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Research Paper

Adsorption characteristics studies on removal of Cr (VI) from aqueous solution by using Casuarina equisetifolla

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Abstract-*In this research, adsorption of chromium (VI) ions on Casuarina equisetifolla has been studied through using batch adsorption techniques. The main objectives of this study are to 1) investigate the chromium adsorption from aqueous solution by Casuarina equisetifolla, 2) study the influence of contact time, pH, adsorbent dose and initial chromium concentration on adsorption process performance and 3) determine appropriate adsorption isotherm and kinetics parameters of chromium (VI) adsorption on Casuarina equisetifolla. The results of this study showed that adsorption of chromium by Casuarina equisetifolla reached to equilibrium after 60 min and after that a little change of chromium removal efficiency was observed. Higher chromium adsorption was observed at lower pHs, and maximum chromium removal (96.1 %) obtained at pH of 2. The adsorption of chromium by Casuarina equisetifolla decreased at the higher initial chromium concentration and lower adsorbent doses. The obtained results showed that the adsorption of chromium (VI) by Casuarina equisetifolla follows Langmuir isotherm equation with a correlation coefficient equal to 0.984. In addition, the kinetics of the adsorption process follows the pseudo second-order kinetics model with a rate constant value of 0.0185 g/mg.min The results indicate that Casuarina equisetifolla can be employed as a low cost alternative to commercial adsorbents in the removal of chromium (VI) from water and wastewater.*

Key words: *Heavy metals, natural adsorbents, isotherm, kinetics, Thermodynamics*

Introduction

One of the heavy metals that have been a major focus in water and wastewater treatment is chromium and the hexavalent form of it has been considered to be more hazardous due to its carcinogenic properties[1]. Chromium has been considered as one of the top 16th. Toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern[2].Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production[3]. Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard[4]. In addition, National Iranian standard for Cr (VI) concentration in drinking water is 0.05 mg/L (ISIRI number 1053, 1991). There are various methods to remove Cr (VI) including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis[5]. These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost[6]. For this purpose in recent years, investigations have been carried out for the effective removal of various heavy metals from solution using natural adsorbents which are economically viable such as agricultural wastes including sunflower stalks[7], Eucalyptus bark[8], maize bran[9], coconut shell, waste tea, rice straw, tree leaves, peanut and walnut husks[10]. The bran of wheat is the shell of the wheat seed and contains most nutrients of wheat. This bran is usually removed in the processing of wheat into flour. Recently a few studies have been done on removing heavy metals such as pb (II) [11], Cu (II) and Cd (II)[12] by Casuarina equisetifolla. In this study, Casuarina equisetifolla had been used for Cr (VI) removal from aqueous solution. The aims of this study are to 1) investigate the chromium adsorption from aqueous solution by Casuarina equisetifolla 2) study the effect of different parameters such as contact time, pH, adsorbent dose and initial chromium concentration on adsorption process and 3) find optimum adsorption isotherm as well as the rate of adsorption kinetics.

Experimental work

Instrumentation

The pH was adjusted with a digital pH meter (Jenway Model 3320) using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). Chromium (VI) was estimated with a UV/VIS spectrophotometer (Labomed UVD 3500) at λmax 540 nm.

Preparation of adsorbent

Casuarina equisetifolla, collected from the Tranquebar coastal area, was crushed with laboratory-scale crushers, powdered with a disk pulverizer, and sieved to 0-63 mesh (ASTM). The powdered adsorbent was washed, dried at 105 ◦ C for 10 h in an oven, and stored in high-density polythene (HDPE) bags. The proximate analysis of the coal was carried out by using standard methods (ASTM D 5142-90). Powdered adsorbent was soaked in HCl (0.1 mol L^{-1}) for 24 h, followed by filtering and washings with distilled water. Afterwards, it was dried in an oven at 105 ◦ C for 10 h and stored in HDPE bags.

Chemicals

All chemicals used during experimental work were of analytical grade and were used as such without purification. Chromium (VI) (Fluka), HCl (E. Merck 11.6 M). Double distilled water was used for the preparation of all types of solution and dilution when required.

Instrumentation

Balance ER-120A (AND), Electric grinder (Kenwood), pH meter HANNA pH 211 (with glass electrode), UV/VIS spectrophotometer (Labomed, Inc. Spectro UV-Vis double beam UVD = 3500).

Standard Solutions

The stock Chromium (VI) solution was prepared by dissolving accurately analar grade of 500 mg of $K_2Cr_2O_7$. in 250 ml of Double distilled water to make it to 700 ppm solution. Form this stock solution, 10,20,30,40, 50 & 60 ppm solutions were prepared by diluting it suitably.

Adsorption

Experiments

The adsorption studies were carried out at 30 ± 1 ^{o}C. pH of the solution was adjusted with 0.1 N HCl. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture were filtered and the remaining metal ion concentration were determined in the filtrate using (Spectro UV-Vis Double Beam UVD- 3500, Labomed.Inco) at λ_{max} = 540 nm.The effect of various parameters on the rate of adsorption process were observed by varying mesh size of adsorbent, contact time, t , initial concentration of metal ion C_o , adsorbent amount , initial pH of solution and temperature. The solution volume (V) was kept constant 50 mL).The metal ion adsorption (%) at any instant of time was determined by the following equation:

Metal ion adsorption (%) =
$(C_o – C_e) \times 100/ C_o$

Where C_o is the initial concentration and C_e is the concentration of the metal ion at equilibrium. To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

Isotherm studies

A series of experiments were carried out for isothermal and kinetic study of Casuarina equisetifolla adsorption of Chromium (VI) metal ion. Langmuir (eq :1) ,Freundlich(eq :2) ,Temkin(eq :3) ,Harkin-Jura (eq :4),Halsey(eq :5),Redlich-peterson(eq :6) and ,Dubinin-Kaganer-Radushkevich(DKR) (eq :7) were plotted by using standard straight-line equations and corresponding parameters were calculated from their respective graphs.

$Ce/X = 1/K{*}K_L + Ce/ K$ -----------------------(1)
$\text{Log } qe = \log K_F + 1/n \log Ce$ -----------------------(2)
$qe = K_T \ln Ce + b_T$ ------------------------ (3)
$1/qe2 = B/A - 1/A \log Ce$ ------------------------ (4)
$\text{Ln } qe = 1/n \ln K – 1/n \ln Ce$ ------------------------ (5)
$qe = K_R Ce / (1+b_RCe\beta)$ ------------------------ (6)
$\text{Log } qe = \log Xm – \beta\varepsilon^2/2.303$ ------------------------ (7)

K(mg/g) : an indicator of the adsorption capacity,1/n (mg/L): adsorption intensity, **ε** (the Polanyi potential) = RT ln (1 + 1/Ce),qe: the amount of metal ions adsorbed per unit weight of Casuarina equisetifolla (mg/g), K′**:** constant related to the adsorption energy (mol2/KJ2),R: gas constant (kJ/K.mol),T**:** temperature (K),Ce is the equilibrium concentration of the adsorbate (mg/L) and X is the amount of adsorbate adsorbed (mg/g). K_L indicates monolayer adsorption capacity (mg/g),K is the Langmuir equation constant(L/mg),K_F and 1/n are constants for a given adsorbate and adsorbent at a particular temperature and bT (KJ/mol) is adsorption potential of the adsorbent . K_T is the Temkin isotherm constant and 1/A is the external surface area for the Harkin –Jura isotherm.K_R, b_R,β are Redlich Peterson constants. Xm is maximum sorption capacity; β is mean sorption energy and ε sorption potential in DKR isotherms

Results and Discussion

Characterization of adsorbent

The adsorbent analysis revealed that it had high moisture content and volatile matter. Ash content was also appreciable. Results are illustrated in Table 1.It was determined by proximate and ultimate analysis as follows:

Proximate analysis

Moisture

About 1g of finely powdered air-dried adsorbent sample is weighed and taken in a crucible. The crucible is placed inside an electric hot-air oven and heated at 100-105’C for 1hour. It is then taken out, cooled in a desicator and weighed. From this, the percentage of moisture can be calculated as follows:

*Percentage of moisture = (loss in weight of adsorbent / weight of air dried adsorbent taken)*100*

Volatile matter

The crucible with moisture free adsorbent sample is covered with a lid and placed in an electric muffle furnace, heated at 905-945’C for seven minutes. It is then taken out, cooled in a desicator and weighed. From this, the percentage of volatile matter can be calculated as follows:

*Percentage of volatile matter = (loss in weight of adsorbent / weight of dried adsorbent taken)*100*

Ash content

The crucible with residual adsorbent sample is placed in an electric muffle furnace, heated without lid at 650-750’C for 30 minutes. It is then taken out, cooled in a desicator and weighed. From this, the percentage of ash content can be calculated as follows:

*Percentage of ash = (weight of ash left / weight of dried adsorbent taken)*100*

Fixed carbon

The fixed carbon content can be calculated from the following equation

Percentage of = 100- % of (moisture+ volatile matter + ash)

Ultimate analysis of Sulphur

A known quantity of adsorbent sample is burnt completely in a Bomb calorimeter. During this process sulphur is converted in sulphate, which is extracted with water. The extract is then treated with $BaCl_2$ solution so that sulphates are precipated as $BaSO_4$.The precipitate is filtered, dried and weighed. From the weight of $BaSO_4$ obtained, the sulphur present in the adsorbent was calculated as follows.

$$\underset{(32)}{S} \xrightarrow{2O_2} SO_4^{2-} \xrightarrow{BaCl_2} \underset{(233)}{BaSO_4}$$

Percentage of sulphur in adsorbent = (32 weight of $BaSO_4$ obtained) / (233* weight Of dried adsorbent taken)*

Results are given in table: 1

Effect of Mesh Size

The effect of adsorbent’s mesh size was studied in the range of 0-200 microns mesh size (0-63, 63-125, 125-200) for checking the maximum adsorption of Chromium (VI), and the smallest mesh size (0-63) was shown to be best for adsorption, as particles with smallest size presents a larger surface area and the results are shown in Fig. 1. Mesh size is inversely related with particle size. As the mesh size is larger, the size of particle is accordingly decreased which results in more surface area available for adsorption.

Effect of contact time on chromium adsorption

Contact time is one of the effective factors in batch adsorption process. In this stage, all of the parameters except contact time, including temperature (30 °C), adsorbent dose (0.15 g/50 mL), pH (2), initial chromium concentration (10 mg/L) and agitation speed (300 rpm), were kept constant. The effect of contact time on chromium adsorption efficiency showed in Fig. 2. As it is shown, adsorption rate initially increased rapidly, and the optimal removal efficiency was reached within about 3 h to 96.1 %. There was no significant change in equilibrium concentration after 1 h up to 4 h and after 1 h, the adsorption phase reached to equilibrium.

Effect of pH on chromium adsorption

The pH of the aqueous solution is clearly an important parameter that controlled the adsorption process. The experiments of this stage were done under the conditions of constant temperature (30 °C), agitation speed (300 rpm), contact time (3 h), adsorbent dose (0.15 g/50 mL) and initial chromium concentration (10 mg/L). pH of solution was changed and the chromium removal was investigated. The experimental results of this stage are presented in Fig. 3. As it is shown, the optimum pH of solution was observed at pH of 2 and by increasing pH, a drastic decrease in adsorption percentage was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent that ultimately lead to the reduction in sorption capacity[13]. Adsorption of hexavalent chromium varies as a function of pH with H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} ions appear as dominant species [14]. At pH of 2, $HCrO_4^-$ is the dominant species. The surface charge of

Casuarina equisetifolla is positive at low pH, and this may promote the binding of the negatively charged HCrO4- ions. The $HCrO_4^-$ species are most easily exchanged with OH- ions at active surfaces of adsorbent under acidic conditions as shown in Eq. 8 (Ar is adsorbent surface) [15].

Ar OH + HCr O_4^- +H+ ArHCr O_4 +H_2O------------- (8)

Effect of adsorbent dose on chromium adsorption

At this stage, the experiments were done under the conditions described at previous stage with constant pH of 2 and variable adsorbent dose (0.5, 0.1,0.15,0.2g/50 mL). The effect of adsorbent dose on the adsorption of chromium by Casuarina equisetifolla was presented in Fig. 4. As illustrated in Fig. 4, chromium removal efficiency increased with increase in adsorbent dose, since contact surface of adsorbent particles increased and it would be more probable for HCrO4- andCr_2O_7 -ions to be adsorbed on adsorption sites and thus adsorption efficiency increased [16].

Effect of initial chromium concentration on adsorption Process

Initial concentration is one of the effective factors on adsorption efficiency. The experiments were done with variable initial chromium concentration (2.5, 5, 7.5, 10, 12.5 and 15 mg/L) and constant temperature (30 °C), pH (2), agitation speed (300 rpm), contact time (3 h) and 0.15 g of adsorbent dose (0.15 g/50 mL). The experimental results of the effect of initial chromium concentration on removal efficiency were presented in Fig. 5. As in Fig.5 is shown, chromium removal efficiency decreased with the increase in initial chromium concentration. In case of low chromium concentrations, the ration of the initial number of moles of chromium ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions which depends upon the initial concentration, decreases [17].

Effect of Temperature

Temperature has an important effect on the rate of adsorption. The percentage of Chromium (VI) adsorption was studied as a function of temperature in the range of 30-60 °C. The results obtained were present in Fig. 6. It was observed that adsorption yield increase with increase in temperature. The minimum adsorption was 94 % at 30 °C and maximum adsorption was 99.67 % at 60 °C for 30 ppm initial concentration of metal ion solution. The increase in adsorption at high temperature because molecules move with great speed and strong interaction was available for metal ion anions with adsorbent material.

Adsorption isotherm

Isotherm parameters, evaluated from the linear plots of equations (1-7) are illustrated in Table 2a,2b and 2c,(Fig:7-13).The K_L value for the Langmuir isotherm, ie. 5.235mg/g, indicated the high adsorption capacity of biosorbent toward chromium adsorption. The R^2 (correlation coefficient) value of 0.984indicated that the Langmuir isotherm is good for explaining the Chromium (VI) adsorption. The R^2 value calculated for the Freundlich isotherm was found to be 0.978, indicating that the experimental data can be explained by the Freundlich isotherm. The Kf (ultimate adsorption capacity) value as calculated from the Freundlich isotherm was 4.395.The Temkin equation was also good to explain the experimental data ,with an R^2 value 0.984.bT (heat of sorption) was calculated from the Tempkin plot as 4.528KJ/mol ,indicating moderately strong cohesive forces between Chromium (VI) and biosorbent. A value less than 8 indicates a weak interaction between the adsorbent and adsorbate .The Harkin –Jura expression of the value of the correlation coefficient was 0.984,providing good suitability for the experimental data of Chromium (VI) on Casuarina equisetifolla. Halsey's expression of the value of the correlation coefficient was 0.978, providing a better fit for the experimental data of Chromium (VI) on Casuarina equisetifolla. The Harkin-Jura and Halsey equations were more suitable to explain the multi layer adsorption of the adsorbate on adsorbent [18]. The R^2 value calculated for the Redlich-peterson isotherm was found to be 0.990, indicating that the experimental data can be explained by the Redlich-peterson isotherm. The β value as calculated from this isotherm was 0.542. The R^2 value calculated for the DKR isotherm was found to be 0.998, indicating that the experimental data can be explained by the DKR isotherm poorly. The β value as calculated from this isotherm was 1.167.

Thermodynamic parameters

Thermodynamic parameters such as standard Gibbs free energy (ΔG^0),Enthalpy (ΔH^0) and entropy (ΔS^0) were also calculated using equations 9 and 10 and the results obtained are illustrated in table-3a,3b (Fig:14).

ΔG^0 =-RTlnK ----------------------------9

lnKc = (ΔS^0/R)-(ΔH^0/RT) -----------------------------10

Here, K denotes the distribution coefficient for the adsorption. R is the universal constant and T is the absolute temperature in Kelvin. The negative value of the ΔG^0at the studied temperature range indicated that the sorption of Chromium (VI) on sorbent was thermodynamically feasible and spontaneous. The increase in the value of $\Delta G^0$with temperature further showed the increase in feasibility of sorption at the elevated temperature for Casuarina equisetifolla. In other words, sorption is endothermic in nature .The positive value of ΔH^0 for Casuarina equisetifolla showed that the sorption was endothermic. The positive value of ΔS^0 showed an increased randomness at the solid Chromium (VI) solution interface during the adsorption of Chromium (VI), reflecting the affinity of Casuarina equisetifolla for Chromium (VI).

Arrhenius equation

Activation energies for adsorption of Chromium (VI) on adsorbent was calculated using the Arrhenius equation (eq11),plotted in Fig 15 and tabulated in table 4.The activation energy obtained(Table 4) in this case ,indicate that physical forces are involved in the sorption mechanism and sorption feasibility.

Arrhenius equation

Log K = Log A – (E_A / 2.303 RT) ------------------ 11

Kinetic study

A linear trace for the plot of log (qe-q) Vs time (Fig:16-19) shows that the adsorption kinetics follow pseudo second order kinetics' additionally pseudo first order,intra particle diffusion and Elovich model of kinetics were verified. (Tables 5a, 5b, 5c)

First order equation

Log (q_e-q_t) = log q_e - (K1t / 2.303) ----------------- 12

Second order equation

t/qt=1/n+t/qe^2 ---13

Intra particle diffusion equation

qt= Kpt1/2+C -------------------------------------14

Elovich model equation

Qt = α + βLnt ---------------------------------------15

Conclusion

In this study, the effect of Casuarina equisetifolla on Cr (VI) removal was examined. The results indicated that the adsorption process reached to equilibrium after 180 min and at this time, the chromium removal was 96.1 %. Among all of the selected parameters, pH of solution was the most effective on chromium removal. The results showed that the highest adsorption of chromium on Casuarina equisetifolla (96 %) was at pH of 2.It was observed that the removal percentage increased at the lower initial chromium concentration and higher adsorbent doses. The results showed that the Langmuir adsorption isotherm was the best model for the chromium removal on Casuarina equisetifolla with a correlation coefficient (R2) of 0.984. The kinetics analysis of the study showed that the adsorption of Cr (VI) ions onto Casuarina equisetifolla could be well described with the pseudo-second-order kinetics model and the rate constant for the process was found to be 0.0185 g/mg.min at 30 °C. Based on the results of this research, Casuarina equisetifolla can be considered as an effective, available and natural adsorbent for removing chromium from aqueous solutions.

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Table:1

Parameters	**Moisture**	**Volatile matter**	**Ash**	**Fixed C**	**S**
Values	4.1%	8.5%	5.7%	80.6%	1.1%

c0	%	ce	c0-ce	qe	ka	Ka C0	ce/qe
10	93.99	0.601	9.40	3.13	5.2130	52.1298	0.1918
20	91.73	1.654	18.35	6.12	3.6973	73.9460	0.2705
30	87.89	3.633	26.37	8.79	2.4192	72.5764	0.4134
40	80.61	7.756	32.24	10.75	1.3858	55.4306	0.7216
50	78.22	10.89	39.11	13.04	1.1971	59.8561	0.8353
60	73.74	15.76	44.24	14.75	0.9360	56.1615	1.0683

Table 2b

logce	log qe	log ce/qe*-1	ceβ	1/ce+1	ε2	1/qe2
-0.2211	0.4960	0.7171	0.75884	2.6639	6.0982	0.101878
0.2185	0.7864	0.5679	1.313549	1.6046	1.4204	0.02674
0.5603	0.9439	0.3837	2.012166	1.2753	0.3756	0.012946
0.8896	1.0313	0.1417	3.035175	1.1289	0.0934	0.008657
1.0370	1.1152	0.0781	3.64812	1.0918	0.0490	0.005884
1.1974	1.1687	-0.0287	4.456724	1.0635	0.0241	0.004598

Table 2c

Langmuir parameters	$K_L = 5.235$	q0 = 17.243	$b_L = 0.3036$	$R^2 = 0.984$
Freundlich parameter	$K_F = 4.395$	n =2.188		$R^2 = 0.978$
Dubinin-kaganer-Radushkevich parameters	β = 1.167	b = 0.615	q0 =4.120	$R^2 = 0.998$
Redlich peterson parameters	β= 0.542	$K_R = 5.649$	$b_R = 0.276$	$R^2 = 0.990$
Tempkin parameters	$k_T = 7.985$	$b_T = 4.528$		$R^2 = 0.984$
Harkin-jura parameters	A= 47.61	B = 1.333		$R^2 = 0.984$
Halsey parameters	n= 2.188	K = 4.08		$R^2 = 0.978$

Table 3a

T,K	c0	%	ce	c0-ce	ka
303.15	50	93.9	3.05	46.95	5.131148
313.15	50	96.87	1.565	48.435	10.31629
323.15	50	98.65	0.675	49.325	24.35802
333.15	50	99.67	0.165	49.835	100.6768

Table 3b

ΔG0	ΔH0	ΔS0	Log 10 Ka	1/T
-4.12167	23.16804	67.20647	0.710215	0.003299
-6.07592			1.013524	0.003193
-8.57816			1.386642	0.003095
-1.27741			2.002929	0.003002

Table: 4

Ea	Log A	R2
81.77744	14.72	0.962

Table 5a

Time, in	%	C0	Ce	ct	qt	t/qt
30	76.22	10	2.4	7.622	2.541	11.808
60	79.89	10	2.0	7.989	2.663	22.531
90	83	10	1.7	8.3	2.767	32.530
120	90.21	10	1.0	9.021	3.007	39.907
150	93.68	10	0.6	9.368	3.123	48.036
180	96.1	10	0.4	9.61	3.203	56.191

Table 5b

qe-qt	Log (qe-qt)	t1/2	1/qt	1/t	Ln t
0.972	-0.0121848	5.477226	0.393597	0.033333	3.401197
0.850	-0.0705811	7.745967	0.375516	0.016667	4.094345
0.746	-0.1270672	9.486833	0.361446	0.011111	4.49981
0.506	-0.2958495	10.95445	0.332557	0.008333	4.787492
0.390	-0.4085644	12.24745	0.320239	0.006667	5.010635
0.310	-0.5091055	13.41641	0.312175	0.005556	5.192957

Table 5c

I Order	K1 = 0.006909	Qe = 1.13769	R2=0.974
II Order	K2 = 0.01846	Qe = 3.4364	R2=0.995
Intra particle diffusion	Kp = 0.088	C = 2.004	R2=0.967
Elovich model	β = 0.385	α = 1.151	R2=0.918

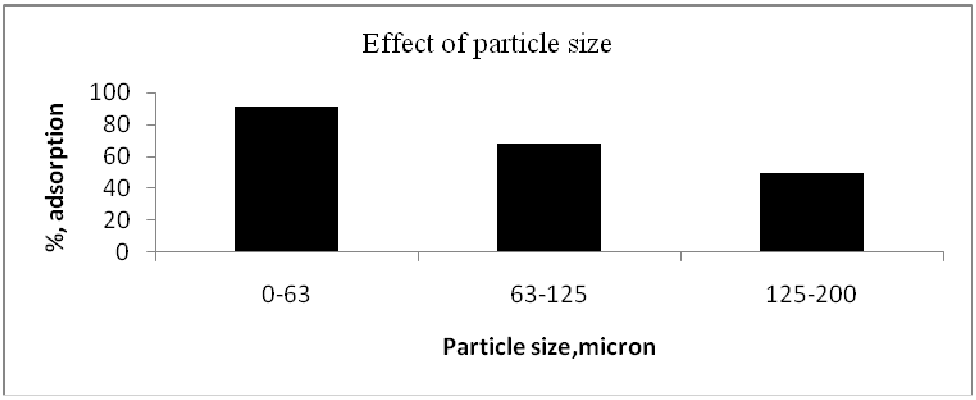


Fig 1

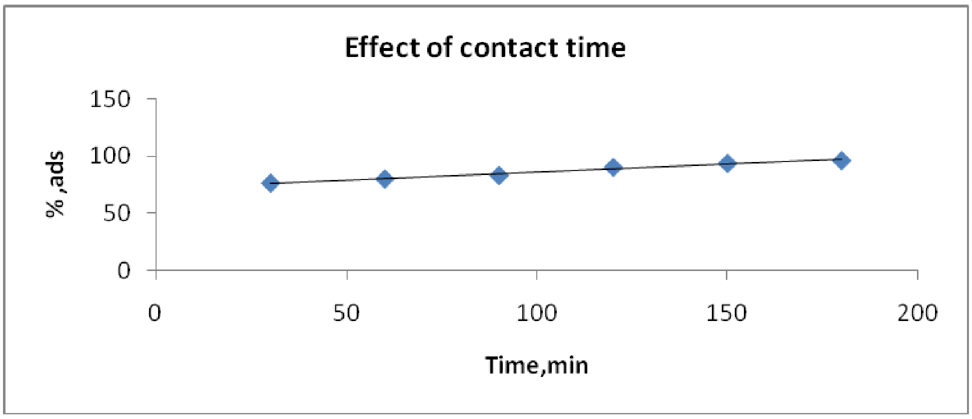


Fig2

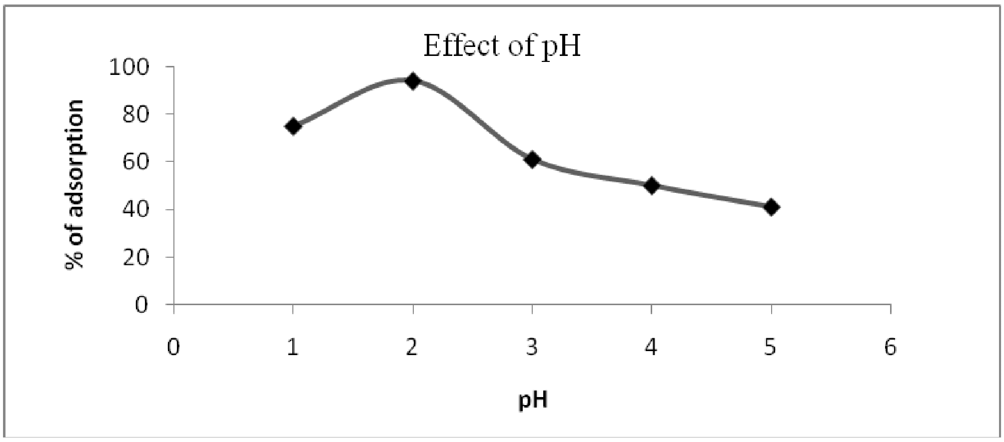


Fig3

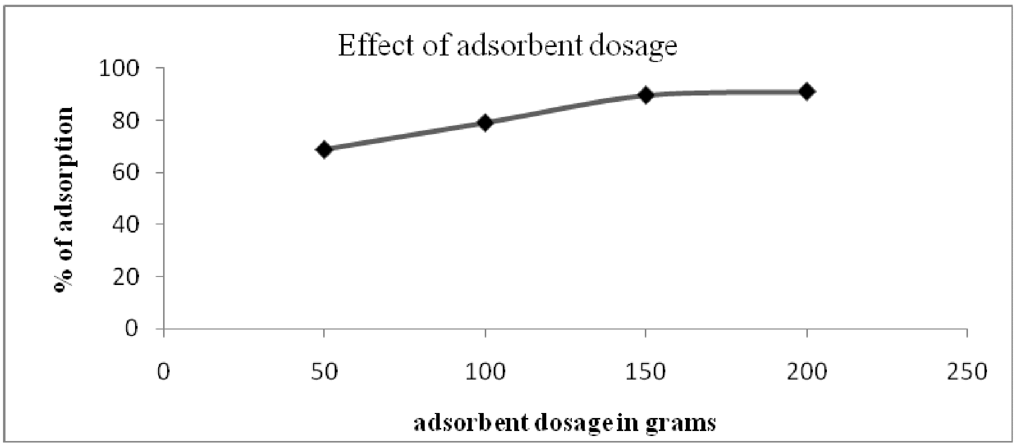


Fig 4

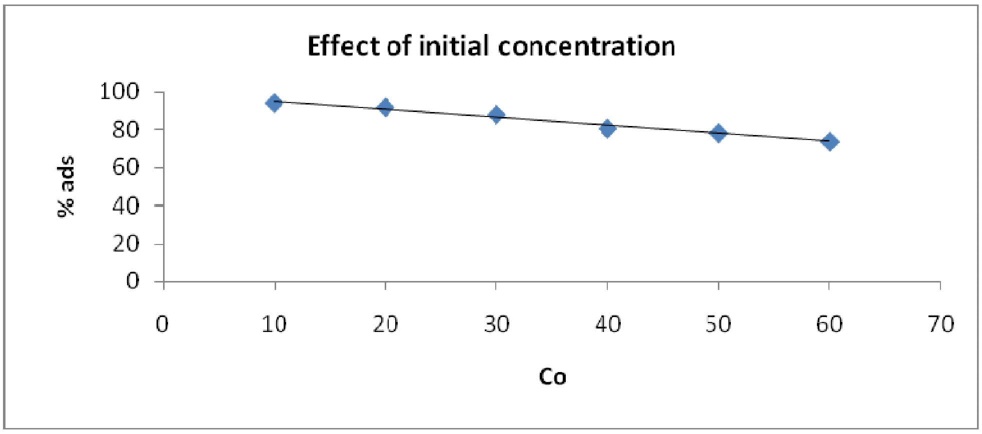
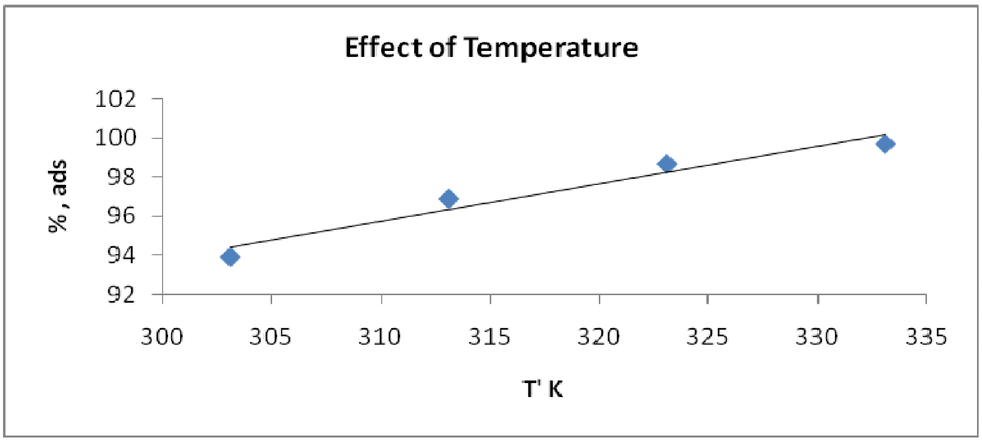


Fig 5



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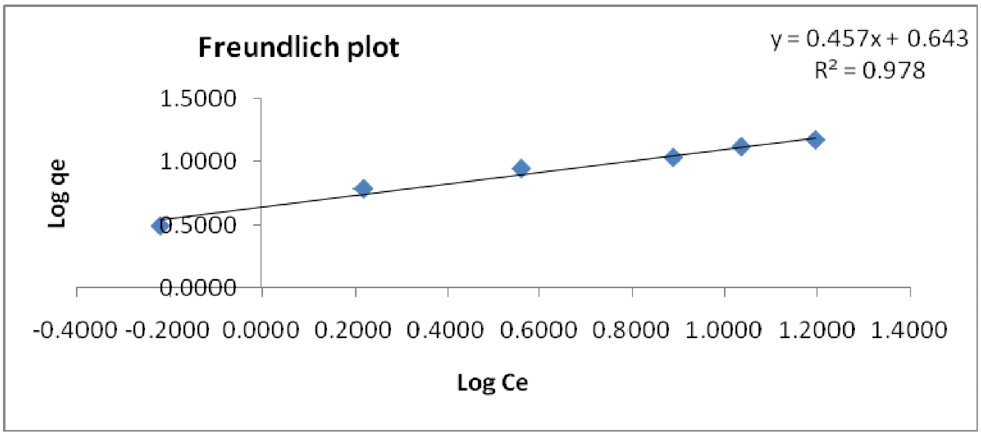

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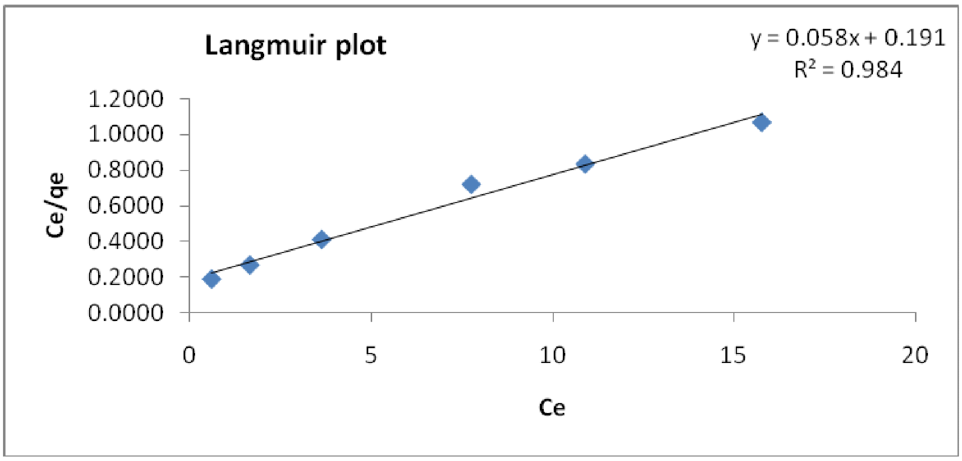

Fig 8

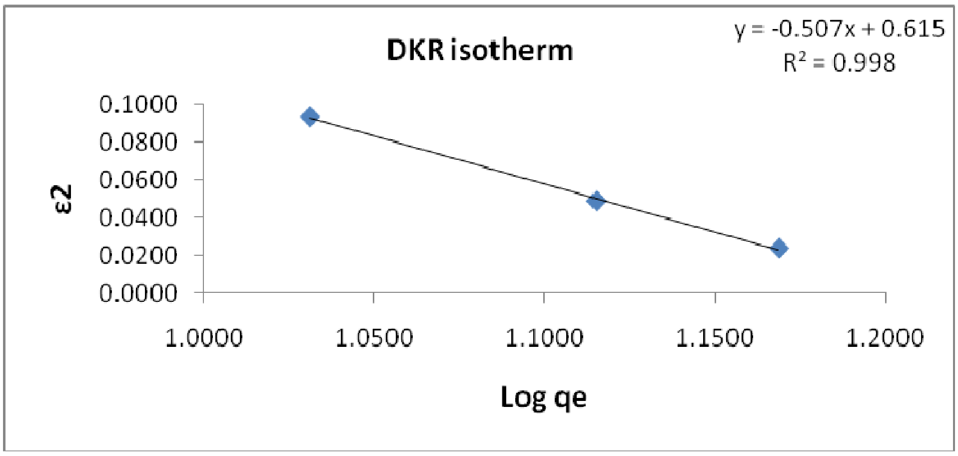

Fig 9

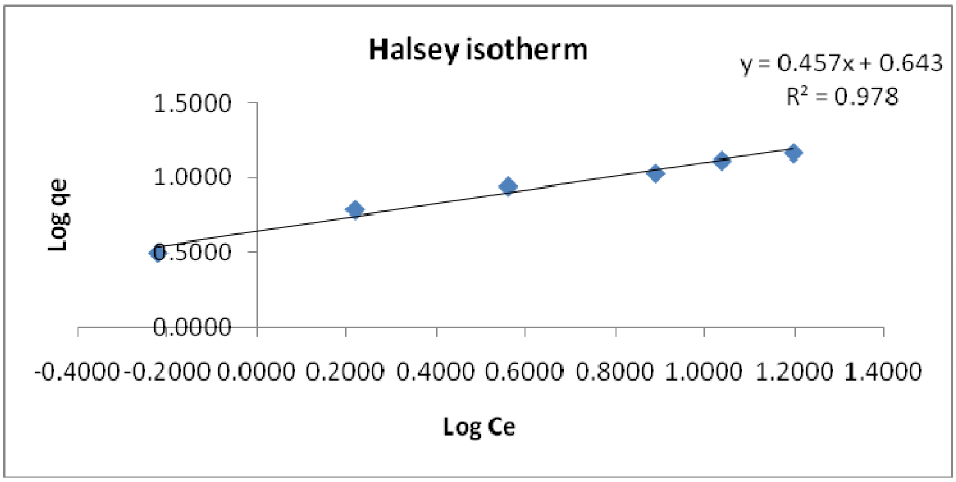

Fig 10

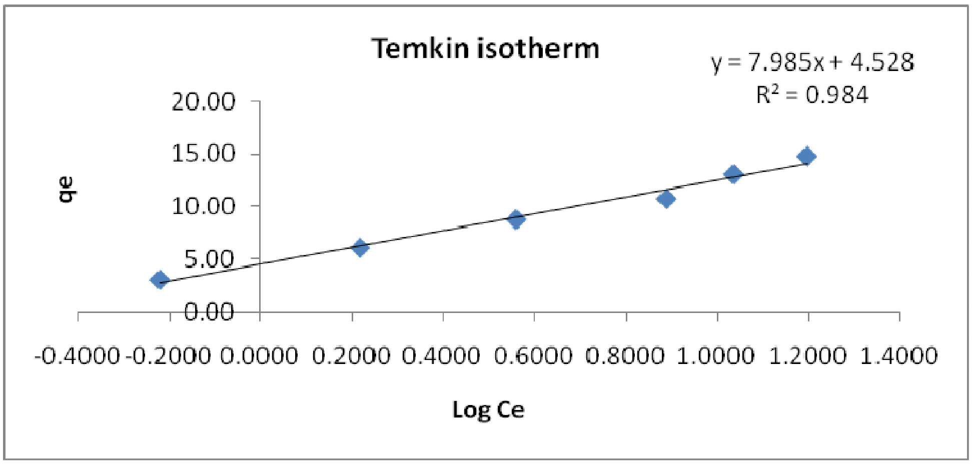

Fig 11

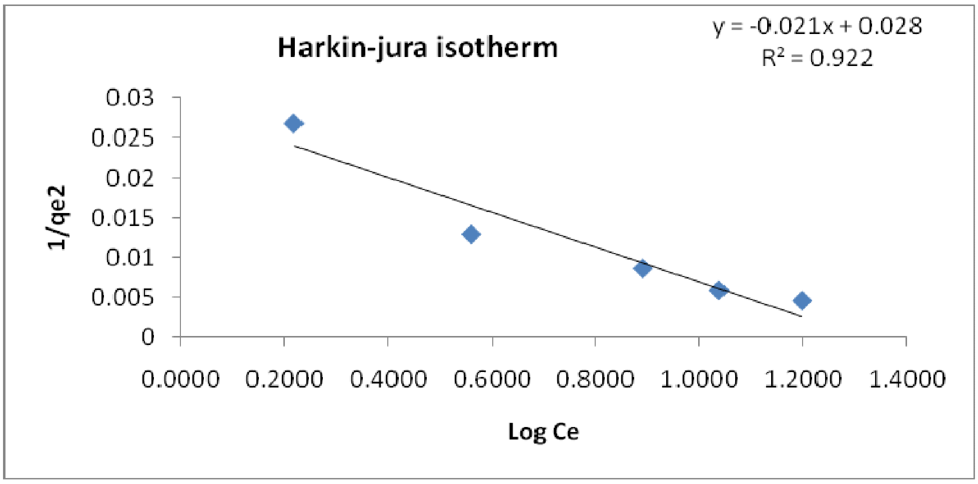

Fig 12

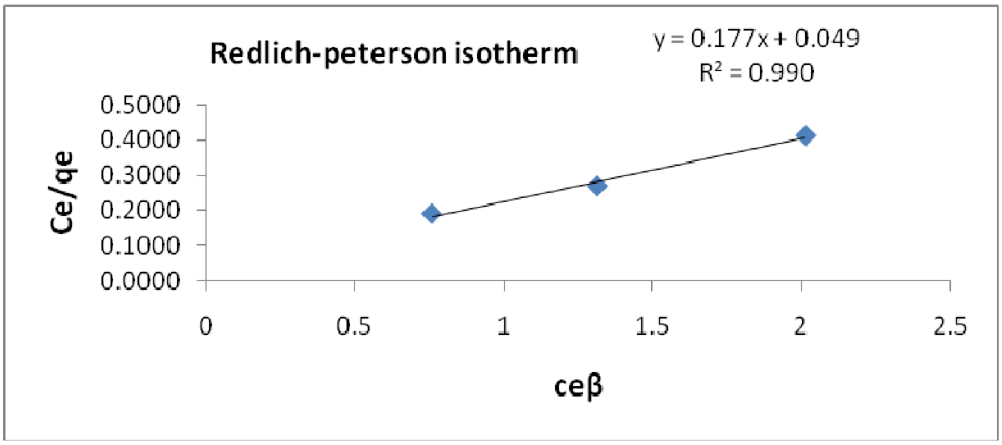

Fig13

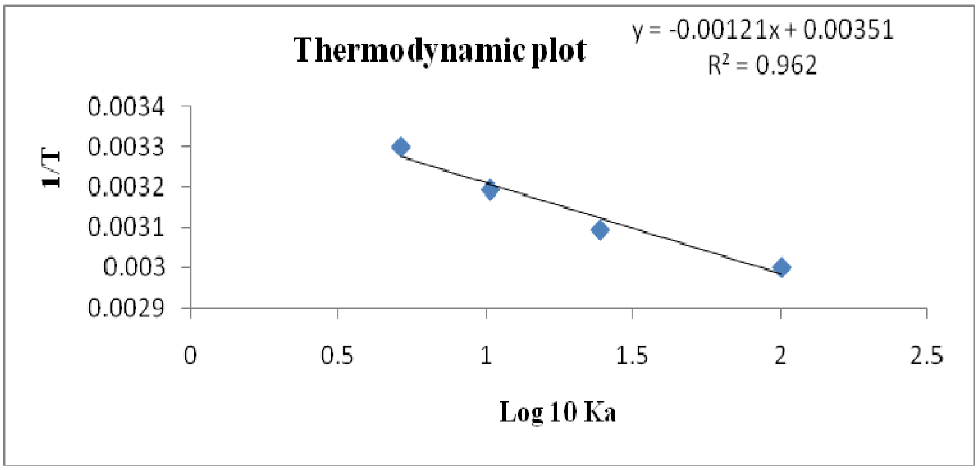

Fig 14

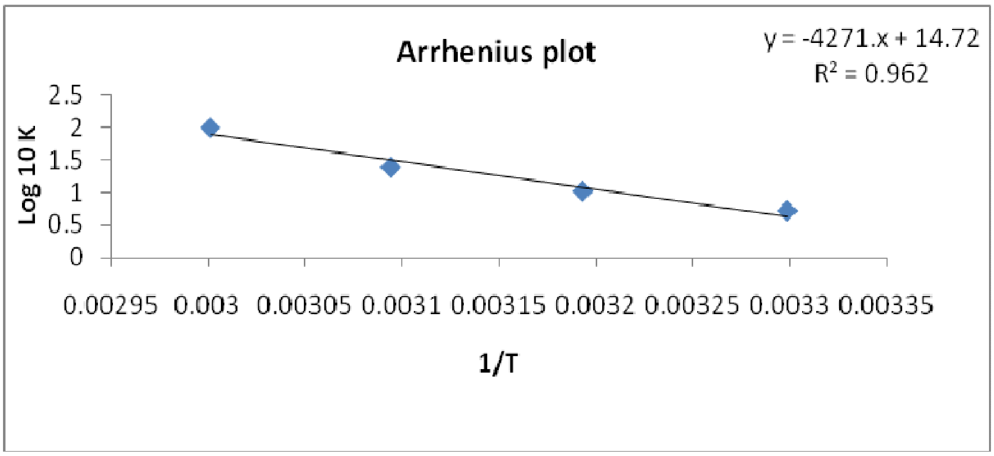

Fig 15

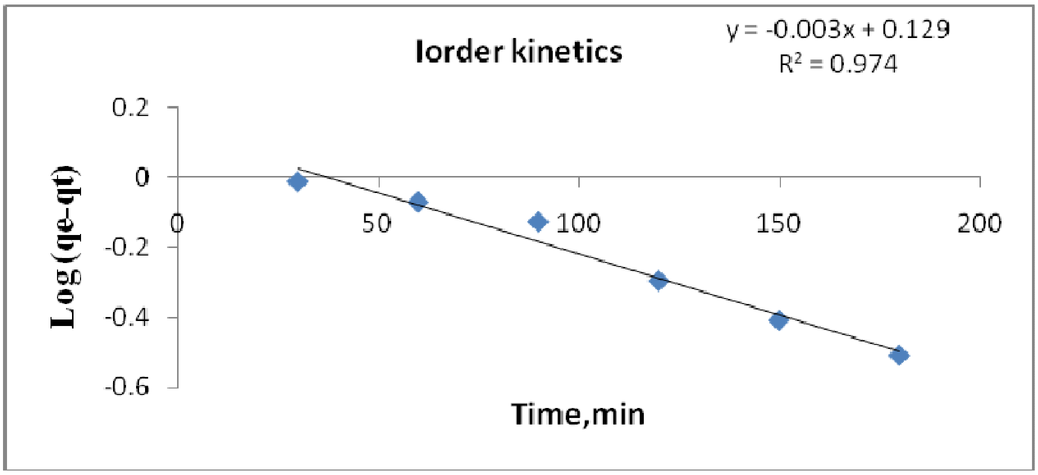

Fig 16

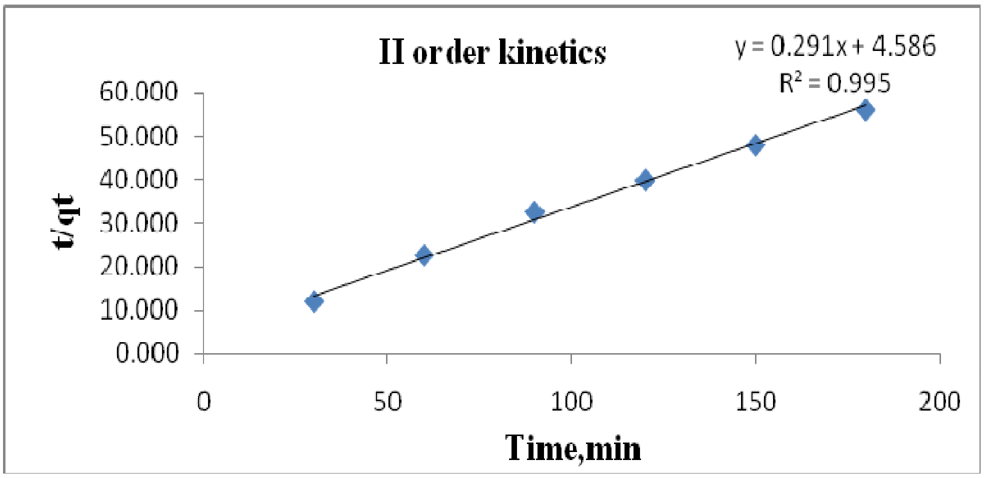

Fig17

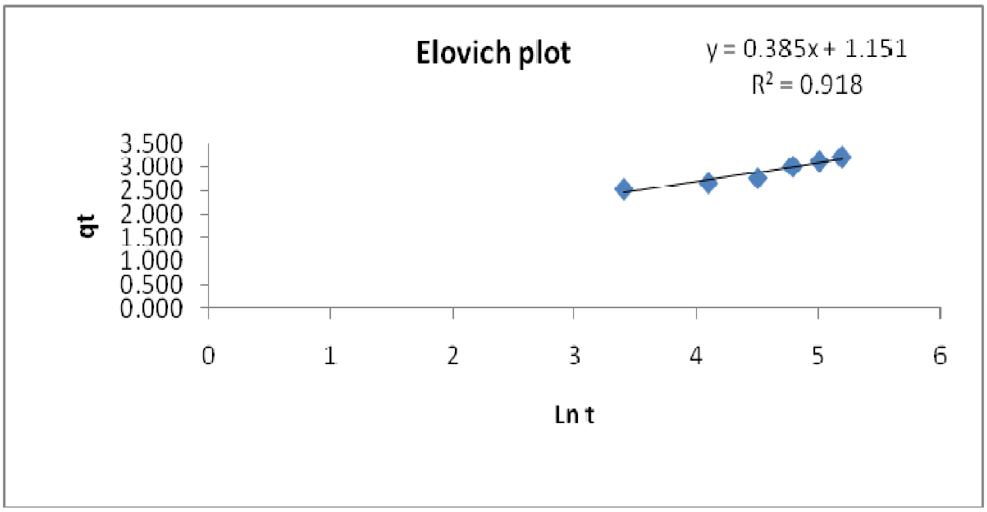

Fig 18

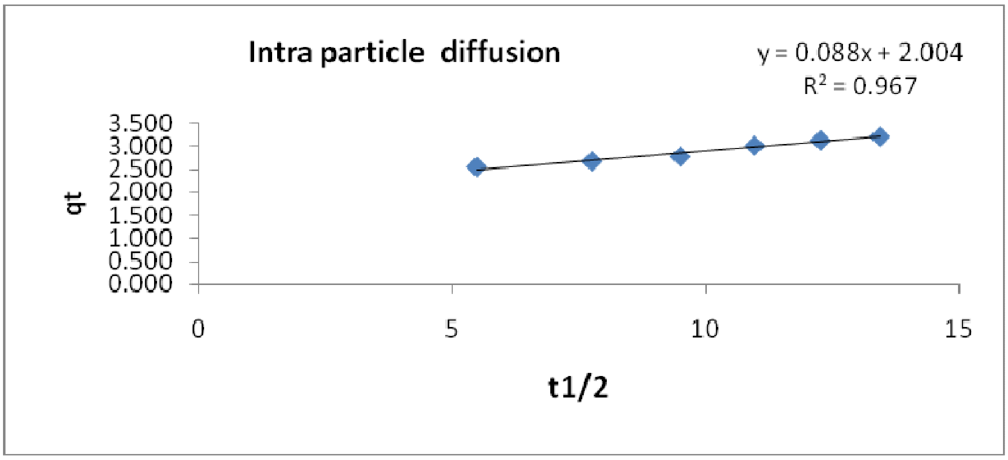

Fig 19