

# Kinetic Studies on the Removal of Cr (VI) using Natural Adsorbent

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## Abstract

*This paper presents the adsorption of Cr (VI) ions in a laboratory batch scale mode by eggshells as a low-cost sorbent, which is available, cheap, and may represent an environmental problem. The adsorption process and extent of adsorption are dependent on the physical and chemical characteristics of the adsorbent, adsorbate and experimental conditions. The effect of process parameters like solution pH, initial concentration of Cr (VI) ions, adsorbent dose, agitation speed and temperature on the adsorption of Cr (VI) was studied. It was found that crushed eggshells possess relatively high sorption capacity, when comparing with other sorbents. The adsorption process follows the second order kinetic equation. Various isotherms were tested and it is found that Langmuir isotherm fits this process.*

**Keywords:** Adsorption, Cr (VI), low-cost adsorbent, Egg shell powder, Kinetics, adsorption isotherm.

and energy requirement, generation of toxic sludge, and high operational cost [16]. In recent years, adsorption has been shown to be an alternative method for removing dissolved metal ions from liquid waste. In order to minimize the cost, extensive research using low-cost adsorbents including various kinds of soils and clay materials has been carried out in several investigations [17, 18]. The main properties of the adsorbents for heavy metal removal are strong affinity and high loading capacity [1]. Large amounts of eggshells are produced in some countries, such as the United States in which annually 120,000 tons of waste eggshells are generated and disposed in landfills [5]. This also represents a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs [15]. Therefore, this paper aimed to present eggshells powder as porous adsorbent. Cr (VI) was successfully removed from effluent under the recommended conditions.

## I. INTRODUCTION

Heavy metals are constantly released into the environment. They are dangerous environmental pollutants due to their toxicity and strong tendency to concentrate in environment and in food chains [1, 2]. Therefore, the best solution is to prevent the entrance of toxic metals into the ecosystem [3]. The source of environmental pollution with heavy metals is mainly industry, i.e. metallurgical, electroplating, metal finishing industries, tanneries, chemical manufacturing, mine drainage and battery manufacturing [4,30]. The presence of trivalent and hexavalent chromium in the environment is the cause of many well-known toxic effects [8]. The main sources of chromium pollution are mining, leather tanning process, cement industries, uses in dyes, electroplating, and production of steel and other metal alloys, photographic material and corrosive paints [8, 10]. Removal of metals from wastewater is achieved principally by the application of several processes such as adsorption [1], sedimentation [13], electrochemical processes [8], ion exchange [14], biological operations [11], cementation [9], coagulation/flocculation [13], filtration and membrane processes [7], chemical precipitation and solvent extraction [6, 12]. The major drawbacks from these technologies include incomplete removal, high reagent

## II. MATERIALS AND METHODS

### A. Preparation of Adsorbents

Initially the raw Egg shell used for this study was collected from nearby hotels. The samples were collected, washed with water and dried for 2 h in large trays in an oven maintained at 60°C, allowed to cool to room temperature, crushed, sieved and those with size (0.15 to 0.048 mm) were used in the experiments. The chemical composition (by weight) of by-product eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [19, 20].

### B. Preparation of Stock Solution

Chromium (VI) stock solution (1000 mg/L) was prepared by dissolving 5.658 g of dried potassium dichromate ( $K_2Cr_2O_7 \cdot H_2O$ ) in 1000 ml double distilled water. The above stock solutions contain few drops of concentrated HCl to prevent hydrolysis of chromium ions.

### C. Analysis of Metal

Hexavalent Chromium was determined spectrophotometrically (ELICO Bio UV Vis-Spectrophotometer) by diphenyl carbazide method. To a series of standard solutions of Chromium (VI), 3 ml of 2N  $H_2SO_4$ , 2 drops of phosphoric acid and 0.5 ml of

diphenyl carbazide solution (0.5% in acetone) were added and made up to 25 ml with water. After few minutes the absorbance was measured at 540nm after against a reagent blank. A calibration graph with absorbance vs. Chromium (VI) concentration was prepared. The concentration in the sample was determined using the calibration chart [21].

#### D. Procedure

This study based on batch process. The concentrated stock solution was diluted by double distilled water to various concentrations like 50 ppm, 100 ppm and 150 ppm. For the experimental study 100 ppm solution was accounted. The pH is varied from 2 to 12. For the different adsorbent dosage (0.5 to 1 gm/100 ml) the experiment is carried out. For different adsorbent size (0.15, 0.112 and 0.061) batch adsorption process carried out. By varying the initial concentration from 50 ppm to 150 ppm the removal of Cr (VI) was examined. The same process was carried out for various effluent volumes (50 ml, 150 ml and 200 ml). For the various agitation speeds (90 rpm, 120 rpm and 180 rpm) and for various temperatures (50<sup>o</sup> C, 60<sup>o</sup> C 70<sup>o</sup> C) the process was carried out.

The percentage adsorption of Cr (VI) ions from the solution was calculated by,

$$\% \text{ Adsorption} = (C_0 - C_r) / C_0 \times 100$$

Where  $C_i$  corresponds to the initial concentration of Cr (VI) ions,

$C_r$  is the residual concentration in the filtrate after shaking for a definite time period.

The metal uptake at a particular time  $q_t$  ( $\text{mg g}^{-1}$ ) was calculated as:

$$q_t = [(C_0 - C_r) / m] * V$$

The amount of metal adsorbed at equilibrium,

$q_e$  ( $\text{mg g}^{-1}$ ) was calculated by:

$$q_e = [(C_0 - C_e) / m] * V$$

Where,

$C_e$  ( $\text{mg l}^{-1}$ ) is the concentrations of metal at equilibrium.

Due to the inherent bias resulting from linearization of the isotherm model and kinetic model, the non-linear regression Root Mean Square Error (RMSE) test was employed as criterion for the quality of fitting [15]. The root mean square error of a model is evaluated by:

$$\text{RMSE} = \sqrt{\frac{1}{n-2} \sum (q_t - q_e)^2}$$

Where,

$q_t$  ( $\text{mg g}^{-1}$ ) is the experimental value of uptake,  $q_e$  is the calculated value of uptake using a model ( $\text{mg g}^{-1}$ ), and  $n$  is the number of observations in the experiment. The smaller RMSE value indicates the better curve fitting [22].

### III. RESULTS AND DISCUSSION

#### A. Effect of pH

The effect of pH on Cr (VI) removal by using Egg shell powder from pH 2.0-12.0 was studied. The effect of pH on adsorption of Cr (VI) onto the adsorbent can be interpreted on the basis of the structure of the sorbent and the speciation of chromium. Chromium solution contains a larger number of  $\text{Cr}_2\text{O}_7^{7-}$  ions and a smaller number of  $\text{HCrO}_4^-$  ions in the regions of lower pH and only  $\text{CrO}_4^{2-}$  ions above pH 8.0. A major fraction of negative sites are occupied by  $\text{H}^+$  ions via electrostatic attraction in the regions of lower pH and these positively charged sites of the adsorbent are occupied by  $\text{Cr}_2\text{O}_7^{7-}$  ions. Hence the maximum chromium removal was observed at lower pH i.e. 6 [23]. Higher removal of chromium at low pH may also be due to reduction of chromium (VI) to chromium (III) which was then adsorbed by the adsorbent. In the table 1 variation of pH is listed. The graphical representation is shown in fig.1.

Table 1 Effect of pH on Removal of Cr (VI)

S.No	pH	% Removal on Cr(VI)
1	2	82.3
2	4	91.9
3	6	93.4
4	8	91.3
5	10	91.8
6	12	91.2

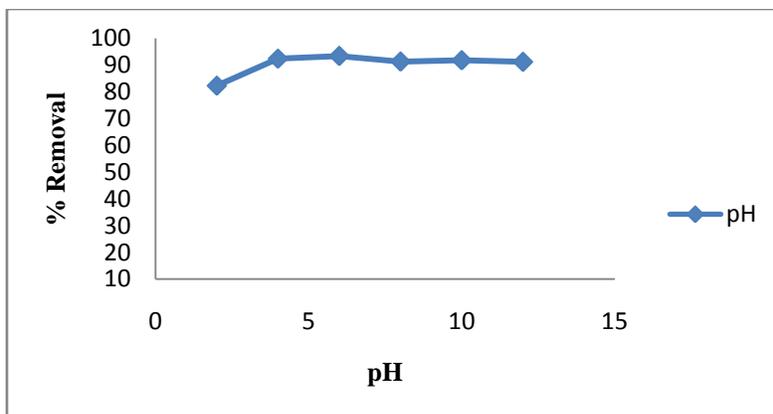


Fig. 1. Effect of pH on the Removal of Cr (VI)

**B. Effect of Adsorbent Dosage**

Adsorbent dose had a very profound effect on Cr (VI) removal. Adsorption experiments were carried out at varying adsorbent dose (0.5 – 2.5gm/100ml), while pH (6.0) was kept constant. The removal of Cr (VI) by Egg shell powder as a function of adsorbent dose is shown in (Fig 2). It was observed from the results that the percentage removal of Cr (VI) increases with increase in adsorbent dose up to some extent, thereafter with further increase in adsorbent dose; there was no appreciable increase in percentage removal. The optimum dose for removal of Cr (VI) was found to be 2.5 gm/100 ml of Egg shell powder. As with increase in

adsorbent dose, more and more binding sites become available for the complex of Cr (VI) ions and this increased the rate of adsorption. However very slow increase in removal beyond an optimum dose may be attributed to attainment of equilibrium between adsorbate and adsorbent at the existing operating conditions [24]. Higher adsorbent dose causes screening effect of dense outer layer of cells, blocking the binding sites from metal ions, resulting in lower metal removal per unit adsorbent [19]. The result is shown in table 2 below.

Table 2 Effect of Adsorbent Dosage on the Removal of Cr (VI)

S.No	Dosage (g)	% Removal on Cr(VI)
1	0.5	51.5
2	1	72.7
3	1.5	82.7
4	2	87.5
5	2.5	93.1

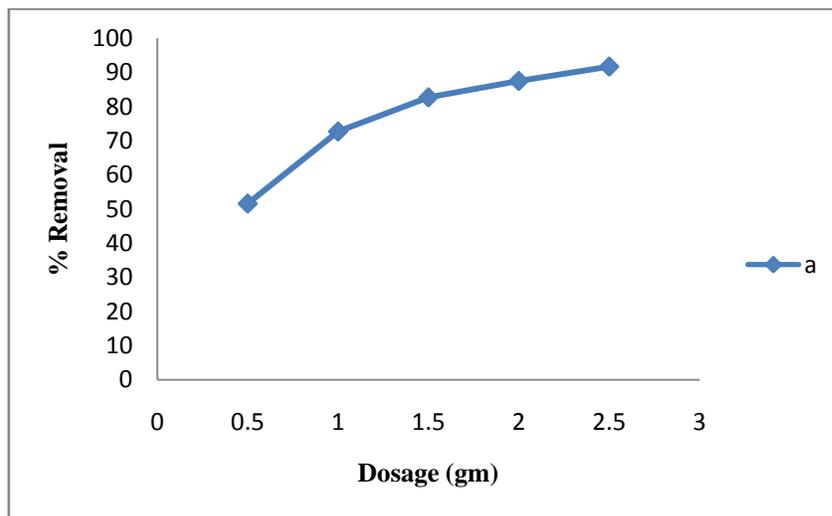


Fig.2. Effect of Adsorbent Dosage on Removal of Cr (VI)

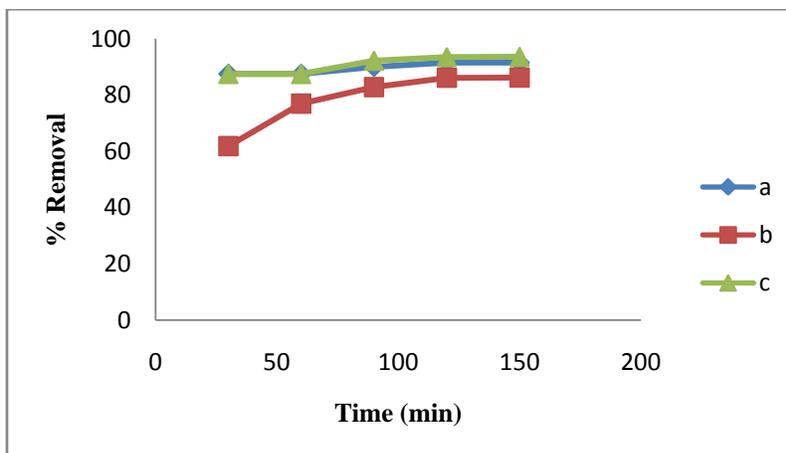
**C. Effect of Adsorbent Size**

The effect of adsorbent size was calculated by varying the size of adsorbent from 0.15 mm, 0.112 mm, 0.061 mm. The study was carried out at the temperature of 30°C and at the optimum pH and adsorbent dosage for the metal. The process is carried out for 120 minutes. After that particular time the adsorption process attains equilibrium. Very slow increase in removal beyond an optimum dose may be attributed to

attainment of equilibrium between adsorbate and adsorbent at the existing operating conditions [24]. Higher adsorbent dose cause screening effect of dense outer layer of cells, blocking the binding sites from metal ions, resulting in lower metal removal per unit adsorbent [19]. Table 3 shows the removal of Cr (VI) ions with respect to the adsorbent size. Figure 3 shows it corresponding graphical representation.

**Table 3 Effect of Adsorbent Size on the Removal Of Cr (VI)**

S.No	Time (min)	% Removal 0.15mm	% Removal 0.112 mm	% Removal 0.062 mm
1	30	87.5	61.8	87.5
2	60	97.5	76.9	87.5
3	90	90	82.8	92.2
4	120	91.5	86.1	93.5
5	150	91.5	86.2	93.6



**Fig.3. Effect of Adsorbent Sizes a – 0.15 mm, b – 0.112 mm & c – 0.061 mm on Removal of Cr (VI)**

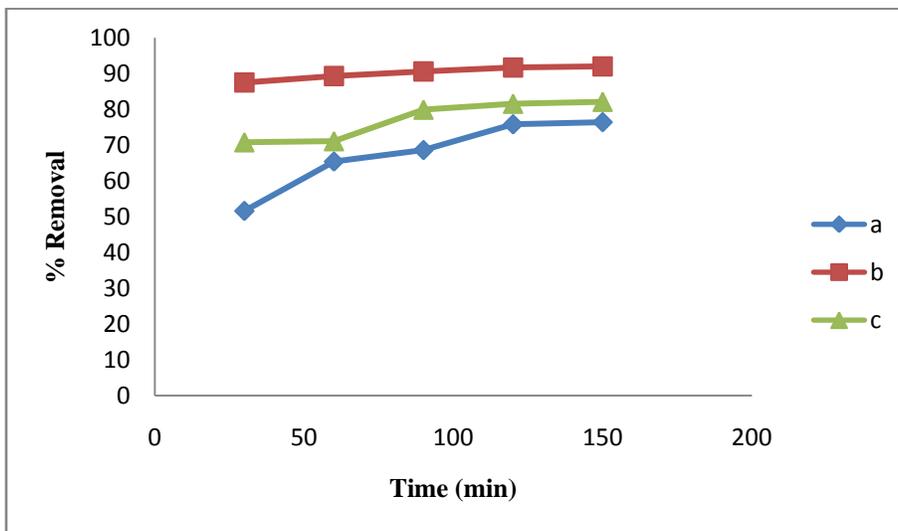
**D. Effect of Initial Concentration**

Effect of initial Cr (VI) ion concentration on its removal was carried out at optimized adsorbent dose and pH by varying the metal ion concentration from 50 to 150 ppm shown in Table 4. Adsorption of Cr (VI) was found to increase with increase in metal ion concentration from 50 to 150 ppm. This is due to increase in number of metal ions competing for available binding sites and due to lack of binding sites

for complexation at higher metal ion concentration. At lower concentration almost all the metal ions could interact with binding sites facilitating maximum adsorption. Maximum Cr (VI) removal was observed at 150 ppm concentration using low cost adsorbents. At higher concentration more chromium ions are left unadsorbed in the solution due to saturation of adsorption sites [28]. Graphical representation for this effect is shown in fig 4.

**Table 4 Effect of Initial Concentration on Removal of Cr (VI)**

S.No	Time (min)	% Removal 50 ppm	% Removal 100 ppm	% Removal 150 ppm
1	30	51.6	87.5	68.86
2	60	65.4	89.3	74.06
3	90	68.6	90.6	83.46
4	120	75.8	91.7	90.06
5	150	76.4	92	90.26



**Fig.4. Effect of Initial Concentrations a – 50 ppm, b – 100 ppm & c – 150 ppm on removal of Cr (VI)**

**E. Effect of Initial Effluent Volume**

A typical result of the functional adsorption of Cr (VI) with time for different initial volume of effluent (50 ml, 150 ml and 200 ml) on Egg shell powder is explained in table 5. As there are more ions for

adsorption, the optimized amount of dosage adsorbs more ions till equilibrium is attained. The increase in the effluent volume tends to more rate of adsorption. Maximum removal is attained at maximum volume. The graphical representation is shown in Fig.5

**Table 5 Effect of Initial Effluent Volume on Removal of Cr (VI)**

S.No	Time (min)	% Removal 50 ml	% Removal 150 ml	% Removal 200 ml
1	30	52.5	70.8	79.1
2	60	53.6	71.1	80.5
3	90	63.3	79.9	82.11
4	120	78.44	81.87	85.4
5	150	79.88	82.1	85.8

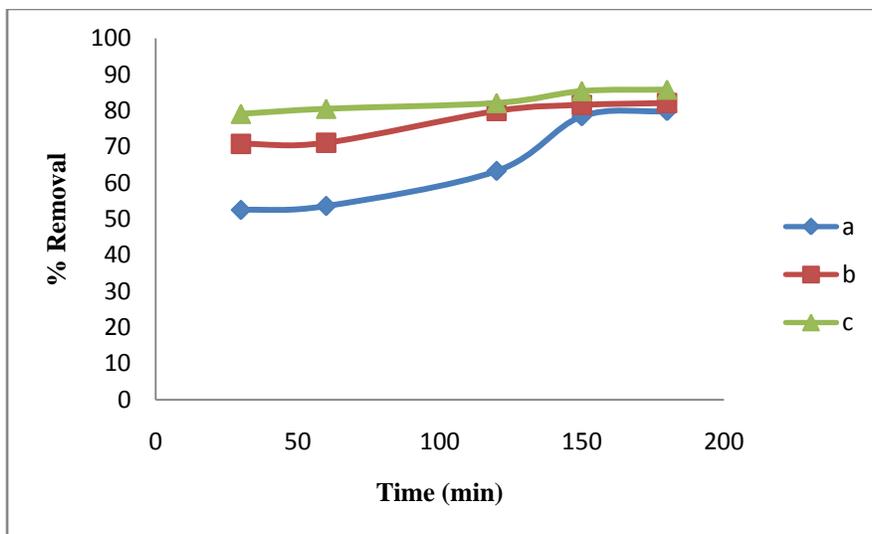


Fig 5 Effect of Initial Volumes a – 50 ml, b – 150 ml & c – 200 ml on Removal of Cr (VI)

**F. Effect of Temperature**

The effect of temperature on the sorption of Cr (VI) on Egg shell powder was investigated in the range of 40 °C to 60 °C in the optimized pH and adsorbent dosage. The influence of temperature on the sorption kinetics is presented in table 6. An increase in

temperature results in increased adsorption. The accelerated ions increase rate of adsorption at higher temperature. After the equilibrium, the removal remains constant. Graphical representation of temperature effect is shown in below fig 6.

Table 6 : Effect of Temperature on Removal of Cr (VI)

S.No	Time (min)	% Removal 40° C	% Removal 50° C	% Removal 60° C
1	30	20.8	19.9	22.4
2	60	22.5	23.5	31.5
3	90	44	66.5	54.1
4	120	87.5	90.3	91.5
5	150	88	90.7	91.8

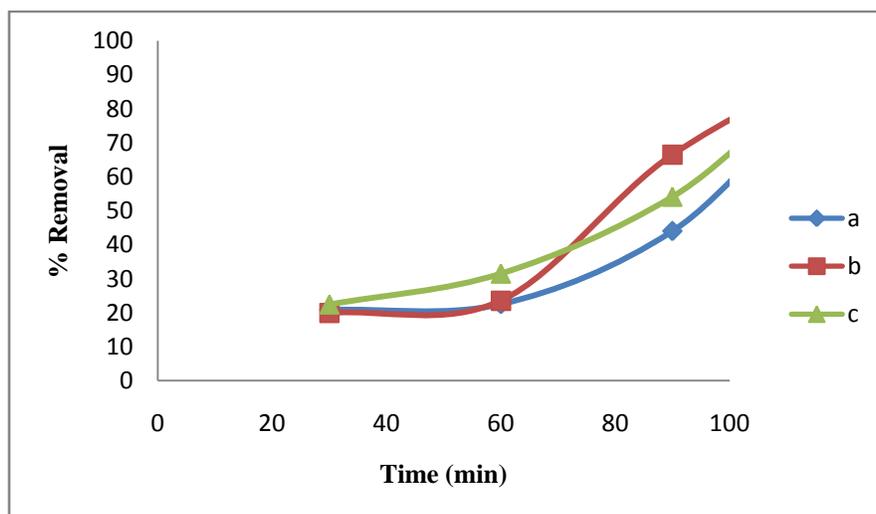


Fig.6. Effect of Temperatures a – 40° C, b - 50° C & c - 60° C on Removal of Cr (VI)

### G. Effect of Agitation Speed

Agitation speed is an important parameter to be considered. For the various agitation speeds like 90 rpm, 120 rpm and 180 rpm the adsorption studies is carried out in room temperature with optimized value. The table 7 shows the results of the experiment. With increase in the agitation speed the metal removal gets

increased. Because of the more forces between the molecules, more metals gets bind to the surface of the adsorbate. There is no further increase in the removal after the equilibrium is attained. Increase in the removal is due to the decrease in the boundary layer thickness. Graphical representation is shown below.

Table 7 Effect of Agitation Speed on Removal of Cr (VI)

S.No	Agitation Speed (rpm)	% Removal
1	90	87.5
2	120	90.3
3	180	93.5

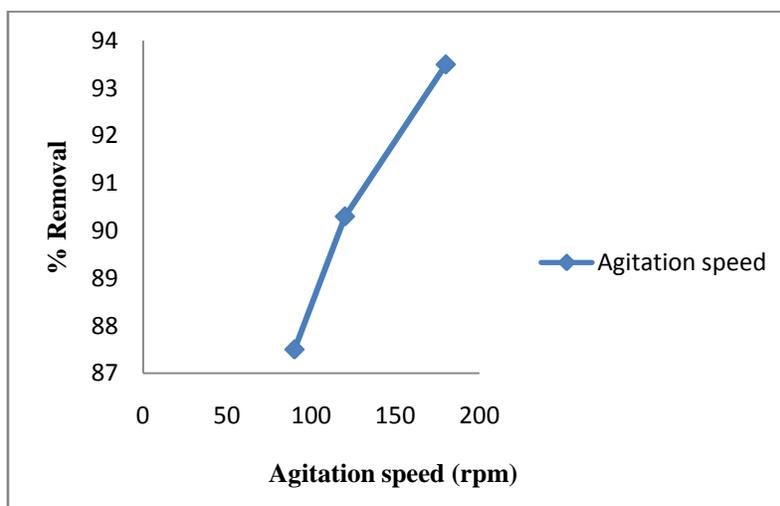


Fig.7. Effect of Agitation Speed on Removal of Cr (VI)

## IV. KINETICS OF ADSORPTION

In order to examine the mechanism of adsorption suitable kinetic model is needed to analyze the rate data. The dynamics of adsorption describes the rate of Cr (VI) uptake on Egg shell powder and this rate controls the equilibrium time. In order to study the mechanism of sorption and potential rate determining steps, different kinetic models have been used to test experimental data obtained from 2 process variables ( Different initial concentration and different temperatures). The adsorption dynamics of the Cr (VI) on Egg shell were tested with the Lagergren pseudo-first order, the chemisorptions pseudo-second order, Elovich kinetic model, the intraparticle diffusion model, and Fractional power model.

### A. Pseudo First Order Equation

The kinetic of Cr (VI) removal on Egg shell powder with pseudo first order equation was explained here. For this analysis, the linear form of Lagergren equation was used. The integrated form can be expressed as

$$\text{Log} (q_e - q_t) = \text{log} q_e - \frac{k_1 t}{2.303}$$

Where  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed at equilibrium and at time  $t$  ( $\text{mg g}^{-1}$ ), respectively, and  $k_1$  is the equilibrium rate constant of pseudo first-order adsorption, ( $\text{min}^{-1}$ ) [29]. The linear plot of  $\text{log} (q_e - q_t)$  versus  $t$  shows the appropriateness of the above equation and consequently the first-order nature of the process involved. This kinetic model not fully describe the adsorption process because, the regression co-efficient for this model is not in acceptable range (0.88).

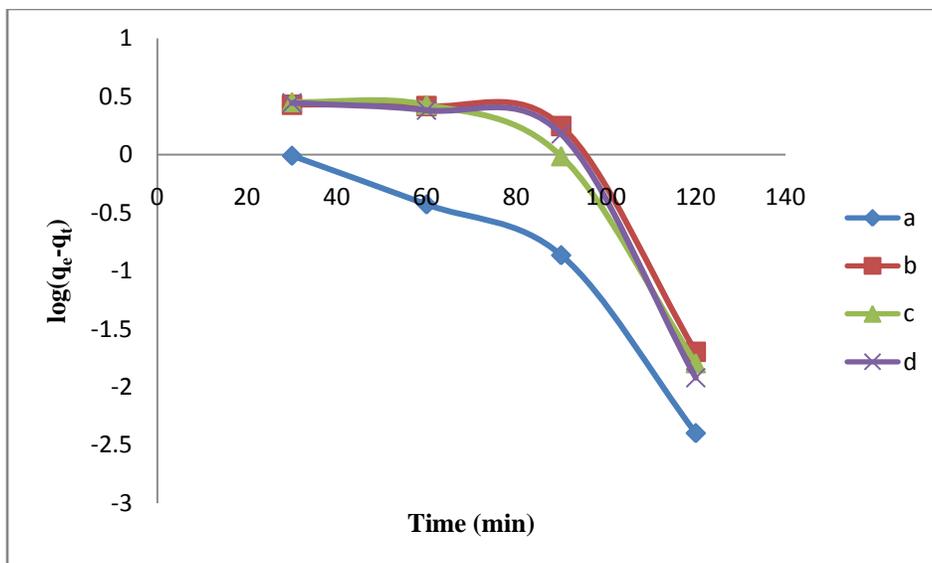


Fig.8 Pseudo First Order Equation for Different Temperatures A – 30<sup>0</sup> C, B – 40<sup>0</sup> C, C - 50<sup>0</sup> C & D - 60<sup>0</sup> C

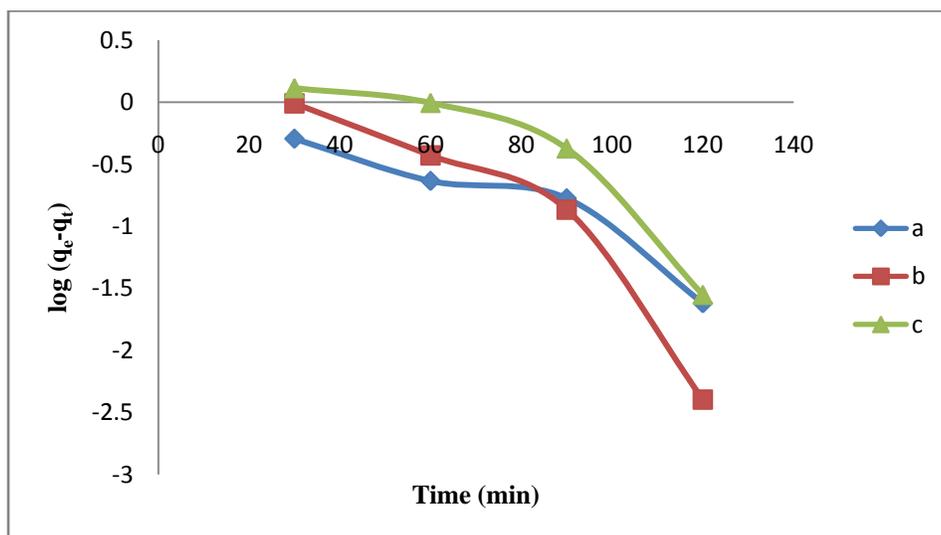


Fig.9. Pseudo First Order Equation for Different Concentrations A – 50 Ppm, B – 100 Ppm & C – 150 Ppm

**B. Pseudo Second Order Equation**

The adsorption kinetics may also be described by a pseudo second-order equation. The linear pseudo second-order equation is the following

$$t/q_t = 1/k_2q_e^2 + 1/q_t * t$$

Where  $k_2$  the equilibrium is rate constant of pseudo second-order adsorption ( $g\ mg^{-1}\ min^{-1}$ ) [30]. The slopes and intercepts of plots  $t/q_t$  versus  $t$  were used to calculate the second-order rate constants  $k_2$  and  $q_e$ . The

plot of  $t/q_t$  versus  $t$  shows good agreement of experimental data with the second-order kinetic model for different initial concentrations and temperature. Table 8 and 9 lists the computed results obtained from the second-order kinetic model. The regression coefficients for the second order kinetic model obtained were in acceptable value (0.99). This shows that this model suits for the adsorption of Cr (VI) ions.

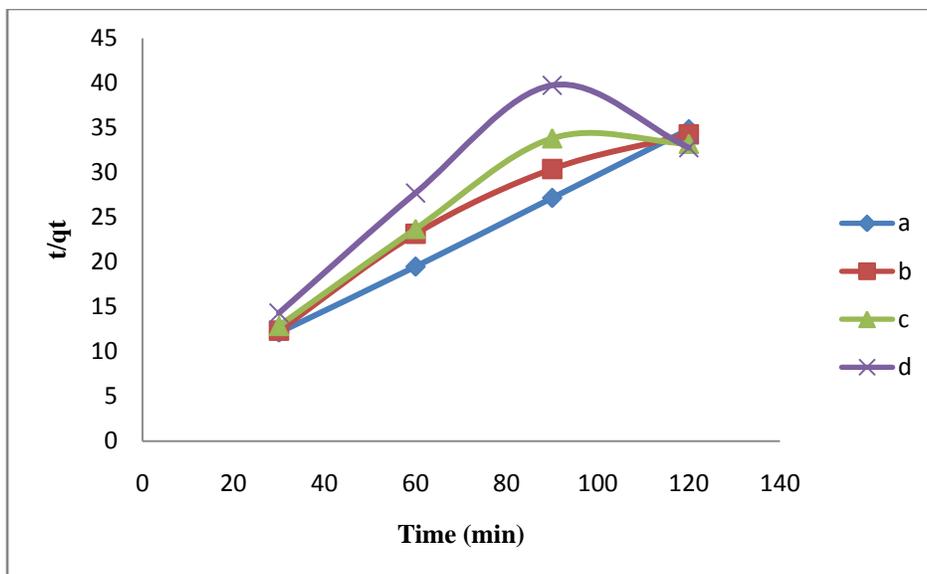


Fig.10. Pseudo Second Order Equation for Different Temperatures A – 30<sup>0</sup> C, B – 40<sup>0</sup> C, C - 50<sup>0</sup> C & D - 60<sup>0</sup> C

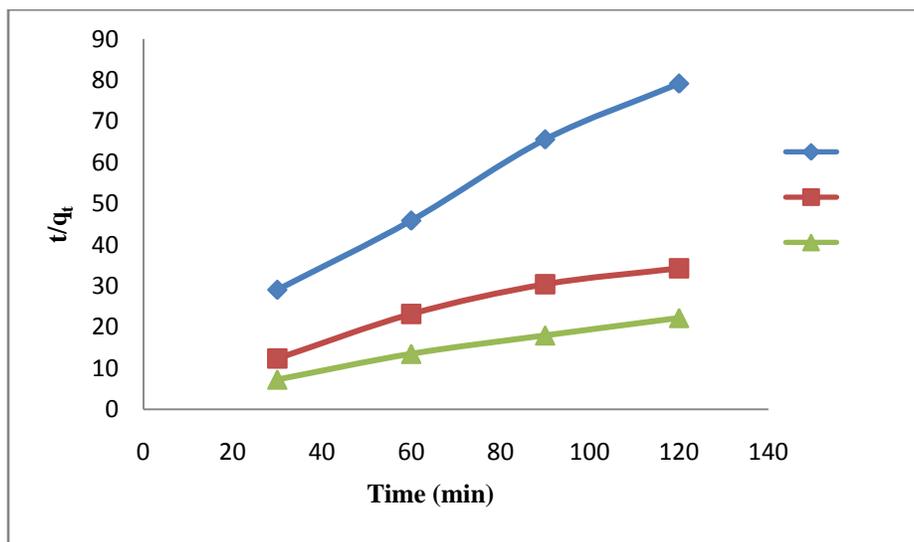


Fig.11. Pseudo Second Order Equation for Different Concentrations A – 50 Ppm, B – 100 Ppm & C – 150 Ppm

### C. Fractional power model

The adsorption kinetics can also be described by power function equation.

The linear power function equation is the following

The equation is given by

$$\ln q_t = \ln k + \mu \ln t$$

The plot  $\ln q_t$  and  $\ln t$  should give linear relationship from which  $\mu$  and  $k$  can be determined from the slope

and intercept of the plot respectively. The results indicate that the power function model described the time-dependent. The kinetic of Cr (VI) ion adsorption can't be satisfactory described by power function model. However, the regression coefficient  $R^2$  is not very high (<0.94) which indicate that power function is not the best model to correlate kinetic data.

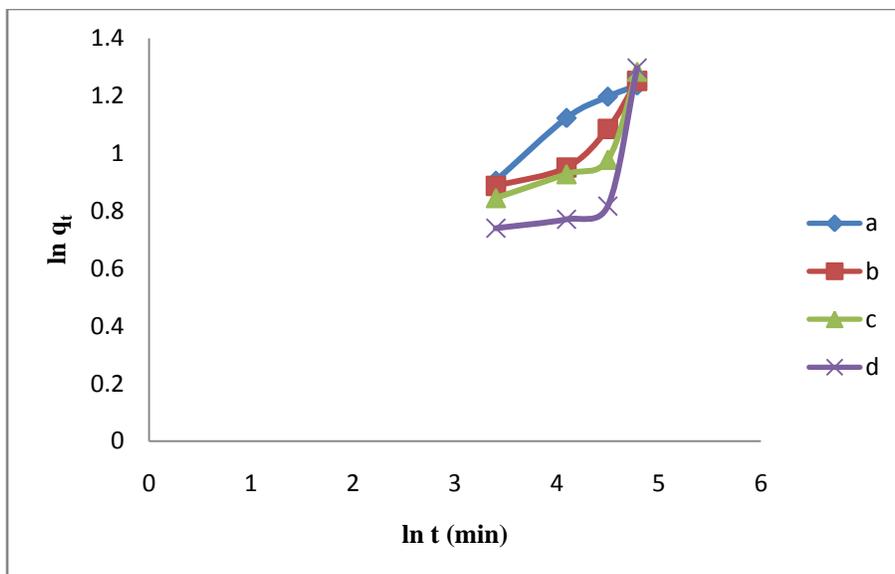


Fig.12. Fractional Model for Different Temperatures A – 30<sup>o</sup> C, B – 40<sup>o</sup> C, C - 50<sup>o</sup> C & D - 60<sup>o</sup> C

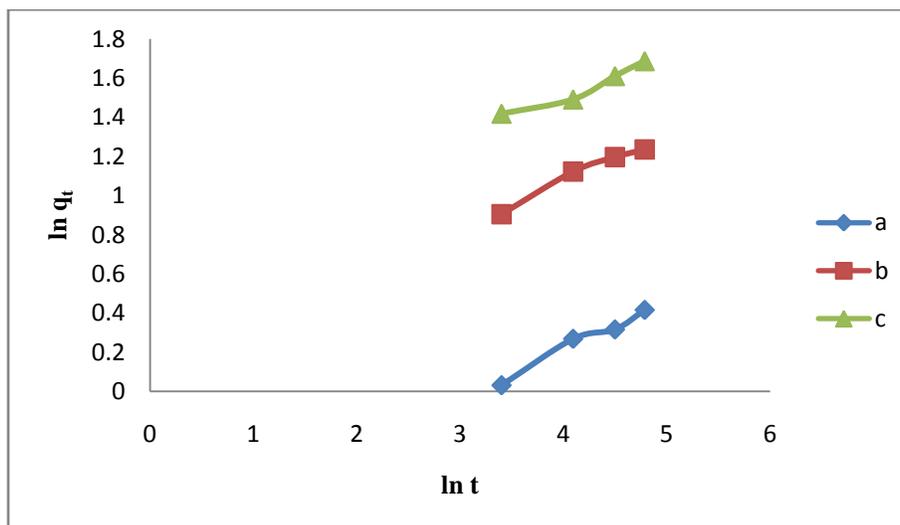


Fig.13. Fractional Model for Different Concentrations A – 50 Ppm, B – 100 Ppm & C – 150 Ppm

#### D. Intra Particle Diffusion

The rate parameters for intraparticle diffusion at different initial concentrations are determined using the following equation.

$$q_t = k_{int} t^{1/2}$$

Where

$k$  is the intraparticle diffusion rate constant, ( $\text{mg g}^{-1} \text{min}^{-1}$ ). The mechanism of adsorption is complex but that intraparticle diffusion is important in the early stages. The slopes of these linear portions can be

defined as a rate parameter and characteristic of the rate of adsorption in the region where intraparticle diffusion is occurring. Initially, within a short-time period, it is postulated that the ion was transported to the external surface of the Egg shell powder through film diffusion and its rate have been very fast. After saturation of the surface, the ion entered into the Egg shell powder by intraparticle diffusion through pore and interior surface diffusion until equilibrium is attained which is represented by the second straight [33].

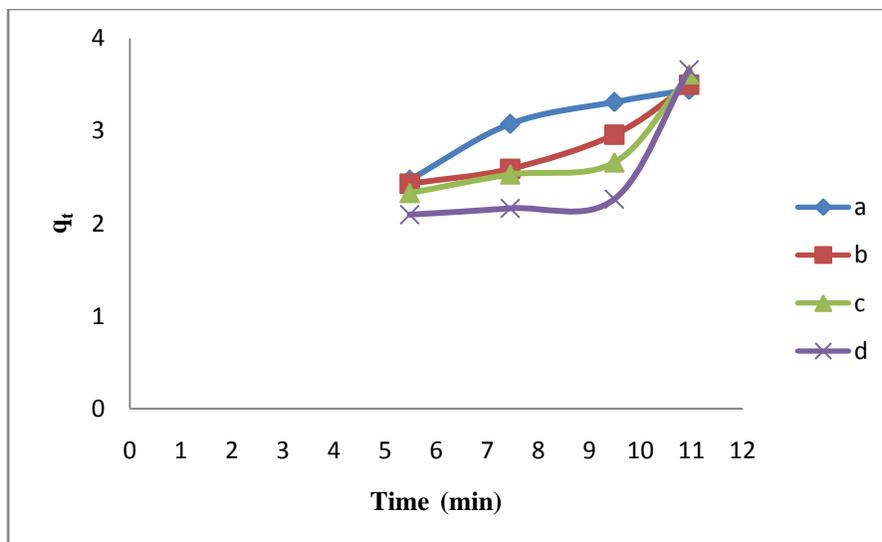


Fig.14. Intra Particle Diffusion for Different Temperatures A – 30<sup>0</sup> C, B – 40<sup>0</sup> C, C - 50<sup>0</sup> C & D - 60<sup>0</sup> C

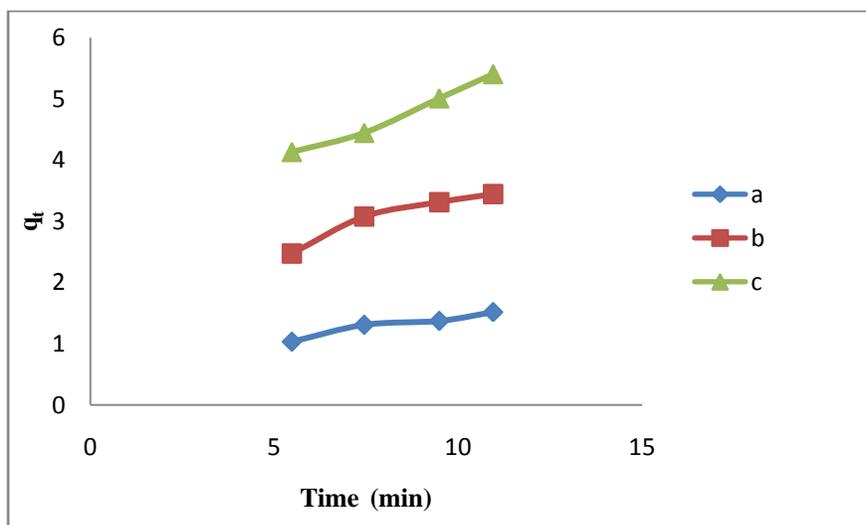


Fig.15. Intra Particle Diffusion for Different Concentrations A – 50 Ppm, B – 100 Ppm & C – 150 Ppm

### E. Elovich Equation

The linear Elovich equation is given as follows

$$q_t = 1/\beta * \ln(\alpha\beta) + 1/\beta * \ln t$$

Where  $\alpha$  is the initial sorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ), and the parameter  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption ( $\text{g mg}^{-1}$ ). The Elovich equation describes predominantly chemical adsorption on highly heterogeneous adsorbents, but the equation does not propose any

definite mechanism for adsorbate–adsorbent interaction [30]. This kinetic also not fit for this adsorption process, because of the low regression co-efficient value (0.97).

For different concentration and temperature, the kinetic values were tabulated for Cr (VI) in table 8, 9 respectively.

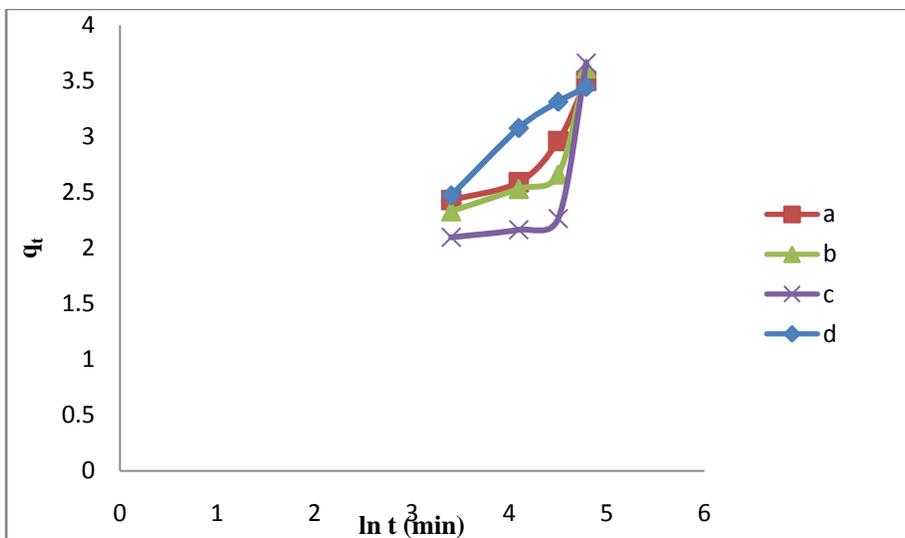


Fig.16. Elovich 'S Model for Different Temperatures A – 30<sup>0</sup> C, B – 40<sup>0</sup> C, C - 50<sup>0</sup> C & D - 60<sup>0</sup> C

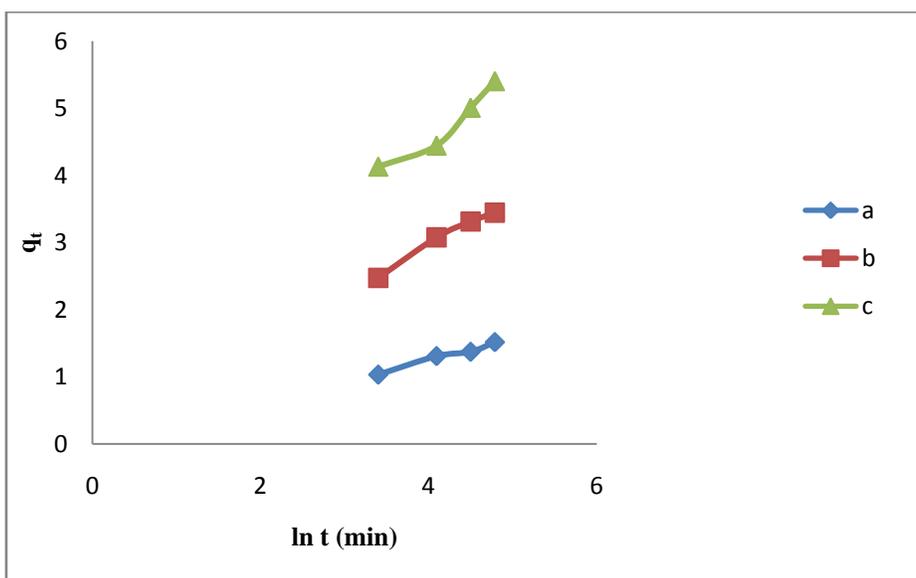


Fig.17. Elovich 'S Model for Different Concentrations A – 50 Ppm, B – 100 Ppm & C – 150 Ppm

Table 8 Kinetic Data for the Removal of Cr (VI) for Different Concentration

Models	Parameters	Concentration at 50 ppm	Concentration at 100 ppm	Concentration 150 ppm
Pseudo first order	R <sup>2</sup>	0.828	0.887	0.828
	K (g.mg <sup>-1</sup> min <sup>-1</sup> )	0.039	0.057	0.039
	q <sub>e</sub> (mg g <sup>-1</sup> )	0.983	0.974	0.015
Pseudo second order	R <sup>2</sup>	0.995	0.999	0.99
	K (g.mg <sup>-1</sup> min <sup>-1</sup> )	0.0258	0.0142	0.009
	q <sub>e</sub> (mg g <sup>-1</sup> )	1.766	3.968	6.097
Fractional power	R <sup>2</sup>	0.973	0.714	0.941
	K	0.421	0.886	2.093
	N	0.267	0.269	0.193

Intra particle diffusion	R <sup>2</sup>	0.935	0.92	0.985
	K	0.082	0.172	0.236
Elovich	R <sup>2</sup>	0.977	0.982	0.927
	α <sub>e</sub>	0.251	0.813	2.511
	β <sub>e</sub>	3.003	1.41	1.097
RMSE	-	0.399	0.744	1.174

Table 9 Kinetic Data for the Removal of Cr (VI) for Different Temperature

Models	Parameters	Temperature at 30 °c	Temperature at 40 °c	Temperature at 50 °c	Temperature at 60 °c
Pseudo first order	R <sup>2</sup>	0.887	0.667	0.76	0.691
	K (g.mg <sup>-1</sup> min <sup>-1</sup> )	0.057	0.048	0.052	0.055
	q <sub>e</sub> (mg g <sup>-1</sup> )	0.974	4.423	4.777	4.933
Pseudo second order	R <sup>2</sup>	0.999	0.956	0.870	0.655
	K (g.mg <sup>-1</sup> min <sup>-1</sup> )	0.0142	0.0086	0.0069	0.0042
	q <sub>e</sub> (mg g <sup>-1</sup> )	3.968	4.115	4.219	4.464
Fractional power	R <sup>2</sup>	0.714	0.857	0.714	0.546
	K	0.886	0.99	0.886	0.638
	N	0.269	0.248	0.269	0.322
Intra particle diffusion	R <sup>2</sup>	0.92	0.915	0.755	0.621
	K	0.172	0.19	0.207	0.246
Elovich	R <sup>2</sup>	0.982	0.825	0.668	0.519
	α <sub>e</sub>	0.813	0.589	0.425	0.231
	β <sub>e</sub>	1.41	1.392	1.291	1.118
RMSE	-	0.744	2.93	2.844	2.810

## V. ADSORPTION ISOTHERMS

Equilibrium isotherm is described by a sorption isotherm, characterized by certain constants whose values express the surface properties and affinity of the adsorbent sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that at the sorbent interface. In order to quantify the affinity of Egg shell powder for the metal studied, i.e. Cr (VI), 4 widely used isotherm models (Langmuir, Freundlich, Temkin and B.E.T isotherm models) were used to analyze the data obtained from the adsorption process.

### A. Langmuir Adsorption Isotherm

The monolayer coverage of the sorbate on a sorbent surface at a constant temperature is represented by the Langmuir isotherm. The basic assumption is that the forces exerted by chemically unsaturated surface atoms do not extend further than the diameter of one sorbed molecule. The Langmuir isotherm hints towards surface homogeneity Langmuir Isotherm:

$$C_e/q_e = [1/K_d q_m] + [1/q_m] C_e$$

Where,

q<sub>e</sub> is the amount of Ni (II) adsorbed at equilibrium per mass of Egg shell powder (mg g<sup>-1</sup>);

C<sub>e</sub> is the concentration of the metal in aqueous phase at equilibrium;

$K_d$  is the sorption equilibrium constant;  
 $q_m$  ( $\text{mg g}^{-1}$ ) is the monolayer capacity.  
 The monolayer coverage is obtained from a plot of  $C_e/q_e$  versus  $C_e$ . The slope and the intercept of the linear

graph obtained from this plot give the value of  $q_m$  and  $K$ . The regression co efficient for this isotherm shows fit for process (0.99).

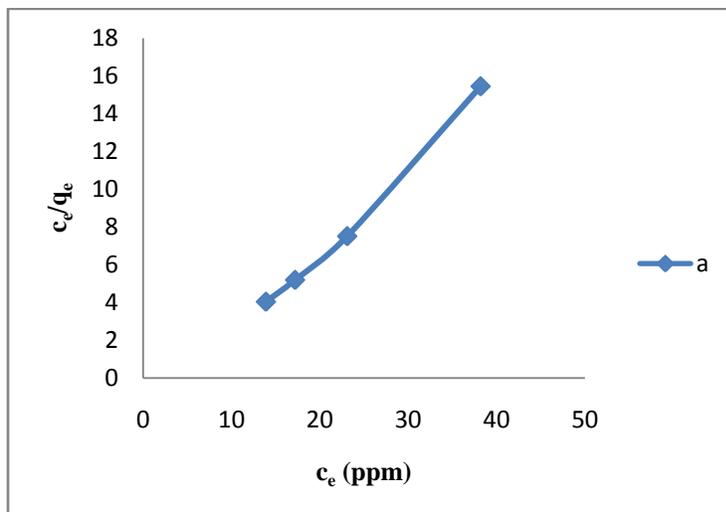


Fig.18. Langmuir Isotherm, Temperature at A – 30<sup>0</sup> C

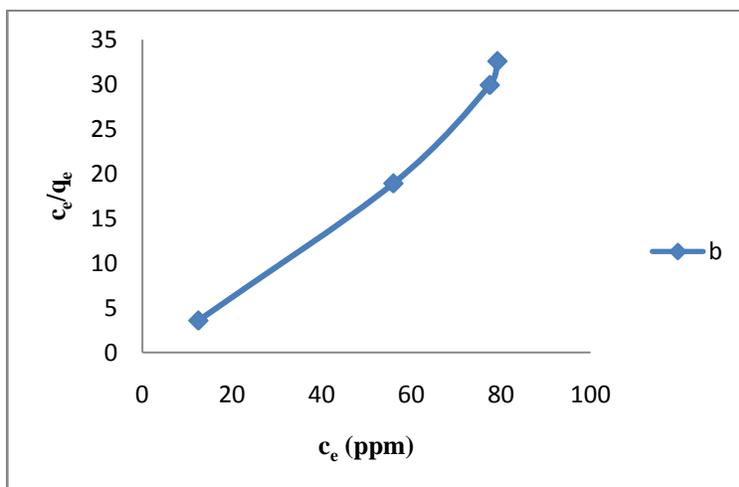


Fig.19. Langmuir Isotherm, Temperature at B – 40<sup>0</sup> C

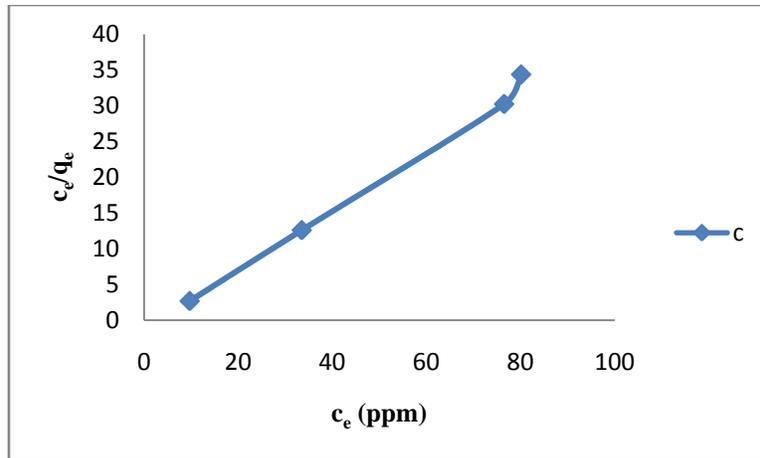


Fig.20. Langmuir Isotherm, Temperature at C – 50<sup>0</sup> C

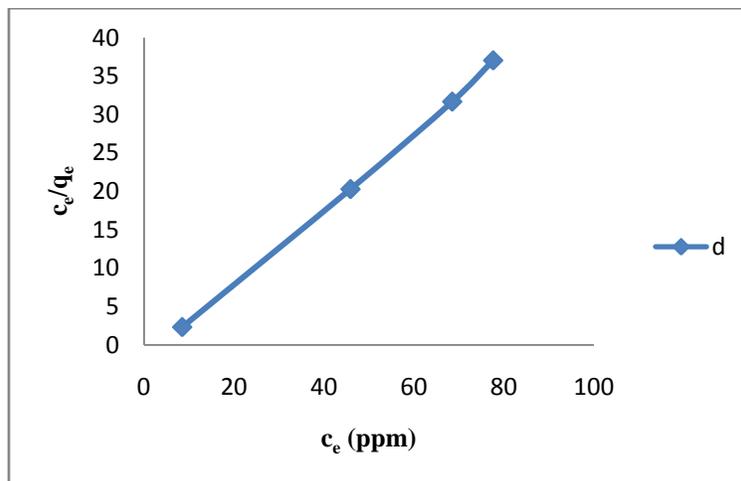


Fig.21. Langmuir Isotherm, Temperature at D – 60<sup>0</sup> C

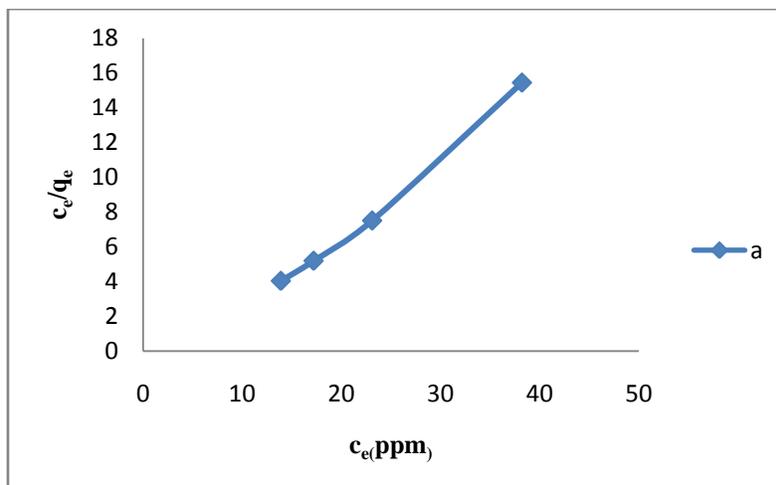


Fig.22. Langmuir Isotherm, Concentration at A – 50 Ppm

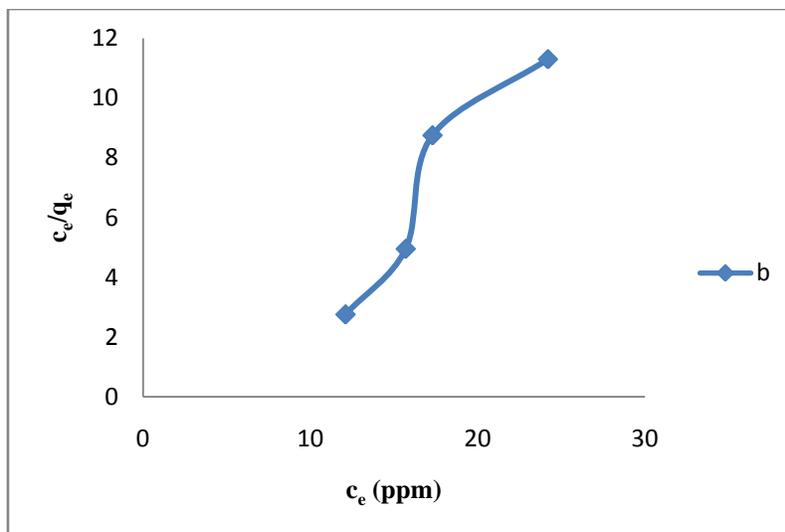


Fig.23. Langmuir Isotherm, Concentration At B – 100 Ppm

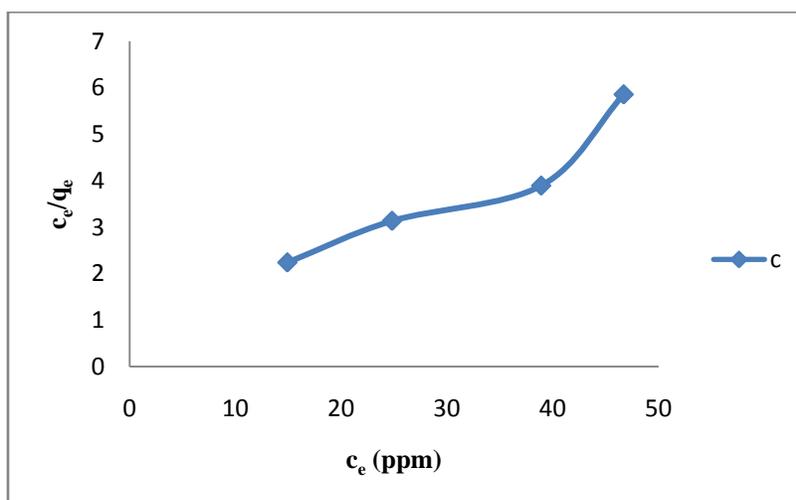


Fig.24. Langmuir Isotherm, Concentration At C – 150 Ppm

**B. Freundlich Isotherm**

Freundlich equation assumes that the uptake of metal ions occur on heterogeneous surface by multilayer adsorption. Linear form of Freundlich equation is

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

Where  $q_e$  - adsorption capacity,  $C_e$  - final concentration,  $n$ = empirical constant

The Freundlich coefficients  $n$  and  $K_f$  are obtained from the plots of  $\ln q_e$  versus  $\ln C_e$ . From the below graph it is cleared that this adsorption process not follows Freundlich isotherm [31].

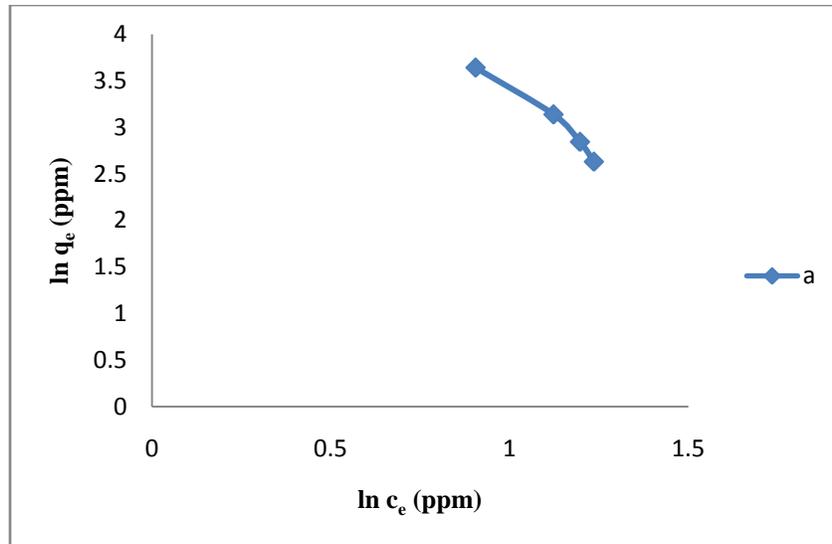


Fig.25. Freundlich Isotherm, Temperature at a – 30<sup>0</sup> C

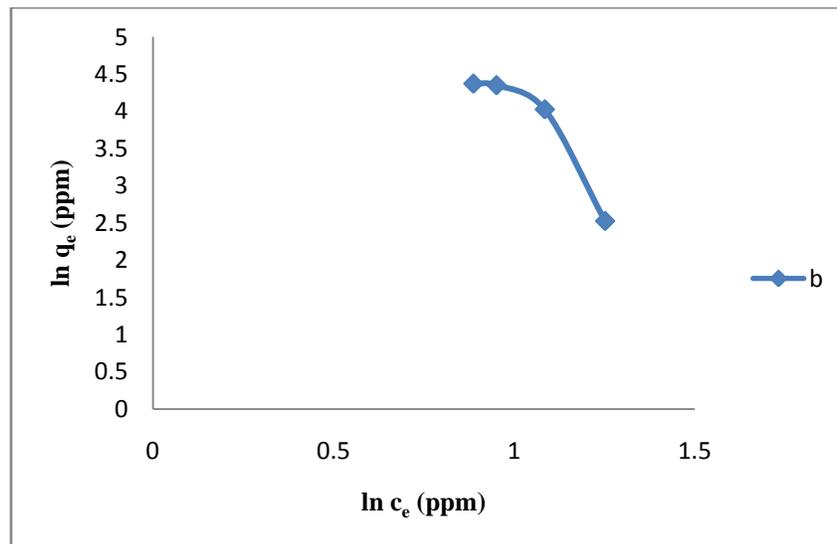


Fig.26. Freundlich isotherm, Temperature at b – 40<sup>0</sup> C

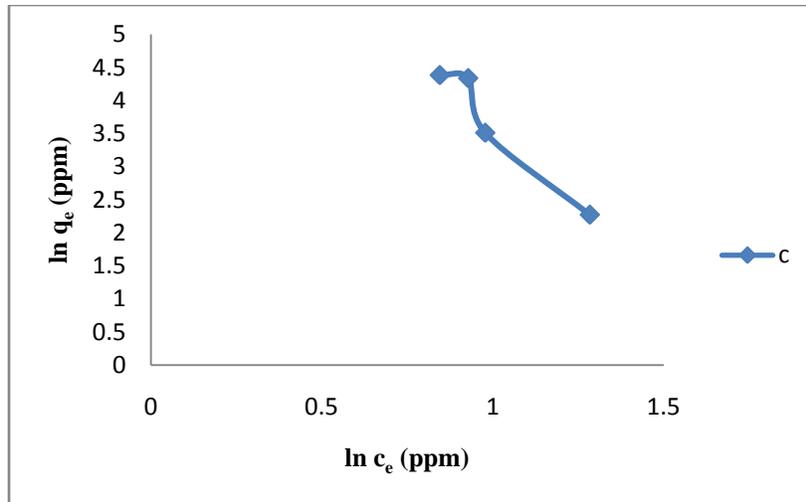


Fig.27. Freundlich Isotherm, Temperature at c – 50<sup>0</sup> C

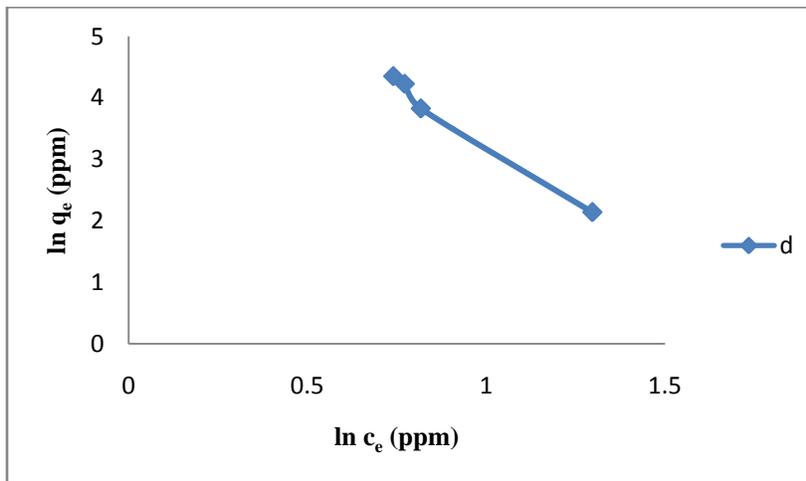


Fig.28. Freundlich Isotherm, Temperature at d – 60<sup>0</sup> C

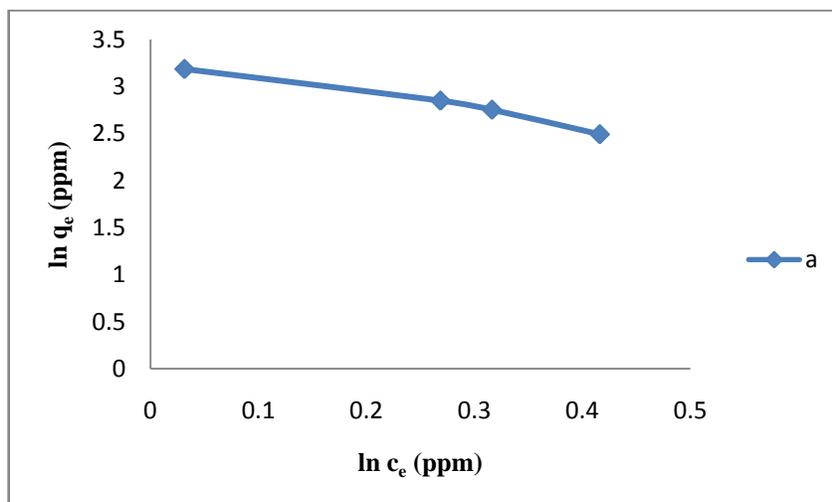


Fig.29. Freundlich Isotherm, Concentration at a – 50 ppm

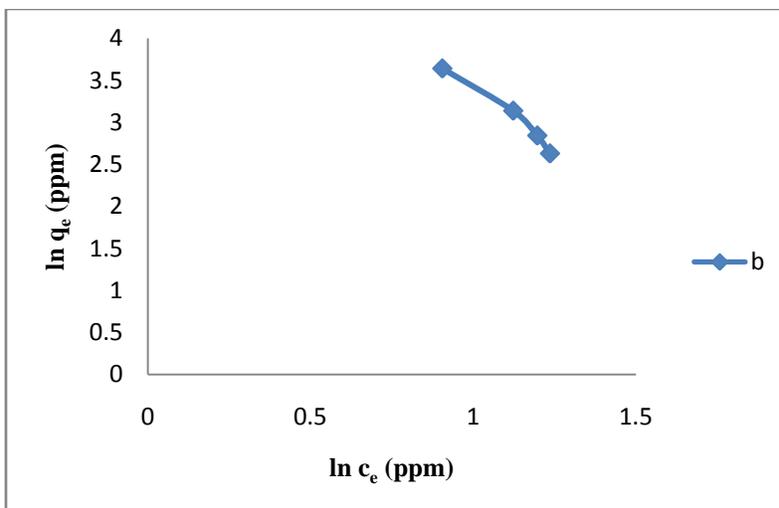


Fig.30. Freundlich Isotherm, Concentration at B – 100 Ppm

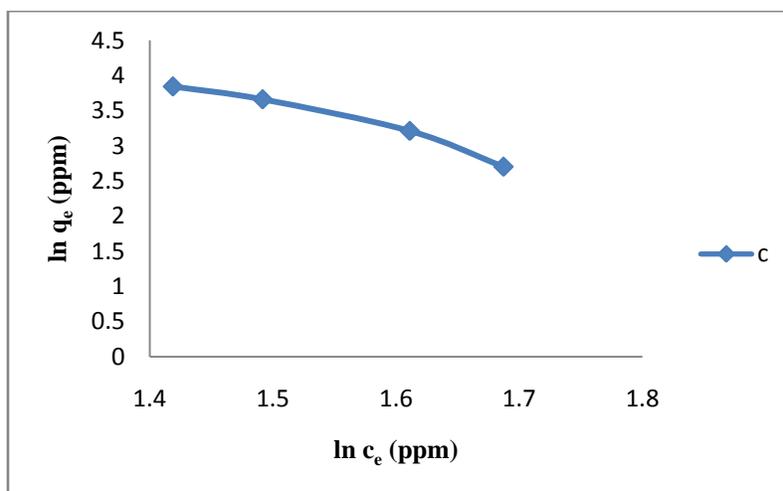


Fig.31. Freundlich Isotherm, Concentration at C – 1000 Ppm

### C. Temkin Isotherm

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy. The Temkin isotherm is given as:

$$X = a + b \ln C$$

Where C - concentration of adsorbate in solution at equilibrium (mg/l), X -amount of metal adsorbed per unit weight of adsorbent (mg/g), a and b are constants related to adsorption capacity and intensity of adsorption and related to the intercept and slope of the plots of  $\ln C$  against X [27]. The Temkin equilibrium adsorption curves relating the solid and liquid phase concentration of metal at equilibrium are given below:

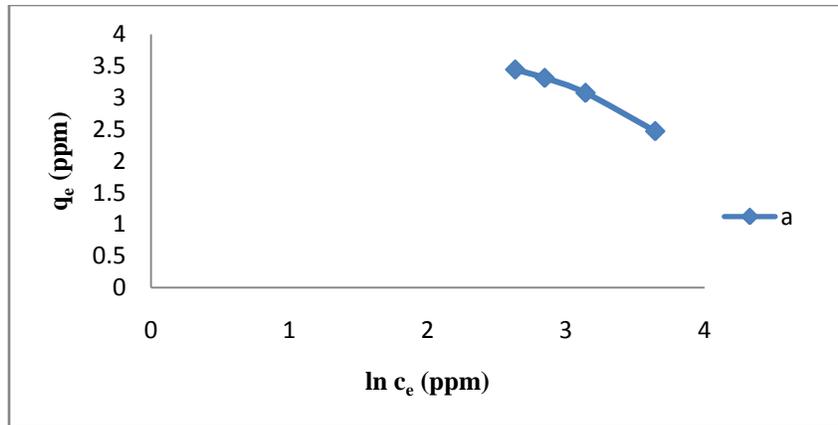


Fig.32. Temkin Isotherm, Temperature at A – 30<sup>0</sup> C

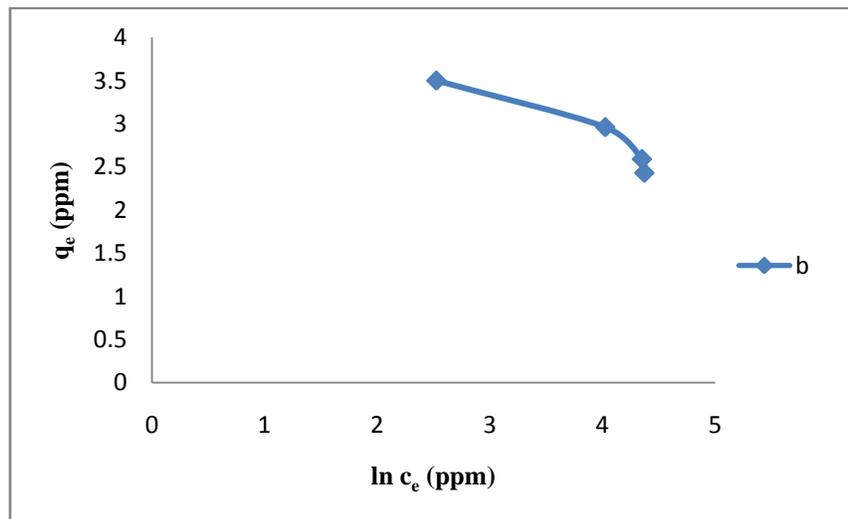


Fig.33. Temkin Isotherm, Temperature at B – 40<sup>0</sup> C

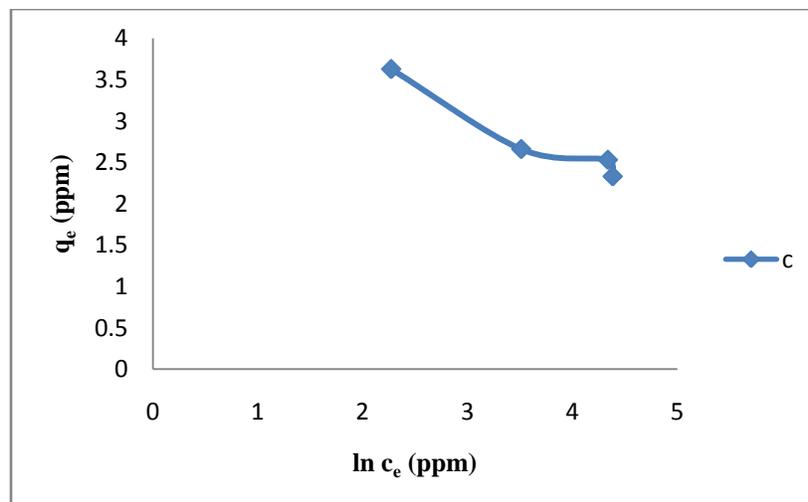


Fig.34. Temkin Isotherm, Temperature at C – 50<sup>0</sup> C

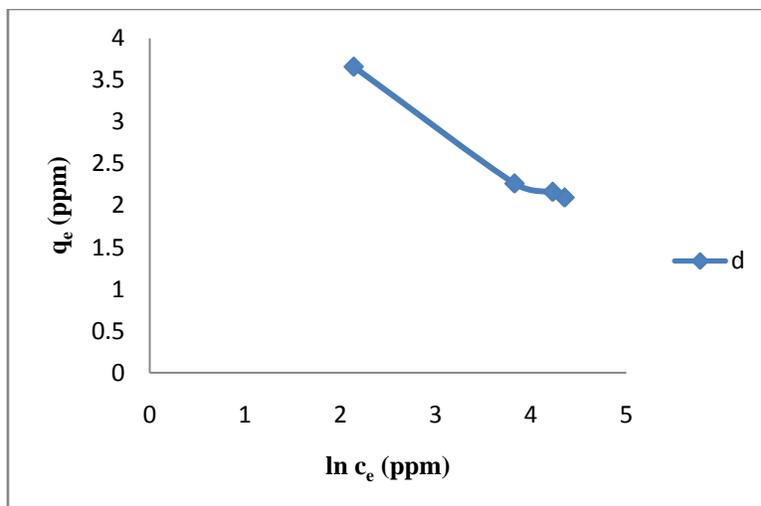


Fig.35. Temkin Isotherm, Temperature at D – 60<sup>0</sup> C

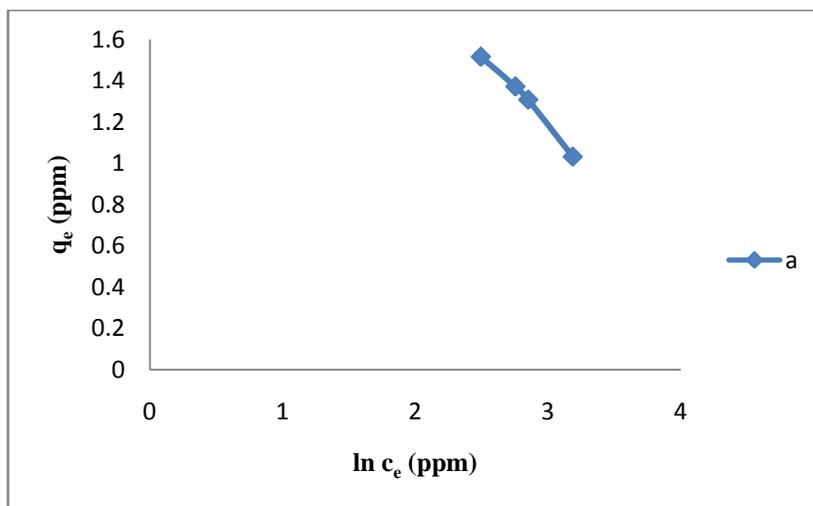


Fig.36. Temkin Isotherm, Concentration at A – 50 Ppm

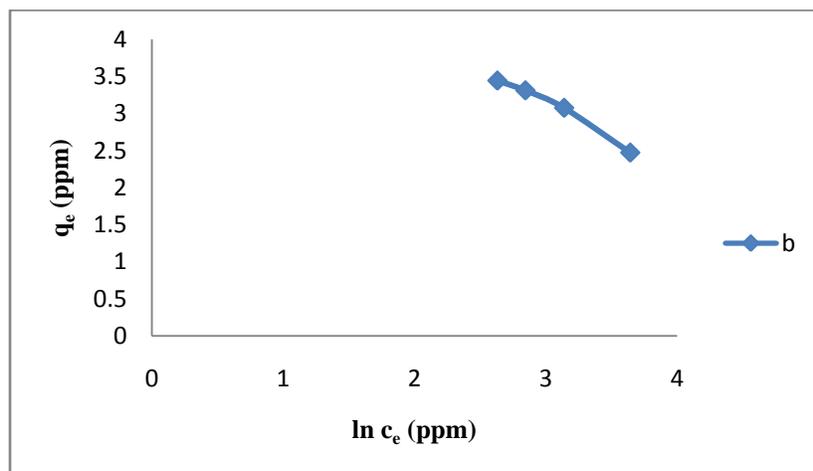


Fig.37. Temkin Isotherm, Concentration at B – 100 Ppm

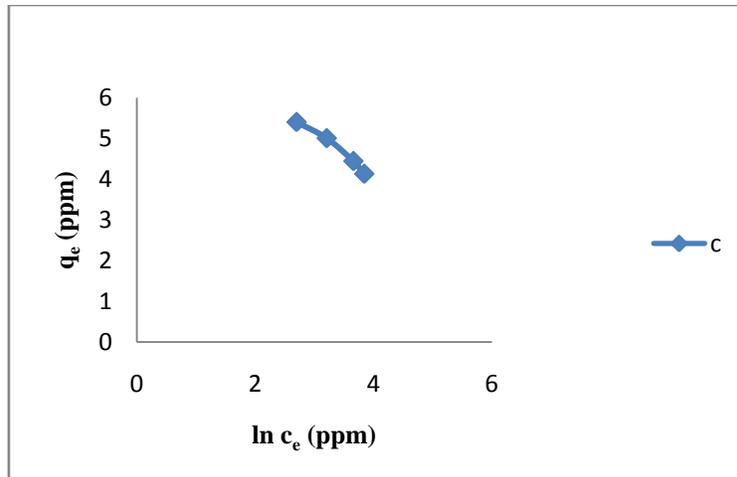


Fig.38. Temkin Isotherm, Concentration at C – 150 Ppm

#### D. B.E.T Adsorption Isotherm

BET isotherm was developed by Brunauer, Emmett and Teller as an extension of Langmuir isotherm, it assumes that first layer of molecules adhere to the surface with energy comparable to heat of adsorption for monolayer sorption and subsequent layers have equal energies. Equation in its linearized form is expresses

$$\frac{C_f}{(C_s - C_f)q} = \frac{1}{Bq_{\max}} - \left( B - \frac{1}{Bq_{\max}} \right) \left( \frac{C_f}{C_s} \right)$$

Where  $C_s$  is the saturation concentration (mg/l) of the solute,  $C_f$  is solute equilibrium concentration. B and  $q_{\max}$  are two constants and can be evaluated from the slope and intercept [32]. The response to this isotherm model is given in below graph.

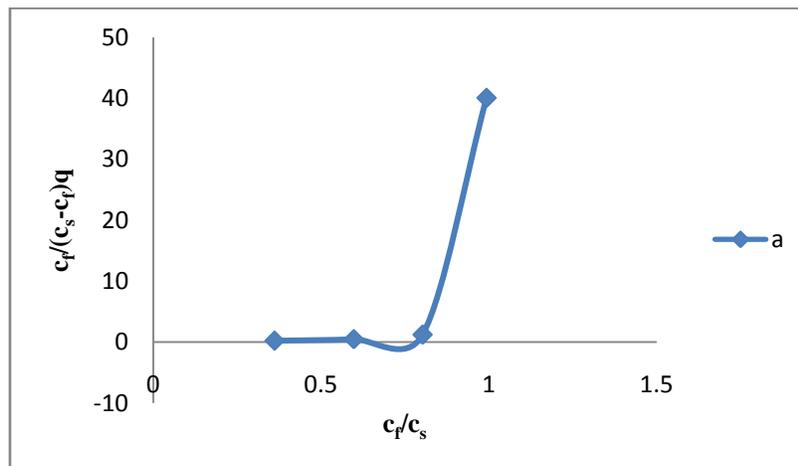


Fig.39. B.E.T Isotherm, Temperature at A – 30<sup>0</sup> C

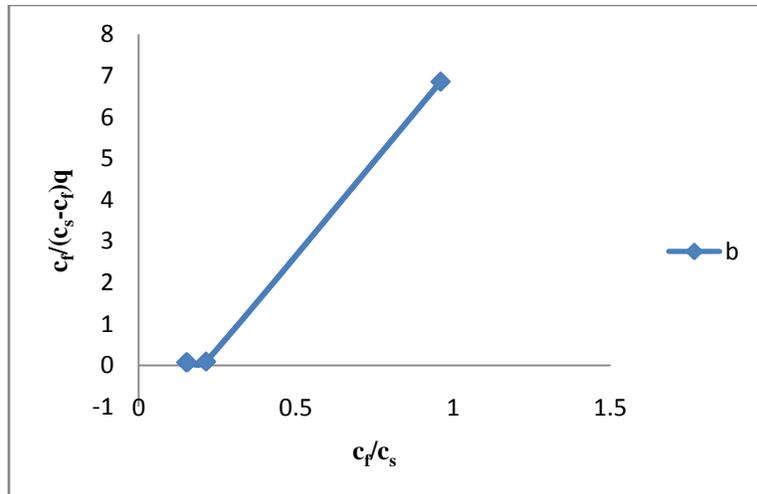


Fig.40. B.E.T Isotherm, Temperature at B – 40<sup>0</sup> C

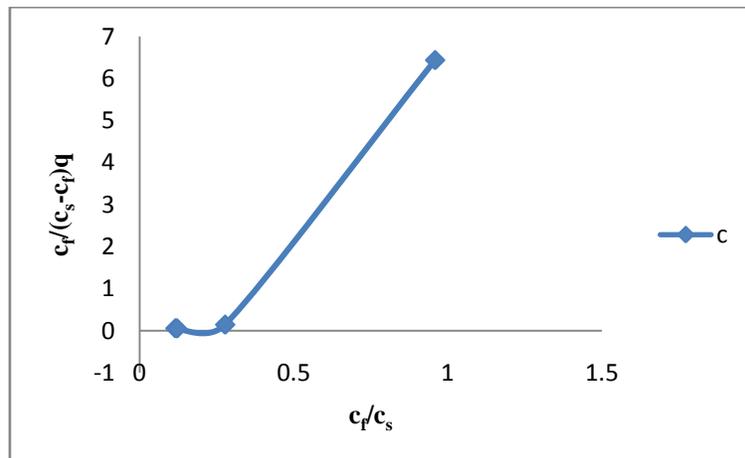


Fig.41. B.E.T Isotherm, Temperature at C – 50<sup>0</sup> C

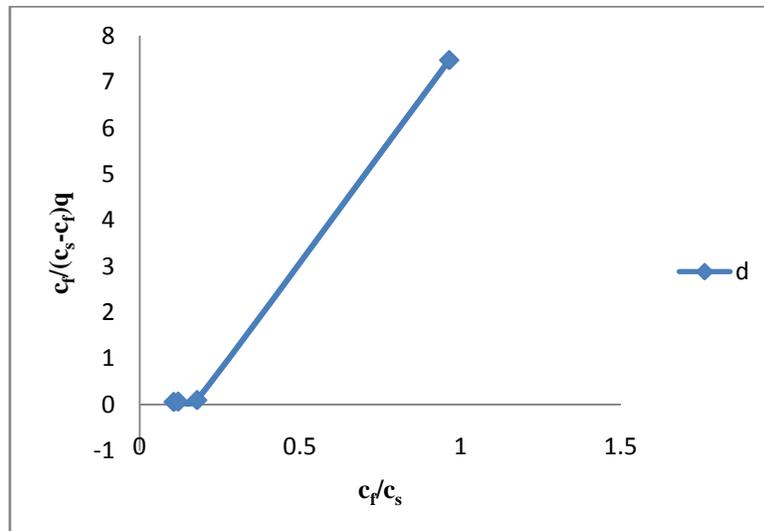


Fig.42. B.E.T Isotherm, Temperature at D – 60<sup>0</sup> C

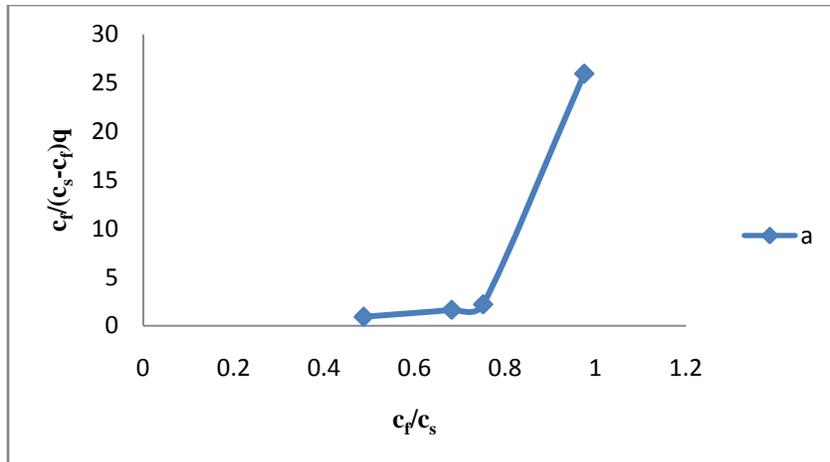


Fig.43. B.E.T Isotherm, Concentration at A – 50 Ppm

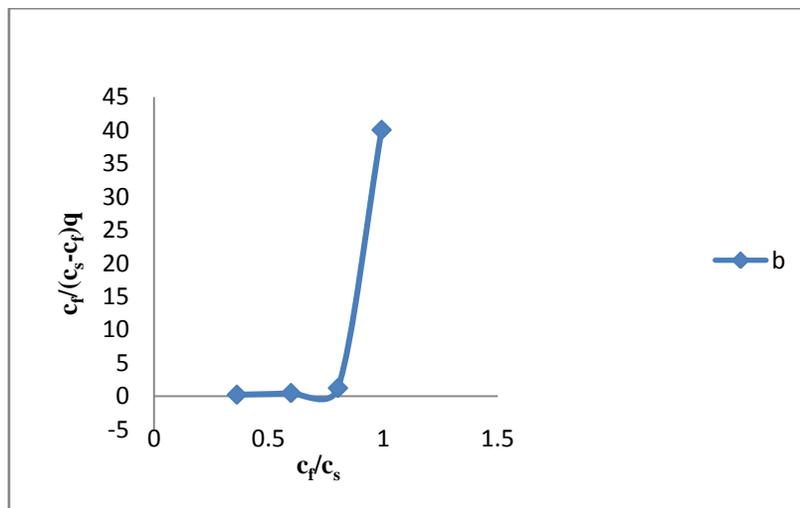


Fig.44. B.E.T Isotherm, Concentration at B – 100 Ppm

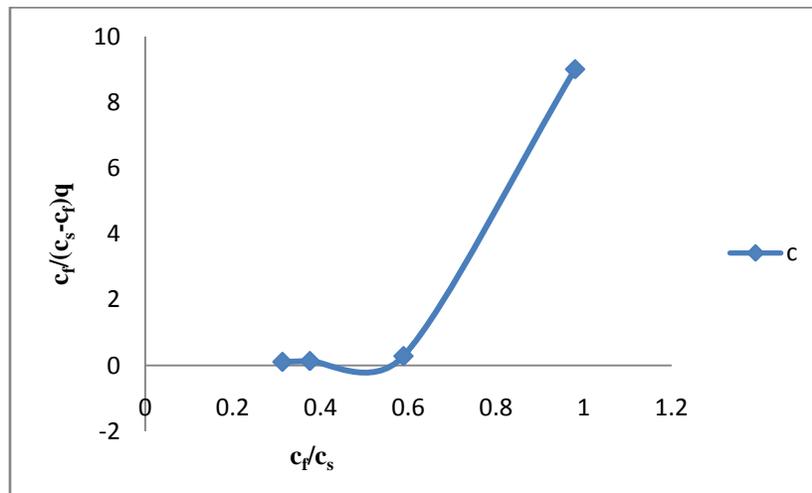


Fig.45. B.E.T Isotherm, Concentration at C – 150 Ppm

**Table 10 Isotherm Data for the Removal Of Cr (VI) For Different Temperature**

Models	Parameters	Temperature at 30 °c	Temperature at 40 °c	Temperature at 50 °c	Temperature at 60 °c
Freundlich isotherm	R <sup>2</sup>	0.969	0.873	0.941	0.989
	K <sub>f</sub>	0.001	0.0001	0.00017	0.0007
	N	0.342	0.197	0.199	0.258
Langmuir isotherm	R <sup>2</sup>	0.994	0.983	0.994	0.999
	Q <sub>o</sub>	2.100	2.375	2.298	2.001
	b	0.161	0.171	0.247	0.231
	R <sub>L</sub>	0.058	0.055	0.039	0.041
Temkin isotherm	R <sup>2</sup>	0.981	0.905	0.935	0.983
	a	6.06	4.84	4.835	5.176
	b	0.973	0.515	0.565	0.723
B.E.T isotherm	R <sup>2</sup>	0.579	0.995	0.969	0.994
	B	3.006	7.124	7.485	8.976
	q <sub>max</sub>	0.011	0.1	0.11	0.1
RMSE	-	0.744	2.93	2.844	2.810

**Table 11 Isotherm Data for the Removal of Cr (VI) for Different Concentration**

Models	Parameters	Concentration for 50 ppm	Concentration for 100 ppm	Concentration for 150 ppm
Freundlich isotherm	R <sup>2</sup>	0.971	0.969	0.966
	K <sub>f</sub>	0.026	0.001	0.00005
	n	0.577	0.342	0.239
Langmuir isotherm	R <sup>2</sup>	0.896	0.994	0.9
	Q <sub>o</sub>	1.404	2.100	9.803
	b	0.131	0.161	0.181
	R <sub>L</sub>	0.132	0.058	0.035
Temkin isotherm	R <sup>2</sup>	0.987	0.981	0.981
	a	3.291	6.06	6.06
	b	0.703	0.973	0.973
B.E.T isotherm	R <sup>2</sup>	0.73	0.579	0.858
	B	2.737	3.006	3.572
	q <sub>max</sub>	0.012	0.011	0.053
RMSE	-	0.399	0.744	1.174

## VI. CONCLUSION

The powdered eggshell has been investigated as a cheap and effective sorbent for the removal of Cr (VI) ions from effluent. The results reveal that the adsorption occurred mainly at the surface of the eggshells and slightly by the internal pores. The optimized pH (6) and adsorbent dosage (2.5 gm) were found and maintained throughout the process. The process followed second order equation. Equilibrium data fits for Langmuir isotherm. From the above studies Egg shell powder is successfully used as low cost

adsorbent for the removal of Cr (VI) from the industrial effluent.

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