used model for a single solute system .It assumes that sorption energy exponentially decreases on completion of the sorptionalcentres of an adsorbent. The Freundlich model describes the adsorption within a small range only. It describes the adsorption of organic and inorganic compounds on a wide variety of adsorbents[40].

This equation has the following form:

$$\log q_e = \log K_f + 1/n \log C_e$$

whereq_e is the amount of adsorbate adsorbed (mg/g) at equilibrium, C_e is the equilibrium concentration of adsorbate in solution (mg/L) and K_f and n are the constants.

Freundlich adsorption isotherms were plotted between log q_e and log C_e as shown in fig. 11 & 12.The values of K_f and n were calculated from the intercept and slope of the plots which were given in Table: 3. The Freundlich isotherm describes reversible adsorption and was not restricted to the formation of monolayer. The isotherm was found to be linear as evidenced from correlation coefficients obtained. The value of $K_f$signifies the adsorption capacity and the value 'n' signifies adsorption intensity. A smaller value of 1/n, points out a better adsorption mechanism and formation of relatively stronger bond between adsorbate. If $1/n < 1$, bond energies increases with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$ all surface sites are equivalent[41]. The similar results were also obtained by Maliyekkalet al[42] while studying the defluoridation by activated alumina and manganus coated alumina. The "n" should have values lying in the range of 1–10 for favorable adsorption. A smaller value of n indicates a weaker bond between adsorbate and adsorbent. The K_f value of ZNAC and SVAC was found to be 3.1 (mg/g) and 1.9 (mg/g) at 33K respectively. The magnitude of K_f showed a good fluoride adsorption capacity by ZVAC and SVAC from aqueous solution at all the temperature studied. It is observed that the correlation coefficient (r^2) value in the Freundlich model was near to unity. Adsorption capacity K_f values are found to be high for ZVAC when compared to SVAC which agrees with the experimental adsorption capacity values. Smaller 'n' values of present study shows that the adsorbent – adsorbate interaction intensity is small which infers the predominance of physisorption.

Table: 3Freundlich isotherm results

Adsorbent	Temperature (K)	n	K_f (mg/g)	R^2
ZVAC	305	1.39	1.8	0.99
	315	1.36	2.2	0.99
	325	1.40	2.7	0.99
	335	1.34	3.1	0.99
SVAC	305	1.46	1.2	0.99
	315	1.44	1.3	0.99
	325	1.45	1.5	0.99
	335	1.48	1.9	0.99

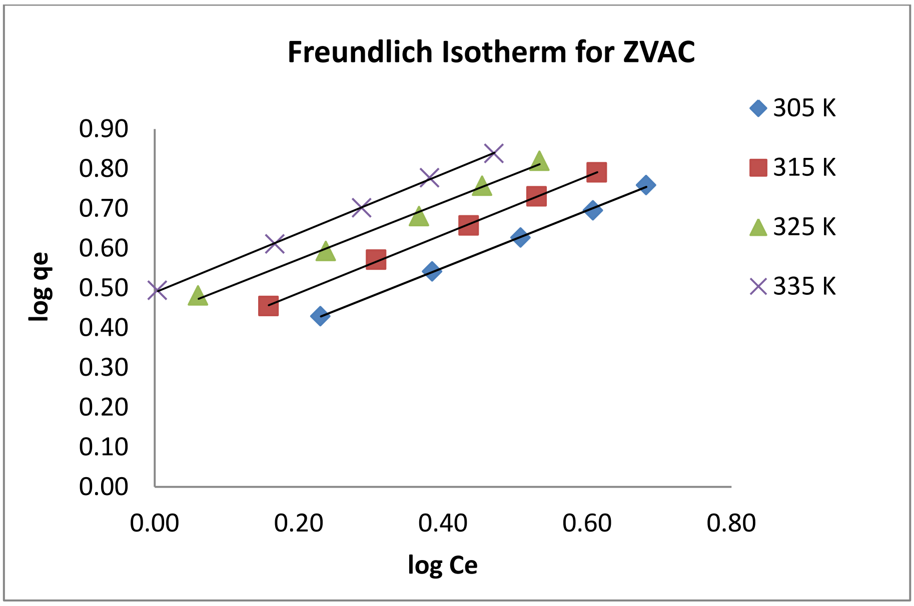

Figure 11.Freundlich Isotherm for ZVAC

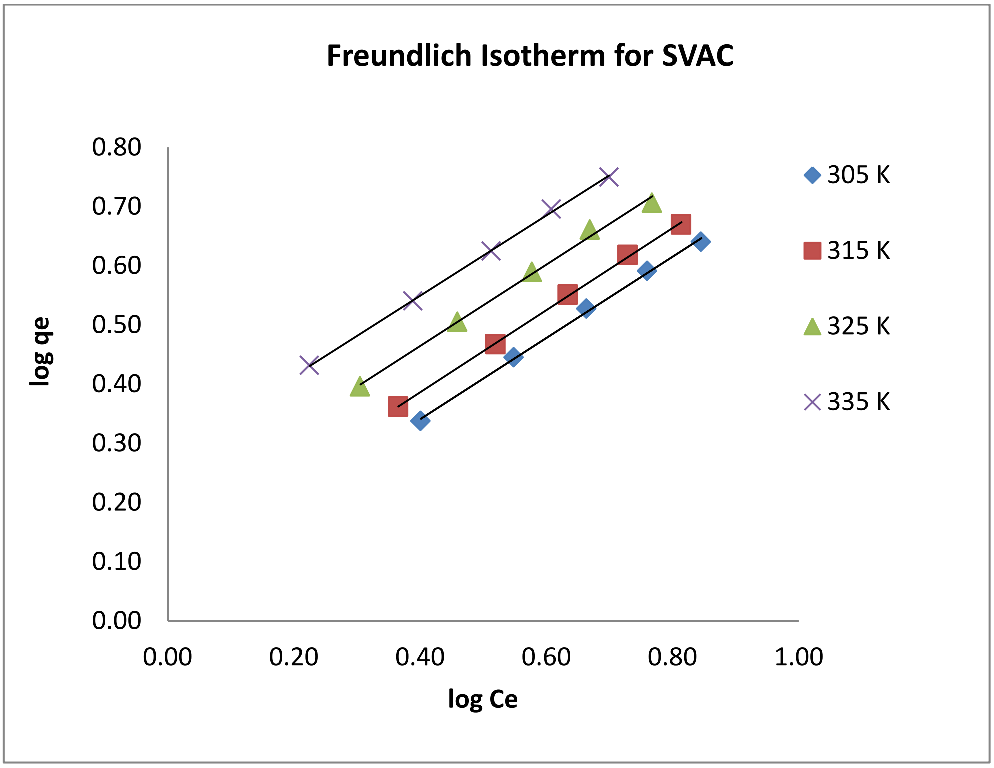

Figure 12.Freundlich Isotherm for SVAC

LANGMUIR ISOTHERM

It is a widespread-used model for describing heavy metal ion sorption onto adsorbent. Langmuir equation relates to the coverage of molecules on a solid surface and the concentration of contacting solution at a fixed temperature.

This isotherm is based on the following assumptions such as adsorption limited to monolayer coverage, all surface sites being alike. One site accommodates one species of the adsorbates and the ability of a molecule to be adsorbed on a given site independent of itsneighbouring sites occupancy[43]. Langmuir equation is written in the following form

$$Q_e = Q_m b\, C_e / 1 + b\, C_e$$

This equation is often written in linear form as

$$C_e/Q_e = 1/Q_m b + C_e/Q_m$$

where $Q_e$is the amount of solute adsorbed per unit weight of adsorbent (mg/g), $C_e$the equilibrium concentration of solute in the bulk solution (mg/L), Q_m is the maximum monolayer adsorption capacity or saturation capacity (mg/g) and b is the adsorption energy, b is the reciprocal of the concentration at which half saturation of the adsorbent is reached. The linear equation is often preferred because of its simplicity and convenience[44].

The essential characteristics of Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation

$$R_L = 1 / (1+ bC_0)$$

Where C_0 is the initial concentration of the adsorbate solution. The separation factor R_L indicates the shape of the isotherm and the nature of the adsorption process as given below:

Table: 4 Nature of the adsorption process

R_L value	**Nature of the process**
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Plots drawn for Langmuir isotherm are shown in fig.13&14. Results obtained from Langmuir model for the adsorption of dyes and metal ions are presented in Table: 5. Regression coefficient values infer the good fitting of data with Langmuir plots. Q_m values of ZVAC & SVAC found to increase with the increase of temperature which support the endothermic nature of adsorption. In the present study, the value of maximum adsorption capacity (Q_m) calculated from the Langmuir isotherm is much higher than that which was mentioned in the previous reported by Karthikeyan*et al*andGopal*et al*[45-46].Q_m values of some adsorbents are collected for comparison sake. Mono layer adsorption capacities (Q_m) are found to be reasonable for ZVAC & SVAC when compared to other adsorbents. Between ZVAC & SVAC, ZVAC found to have higher Q_m values.

Separation factor $R_L$valuescalculated are given in the Table: 4.All the values are in between 0 and 1 which indicates the favourable adsorption processes.

Alagumuthuet al[32] reported the Langmuir constant b is an energy term which varies as a function of surface coverage strictly due to variation in the heat of adsorption. The Langmuir constant b value of CNSC and ZICNSC are 24.33-108.0 and 20.16 – 6.3 (L/g) at 303K – 333K respectively. The magnitude of the Langmuir constant b has small value which indicates a low heat of adsorption [47-48]. The Langmuir constant b value of CNSC was much higher than that of ZICNSC. The higher energy sites with high equilibrium constant (b value of CNSC) has a lower affinity than the lower energy sites with low equilibrium constant (b value of ZICNSC). The similar results have been reported by various researchers[39,49-51]. The essential characteristics of the Langmuir isotherm canbe expressed by dimensionless constant separation factor called equilibrium parameter R_L[51].

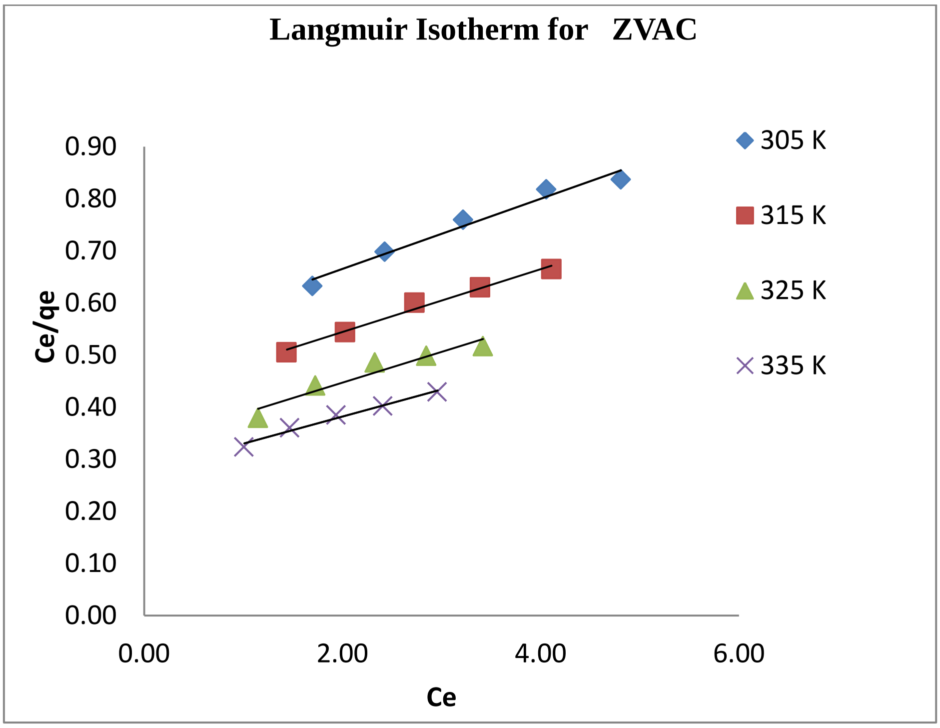

Figure 13. Langmuir Isotherm for ZVAC

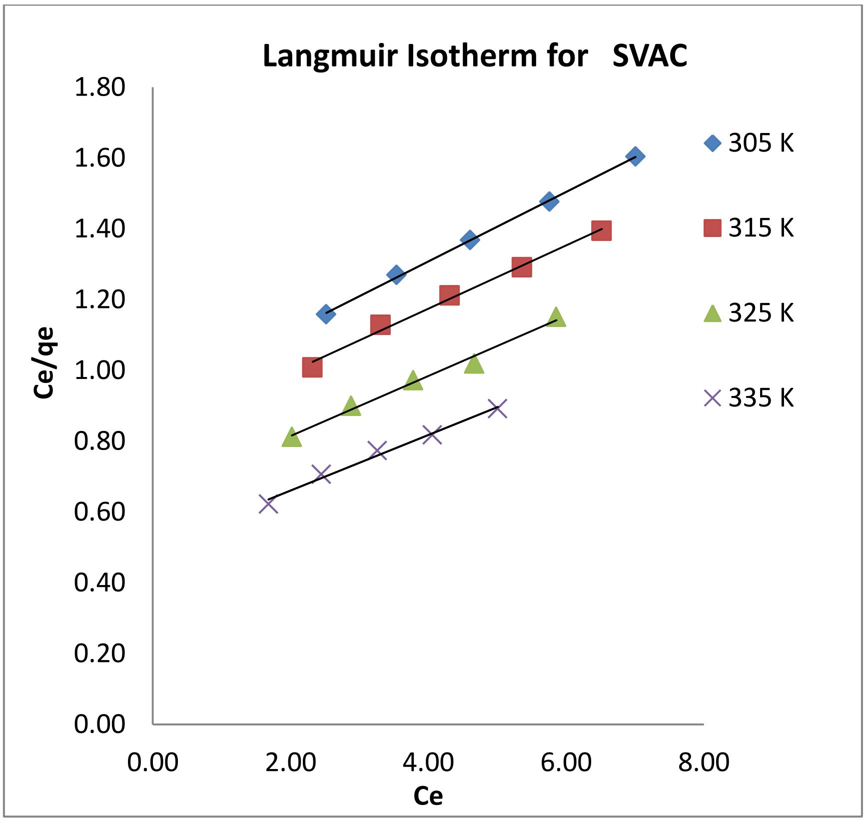

Figure 14. Langmuir Isotherm for SVAC

Table: 5 Langmuir isotherm results

Adsorbent	Temperature (K)	Q_m (mg/g)	b (L/mg)	R^2
ZVAC	305	14.8	0.127	0.97
	315	16.6	0.143	0.98
	325	16.9	0.180	0.91
	335	19.2	0.187	0.98
SVAC	305	10.2	0.107	0.99
	315	11.2	0.109	0.99
	325	11.8	0.131	0.98
	335	12.7	0.156	0.98

PSEUDO FIRST ORDER KINETICS MODEL

Largergren (1898) introduced this model for the adsorption in solid/liquid systems based on the chemical kinetic first-order equation .It is simple kinetic model that describes the process of adsorption[34].

The integral form of the model equation expressed as follows

$$\log (q_e - q_t) = \log q_e - k_1 / 2.303 \times t$$

Where, q_e and q_t (mg/g) are the amount of fluoride that was adsorbed at the equilibrium and at time t (min), respectively and K1 (1/min) is the rate constant. The Pseudo first order rate constant (K_1) for fluoride adsorption onto ZVAC was 2.35 to 3.16 and for SVAC 2.35 to 3.16 at 6-14 mg/L of fluoride. The pseudo-first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The values of log (q_e – q_t) were linearly correlated with t. The values of k_1 and q_e were calculated from the slopes and intercepts of log (q_e – q_t) against the *t* plots. The pseudo first order plots of fluoride adsorption are shown in Figures 15 and 16.Different parameters of pseudo first order kinetics are given in Table 6 & 7.

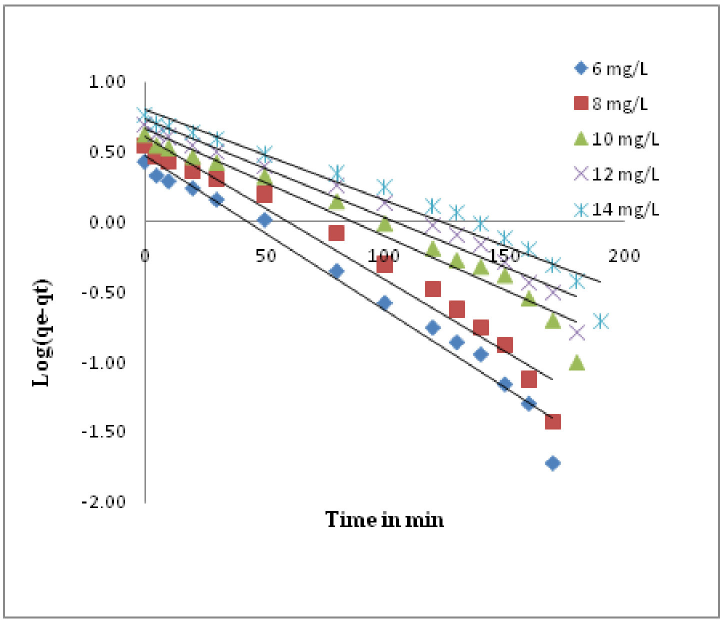

Figure 15.Lagergren plot for ZVAC

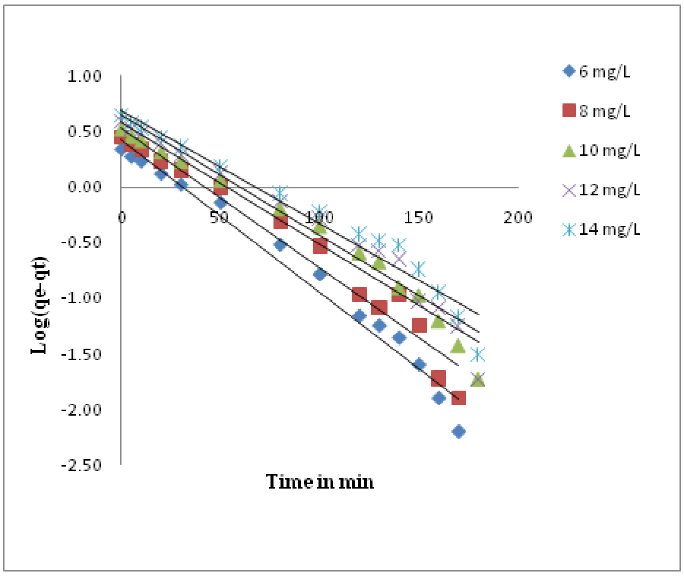

Figure 16.Lagergren plot for SVAC

Table: 6 Pseudo first order Kinetics results for ZVAC

C_i (mg/L)	$k_1 \times 10^{-2}$ (min^{-1})	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	Δq_e	R^2	MSSE
6	3.16	3.0	2.7	0.3	0.97	0.2
8	2.90	4.0	3.5	0.6	0.96	
10	2.56	4.6	4.2	0.4	0.95	
12	2.51	5.4	5.0	0.4	0.95	
14	2.35	6.3	5.7	0.5	0.95	

Table: 7Pseudo first order Kinetics results for SVAC

C_i (mg/L)	$k_1 \times 10^{-2}$ (min^{-1})	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	Δq_e	R^2	MSSE
6	3.16	2.7	2.2	0.5	0.97	0.25
8	2.90	3.4	2.8	0.6	0.96	
10	2.56	3.9	3.4	0.5	0.97	
12	2.51	4.5	3.9	0.6	0.96	
14	2.35	4.9	4.4	0.5	0.96	

PSEUDO SECOND ORDER KINETIC MODEL

The pseudo second-order adsorption kinetic rate equation is expressed in linearized integral formas;

$$t/q_t = 1/ k_2.q_e^2 +1/q_e\ t$$

The values of (t/qt) were linearly correlated with t and gave a linear relationship from which qeandk_2 can be determined from the slope and intercept of the plot, respectively[52]. Plots drawn for Pseudo second order kinetic model are shown in Fig 17 & 18. Different parameters of pseudo first order kinetics are given in Table 8 & 9. The initial sorption rate increased with an increase in the temperature. The value of h was varied from 0.06 to 0.09 mg g^{-1} for ZVAC and 0.05 to 0.09 mg g^{-1} for SVAC respectively[53] also reported the similar result when increasing sorption rate was obtained with increasing initial concentration. This could be probably due to different available surface sites with initial concentration resulting in variation of rate constants.

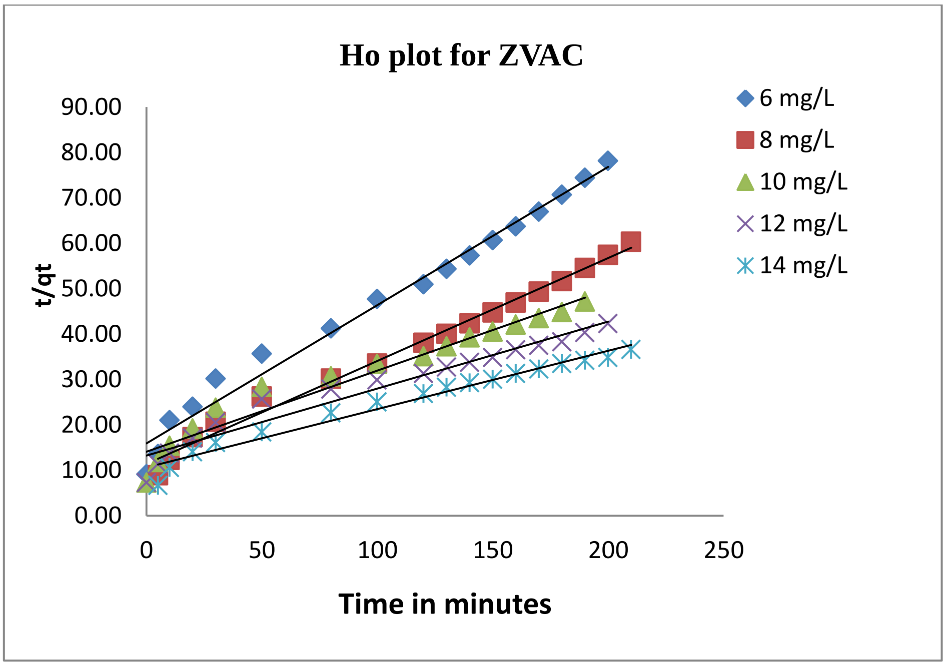

Figure 17. Ho Plot for ZVAC

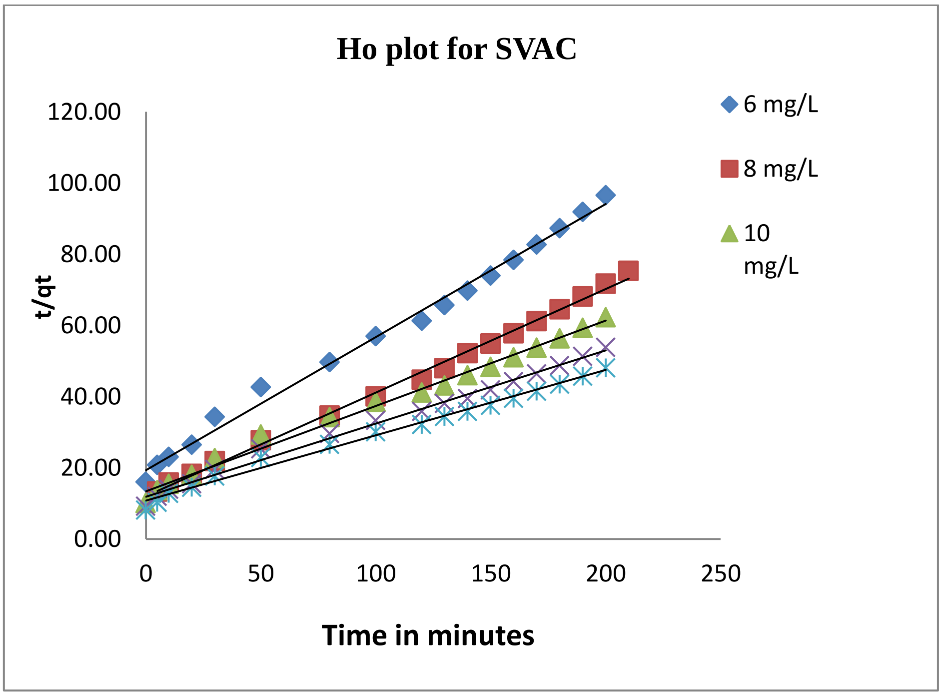

Figure18. Ho Plot for SVAC

Table: 8 Pseudo second order Kinetics results for ZVAC

C_i (mg/L)	$k_2 \times 10^{-3}$ (g/mg.min)	h mg g^{-1} min^{-1}	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	Δq_e	R^2	MSSE
6	5.8	0.06	3.28	2.69	0.6	0.98	0.65
8	4.5	0.09	4.41	3.48	0.9	0.98	
10	2.3	0.07	5.60	4.24	1.4	0.94	
12	1.6	0.08	6.78	4.96	1.8	0.94	
14	1.5	0.09	7.79	5.74	2.1	0.97	

Table: 9 Pseudo second order Kinetics results for SVAC

C_i (mg/L)	$k_2\times10^{-3}$ (g/mg.min)	h mg g^{-1} min^{-1}	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	Δq_e	R^2	MSSE
6	7.2	0.05	2.67	2.2	0.5	0.99	0.37
8	7.0	0.08	3.44	2.8	0.6	0.99	
10	4.3	0.07	4.18	3.4	0.8	0.99	
12	3.6	0.08	4.86	3.9	1.0	0.99	
14	3.1	0.09	5.44	4.4	1.1	0.99	

CONCLUSION

In this work, two types of activated carbons were prepared from the leaves of *VitexNigundo*. One type by impregnating with Zirconyloxychloride solution and the other is by impregnating with Sodium hydroxide and they are designated as zirconium-impregnated *VitexNigundo* activated carbon (ZVAC) and Sodium hydroxide impregnated *VitexNigundo* activated carbon (SVAC) respectively. Removal of fluoride ions from synthetic aqueous solution has been investigated using these activated carbons. The experimental parameters were adsorbent dosage, contact time, initial concentration and temperature. The results indicated that increase in adsorption with the increase of contact time and adsorbent dosage. The equilibrium time was found to be around 3 hours. Initial solution pH was maintained as 7 because acidic and alkaline solutions reduce the F^{-} ion concentration in the solution. ZVAC and SVAC found to remove 71.6 % and 58 % of F^{-} ions respectively from F^{-} ion solution of 6 mg/L concentration when the adsorbent dose was1.6 g/L and the contact time was 210 minutes. The concentration of fluoride found to affect the defluoridation capacity of the adsorbent. The fluoride adsorption capacity was increased with the increase of initial concentration of fluoride ion solution as well as with the increase of temperature. Adsorption capacity of ZVAC found to be high when compared to SVAC under similar experimental conditions. Equilibrium adsorption study data were fitted into Langmuir and Freundlich isotherms. Significances of values of constants obtained from these isotherms were discussed well .Theoretical adsorption capacities calculated from the isotherm plots were found to be high for ZVAC than SVAC. The adsorption kinetics was investigated and best kinetic model describing each adsorbate – adsorbent system was determined by the statistical tool 'Mean of Sum of Squared Error' which indicated that both the adsorbent – adsorbate system followed pseudo first-order reaction kinetics. The carbon loaded with fluoride ions indicates that existence of some chemical interactions though majority adsorptions took place via physisorption. This study confirmed that leaves of *VitexNigundo* could be used for the production of activated carbon for the removal of fluoride from water.

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