

STUDIES ON ISOTHERM AND KINETIC CONSTANT FOR REMOVAL OF LEAD FROM WATER

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ABSTRACT

This work deal with isotherm and kinetics study of removal of lead, a heavy metal from polluted water. Samples of polluted water was obtained treated with adsorbent of varied mass, Concentration of lead in treated and untreated water was measured with atomic adsorption spectrometer. Langmuir isotherm constant value obtained for sample of water collected from river are 38.5 mg/g for q_m , 0.0373 l/mg for K_d , 0.908 for R^2 and K_L to be 0.97. The Temkin constant values obtained are 10.77 J/mol for B, 0.2704 l/mg for A, 233.9 for b and 0.75 for R^2 . Comparison of the two model shows Langmuir fitted the adsorption very well while the kinetic analysis suggested the reaction to be first order.

KEYWORDS: Isotherm, Pollution, Adsorption, Adsorbate, Spectrometer, Langmuir isotherm, Temkin isotherm, Gibbs free energy and Langgren equation.

INTRODUCTION

Stream and wells are the main source of potable water to the rural populace in Nigeria, and many third world countries. The activities of this populace centre on farming, local mining, skin and hides etc. These activities uses water which are later discharged back into the stream as waste water. Local mining activities are usually associated with waste water containing heavy metals. Lead a heavy metal ion has been found to pollute stream in areas where local mining activities of Gold is predominant. Ingestion of lead above the limit value resulted in lead poisoning. Its toxicity affects organ such as hearth, bones, intestine, kidney reproductive system and nervous system, etc.

Different numbers of ways of removing waste are available, physical, chemical destruction and biological method. Adsorption onto clay, fullers earth, silica, bauxite has long being investigated clays linings have been used as barriers in landfills to prevent contamination of ground water and subsoil by leachates containing metals. Generally these linings are constituted of bentonite and in particular, montmorillonite. (Abollino et al, 2003). Adsorption using Activated carbon is an effective separation and purification technique used in waste water treatment. This is linked to (i) the pore size that determines its adsorption capacities (ii) chemical structure that influences its interaction with polar and non polar adsorbents, (iii) active sites which determine the type of chemical reaction with other molecules and probably (iv) the sorption energy which account for spontaneity, feasibility and the degree of phase interaction. (Itodo and Itodo, 2011) In this study, focus is on the adsorption process because it is inexpensive, widely applicable, efficient, and creates relatively little sludge. Activated carbon is inexpensive adsorbent and has been widely used in various industries to purify water. Activated carbon removes heavy metals by complexation or by electrostatic attraction of metal ions to various surface oxygen-containing functional groups (Chik et al, 2009). It is the aim and objective of

this work to study the Kinetics and Adsorption Isotherm of removal of Lead from reported water pollution in Zamfara State. This is to enable us to come up with a solution for the removal and remediation of the reported Lead pollution.

The Langmuir isotherm

Langmuir Isotherm:

$$1/q_e = 1/q_m + 1/k_d q_m C_e \quad (1)$$

where q_e is the amount of solute adsorbed at equilibrium per mass of adsorbent (mg/g); C_e is the concentration of the solute in aqueous phase at equilibrium; K_d is the adsorption equilibrium constant; q_m (mg/g) is the monolayer capacity. The monolayer coverage is obtained from a plot of $1/q_e$ versus $1/C_e$. The slope and the intercept of the linear graph obtained from this plot give the value of $1/q_m$ and $1/K_d q_m$, (Hawaiah et al, 2004). Predicting the favourability of an adsorption system, the Langmuir equation can be expressed in term of dimensionless separation factor.

$$R_L = 1/(1 + K_d C_e)$$

The R_L values implied the adsorption to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Lotfi et al, 2007).

The amount of lead retained in the adsorbent phase, q_e , can be calculated by eq. (2) as the difference between the amounts present in the initial lead solution and that remaining in the solution after equilibrium

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of metal in solutions (mol /l), V is the volume of solution (l), and m is the mass of the adsorbent (g). (Svilovic, et a.2008).

The Temkin isotherm equation

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 model is linearly represented as equation (3) and generally applied in the form:

$$q_e = B \ln A + B \ln C_e \quad (3)$$

Where A and B are the Temkin isotherm constant (L/g) and heat of sorption (J/mol) respectively.

R is the gas constant (J/mol/k), b is the Temkin isotherm constant linked to the energy parameter, B, as shown on equation (4)

$$b=RT/B \quad (4)$$

T is the absolute temperature in Kelvin. The quantity, b has no unit (Itodo and Itodo, 2011). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B and A from the slope and intercept of the straight line plot (Oladoja et al, 2008)

The Gibbs Free Energy of Adsorption

The Gibbs free energy of adsorption in KJ/mol is given by

$$\Delta G_{ad} = -RT \ln K_c \quad (5)$$

Where

R is the universal gas constant (8.314 J/mol K).T is the absolute temperature in Kelvin and K_c is the equilibrium constant.

$$K_c = \frac{C_s}{C_e} \quad (6) \text{ (Itodo et al, 2011; Adesola et al, 2008)}$$

It can be taken as Langmuir constant.

KINETICS OF ADSORPTION

The following equations are useful for studies of kinetics in the adsorption process

Natarajan- Khalaf equation which is given thus
 $\text{Log}(C_i/C_e) = (K/2.303)t \text{ -----(7)}$

Lagergren equation which is given thus
 $\text{Log} (q_e - q_t) = \text{Log} q_e - (K/2.303)t \text{ -----(8)}$

Where: C_i and C_e are concentration of metal at time t and at equilibrium condition in mg/L. q_e and q_t are the amount of adsorbed solute at equilibrium and at time t, in mg/g. Plot of $\text{Log}(C_i/C_e)$ vs t enable evaluation of kinetics constant, K. In equation (7) while plot of $\text{Log} (q_e -$

$q_t)$ vs t also enable evaluation of K . (Pragnesh et al, 2012)

EXPERIMENTAL

The following experimental procedure were adopted for this study;

Experimental Procedure

(1) Collection and Preparation of Samples

Two samples were collected. Sample A at the point where mined Gold is being washed in a stream and sample B at a well about 150 meters from the stream. The two samples are from ANKA Village in ZAMFARA STATE, NIGERIA.

Collected samples were stored in a refrigerator for subsequent analysis.

(2) Determination of Metal Concentration

100ml of each samples collected was digested and analysed with AAS machine to determine the initial concentration of heavy metal in the samples and the same procedure was carried out for samples of water treated with Activated Carbon .

(3) Removal of Lead Using Various Mass of Activated Carbon.

50ml of water sample collected was measured into a flask and 1gram of activated carbon added. The whole content was mounted on to a stirrer and stirred for 20minutes.The content was filtered and the filtrate was digested and analysed for Lead concentration using AAS machine. The same procedure was repeated using 2, 3 and 4gram of activated carbon.

(4) Effect of Varying Adsorption Time.

50ml of water sample collected was measured into a flask and 3gram of activated carbon was added, the flask was mounted to a stirrer and stirred for 10 minute. The content was filtered and filtrate was digested and analysed for lead concentration using AAS machine. The same procedure was repeated for 15, 20 and 25 minute duration. Note both sample A and B were given the same treatment.

RESULTS

The following results were obtained from the experimental analysis carried out.

Table1. Effect of Variation of Adsorbent on Removal of Lead from Water Sample Collected at Gold Washing Point.

Mass of activated carbon. g	1	2	3	4
Quantity of Lead removed. $C_i - C_e$.mg/l	0.8695	0.9006	0.9565	0.9616
Percentage removal of lead. $\frac{C_i - C_e}{C_i} \times 100\%$	89.45	92.65	98.40	98.93
Quantity of Lead adsorbed per unit mass. $q_e = \frac{(C_i - C_e)V}{M}$ mg/g	43.48	22.515	15.94	12.02
1/q	0.02300	0.04441	0.06273	0.0832
1/C	9.756	14.01	64.52	96.15
LnC	-2.28	-2.64	-4.17	-4.57
Volume of water. $\times 10^{-3}$ l	50	50	50	50
Adsorption period. mint	20	20	20	20

Initial Concentration of lead is denoted as C_i mg/l
 Equilibrium Concentration of lead is denoted as C_e , mg/l

Table2: Effect of Variation of Adsorbent on removal of Lead from Water Sample Collected at Nearby Well.

Mass of activated carbon. g	1	2	3	4
Quantity of Lead removed. $C_0 - C_e$.mg/l	0.0033	0.0062	0.0069	0.0075
Percentage removal of lead. $\frac{C_0 - C_e}{C_0} \times 100\%$	35.5	66.7	74.2	80.6
Quantity of Lead adsorbed per unit mass. $q_e = \frac{(C_0 - C_e)V}{M}$ mg/g	0.165	0.155	0.115	0.094
1/q	6.061	6.452	8.70	10.64
1/C _e	166.7	322.6	416.7	555.5
LnC _e	-5.12	-5.78	-6.03	-6.32
Volume of water.×10 ⁻³ l	50	50	50	50
Adsorption period. mint	20	20	20	20

Initial Concentration of lead is denoted as C₀ mg/l
 Equilibrium Concentration of lead is denoted as C_e.mg/l

Table 3:Effect of Variation of Adsorption Contact Time for the Sample Collected at Gold Washing Point.

Time (Mints)	10	15	20	25
Quantity of Lead removed. $C_0 - C_e$.mg/l	0.9099	0.9378	0.9385	0.9409
Percentage removal of lead. $\frac{C_0 - C_e}{C_0} \times 100\%$	93.6	96.5	96.6	96.8
Quantity of Lead adsorbed per unit mass. $q_e = \frac{(C_0 - C_e)V}{M}$ mg/g	15.20	15.66	15.67	15.71
C/C _e	0.0639	0.0352	0.0345	0.0320
$q_t = \frac{(C_N - C_{N+1})V}{M}$, mg/g	0	0.466	0.0117	0.0401
q _e - q _t	15.20	15.194	15.66	15.67
Log q _e - q _t	1.182	1.182	1.195	1.1951
Mass of adsorbent. g	3	3	3	3
Volume of water.×10 ⁻³ l	50	50	50	50

Initial concentration of lead is denoted as C₀ mg/l
 Equilibrium concentration of lead is denoted as C_e, mg/l

Table 4: Effect of Variation of Adsorption Contact Time for The Sample Collected at a Nearby Well.

Time (Mints)	10	15	20	25
Quantity of Lead removed. $C_0 - C_e$.mg/l	0.0033	0.0049	0.0054	0.0092
Percentage removal of lead. $\frac{C_0 - C_e}{C_0} \times 100\%$	35.5	52.7	58.1	98.9
Quantity of Lead adsorbed per unit mass. $q_e = \frac{(C_0 - C_e)V}{M}$ mg/g	0.05511	0.08183	0.09018	0.1536
C/C _e	0.6452	0.4731	0.4194	0.01075
$q_t = \frac{(C_N - C_{N+1})V}{M}$, mg/g	0	0.02672	0.00835	0.06346
q _e - q _t	0.05511	0.05511	0.08183	0.09014
Log q _e - q _t	-1.25877	-1.25877	-1.08709	-1.04508
Mass of adsorbent. g	3	3	3	3
Volume of water.×10 ⁻³ l	50	50	50	50

Initial Concentration of lead is denoted as C₀ mg/l
 Equilibrium concentration of lead is denoted as C_e, mg/l

Table 5: Summary of Constant Values Obtained For Various Model Equation Used.

MODEL EQUATION USED AND CONSTANT	SAMPLE COLLECTED AT GOLD WASHING POINT	SAMPLE COLLECTED AT A NEAR - BY WELL
Langmuir Isotherm	VALUES OBTAINED	VALUES OBTAINED
q_m mg/g	38.5	0.2915
K_d l/mg	0.0373	0.2859
R^2	0.908	0.897
K_L	0.97	0.997
Tempkin Isotherm	VALUES OBTAINED	VALUE OBTAINED
B J/mol	10.77	0.059
A l/mg	0.2704	3.244
B	233.9	42697.3
R^2	0.75	0.824
Langagren	VALUES OBTAINED	VALUES OBTAINED
q_e mg/g	14.79	0.0358
K mint ⁻¹	-0.002303	-0.03685
R^2	0.803	0.868
ΔG KJ/mol K	-8.284	-3.154

DISCUSSION

The study of removal of Lead from sample of water collected from Gold washing point as shown in Table 1. Indicate that, initial lead concentration stood at 0.9720mg/l. This value of concentration exceed the limit value of 0.05 mg/l for lead in drinking/surface water as specified by Federal Environmental Protection Agency(FEPA), which is now the Federal ministry of Environment in Nigeria,. Using this water as a potable water pose a risk to health of people , animals and aquatic lives living around the stream, unless remediation is adopted. Similarly from, table 2. The value of 0.0093mg/l obtained for concentration of lead in a near-by well water was found to be within acceptable limit nevertheless analysis of the sample will be done as to provide a data for references.

The studies of effect of varying the dosage of adsorbent from 1g to 4g in removal of lead from the water as shown in table 1 .indicates percentage lead removal to increase rapidly from 89.45% to 98.72%. Increased in amount of adsorbent increases the available surface area and active site presented for adsorption of lead from the water. Similar observation was made in table 2 amount of lead in well water was removed from 35.5% to 80.6%.

The quantity of lead adsorbed per unit mass q_e in table 1 decreases from 43.48 mg/g to 12.02 mg/g, as mass of adsorbent increases from 1g to 4g. This implied that there are available more un-exhausted surface area and site for adsorption with increased in adsorbent masses .Similar observation was made for sample collected from a well as seen in table 2 as q_e decreases from 0.165 mg/g to 0.094 mg/g.

The Langmuir isotherm analysis as shown in table5, for samples collected at gold washing point has a value of q_m to be 38.5mg/g , K_d to be 0.0373 l/mg this valve is within the range of values obtained for similar study done by (Pragnesh et al, 2012). The value of R^2 was found to be 0.908.While K_L the separation factor of 0.97

obtained shows that the adsorption process is almost linear. Similar observation was made for sample collected at near-by well with q_m to be 0.915mg/g, K_d to be 0.2859, R^2 to be 0.897 and K_L to be 0.997.Based on the value of R^2 and linearity of figure 1&2 Suggest that Langmuir isotherm is suitable to described the adsorption process of lead removal.

Tempkin isotherm analysis as shown in table5, for sample collected at gold washing point has a value of 10.77 J/mol for heat of adsorption (B). 0.2704 l/mg for A and 233.9 for b. Similar observation was made for sample collected at a near-by well. 0.059 J/mol for B, 3.244 l/mg for A and 42697.3 for b. Plot of Tempkin isotherm is linear in nature, as shown in figure 3&4

Langargren kinetics analysis as presented in table 5 shows sample collected at gold washing point has q_e to be 14.79 mg/g, K to be -0.0023 mint⁻¹.Similarly sample collected at near-by well has 0.0358 mg/g for q_e and -0.03685 mint⁻¹ for K . The linearity of Langargren as shown in figure 5&6, the values of K obtained and R^2 . Suggest that the adsorption is of first order in nature. This suggestion is further consolidated with the value of ΔG KJ/mol K obtained which is -8.284 and -3.154 respectively. These value falls below 20 KJ/mol. It confirms the adsorption is a physical adsorption in nature.

The concentration profile graph as presented in figure 7&8 shows that residual concentration of lead in water per initial concentration decreases with passage of time. The graph slope from top-left to bottom- right.

CONCLUSIONS

The following conclusions were drawn from the analysis carried out

- (1) Based on the values of constant obtained from Langmuir isotherm and the linear nature of the isotherm it can be said that Langmuir fits and is more suitable isotherm out of the two used in this analysis.

(2) Based on the values of constant obtained from Tempkin isotherm and the linear nature of the isotherm it can be said that Tempkin can also be used to evaluate lead adsorption.

(3) Based on the values of constant obtained from Langargren first order kinetic plots and the linear nature of the plots it can be said that adsorption of lead is that of first order.

(4) Based on the values obtained for the Gibbs free energy of adsorption it can be said that the adsorption is physical adsorption in nature.

(5) It can be concluded that Activated carbon is a suitable adsorbent to be used in removal of lead from water.

RECOMENDATIONS

i. It is recommended that small water treatment plant should be established for

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community along the stream and activated carbon filtration unit to be integrated into the plant.

ii. It is recommended that the values of isotherm constant found can be used in evaluating the required quantity of activated carbon needed for the treatment of water.

iii. It is recommended that bore hole can be an alternative sources of potable water since concentration of lead in near- by well is below FEPA limit

iv. Borehole water should be adequately analysed before use.

v. Sample of water was collected for this analysis around August when volume of water in the stream was high .It is recommended that analysis of sample collected during dry season and other months should be done, as to have an adequate data available for used.

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APPENDIX

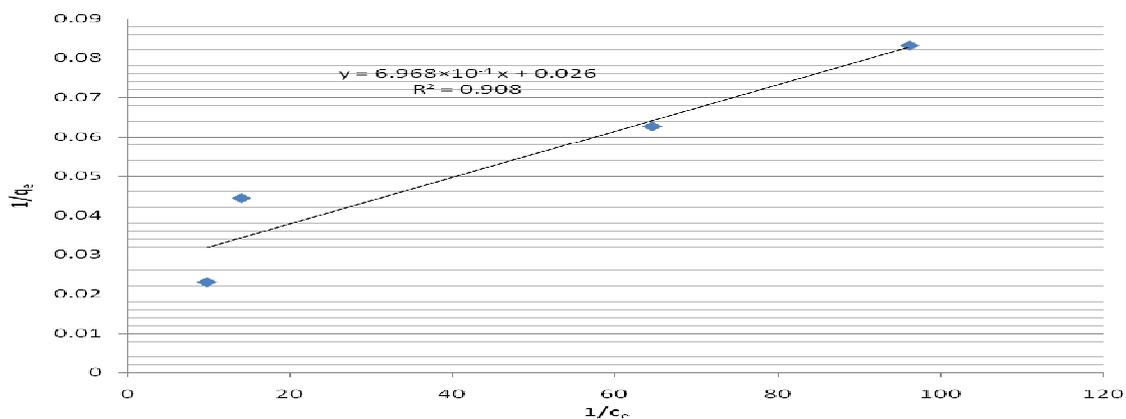


Fig.1 Langmuir Isotherm plot for sample of water collected at the Gold washing point

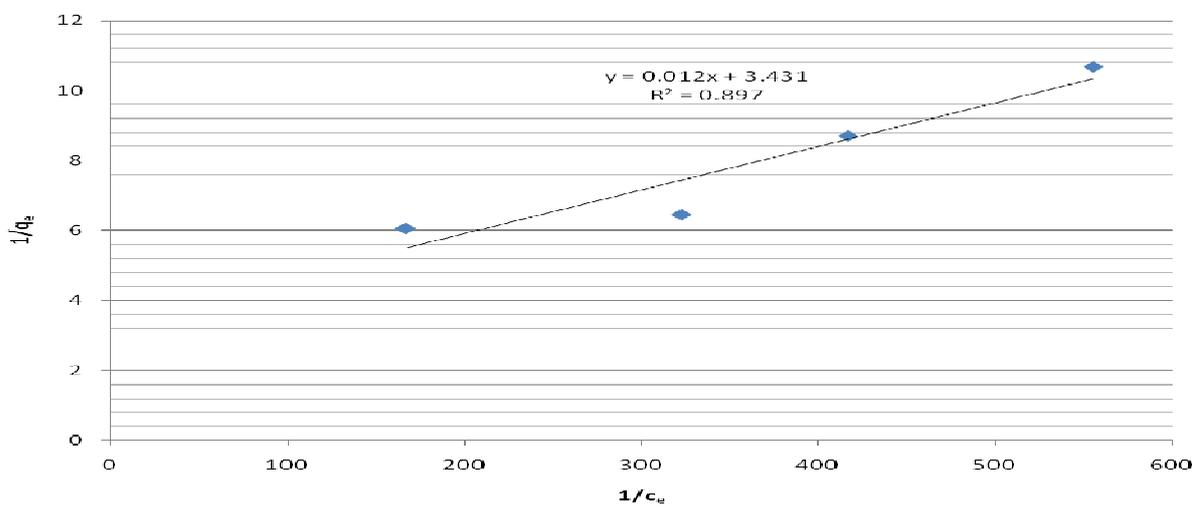


Fig.2 Langmuir Isotherm plot for sample of water collected at a near-by well

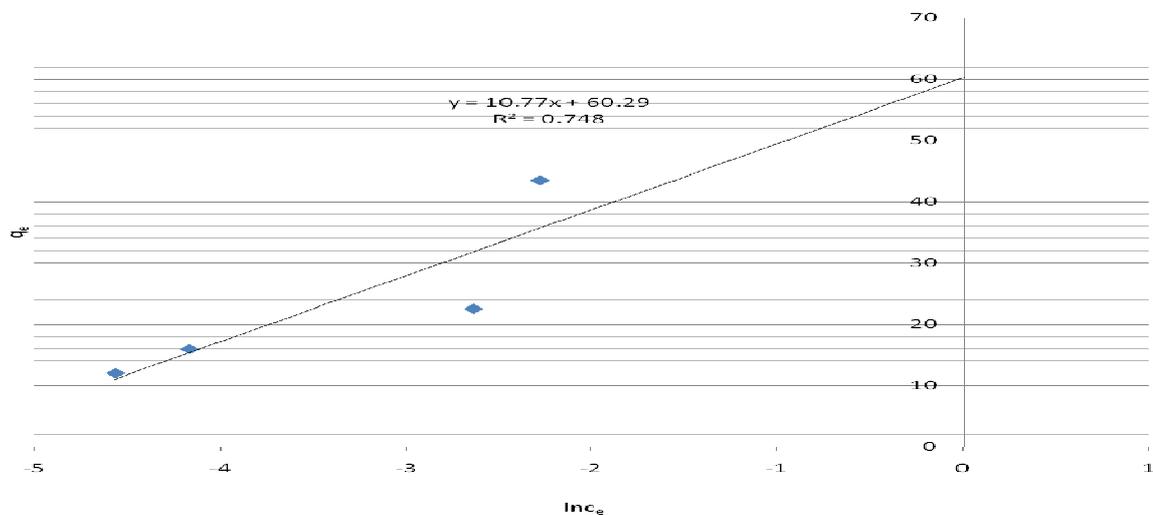


Fig.3 Templkin Isotherm plot for the sample collected at the Gold washing point

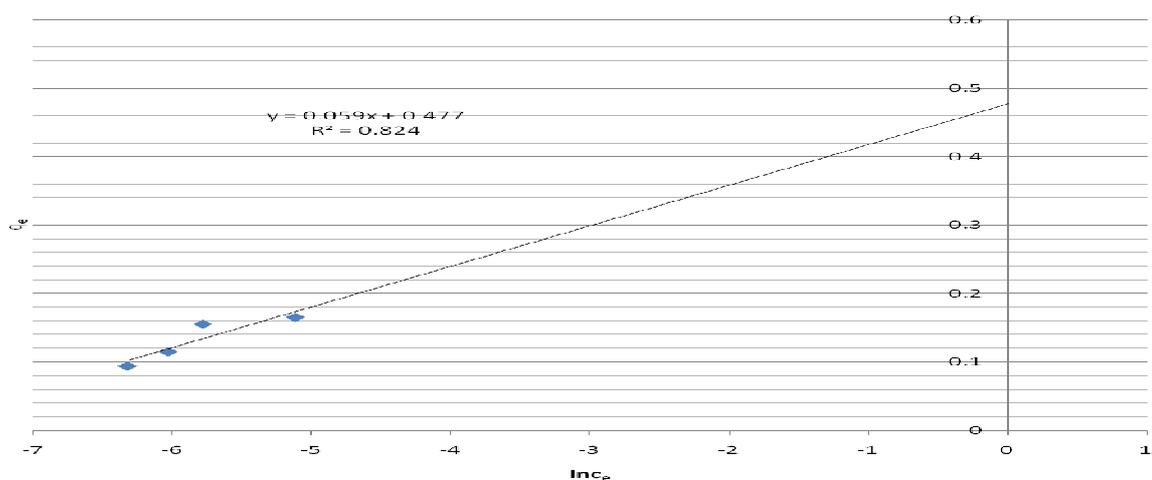


Fig.4 Tempkin Isotherm plot for sample of water collected at near-by well

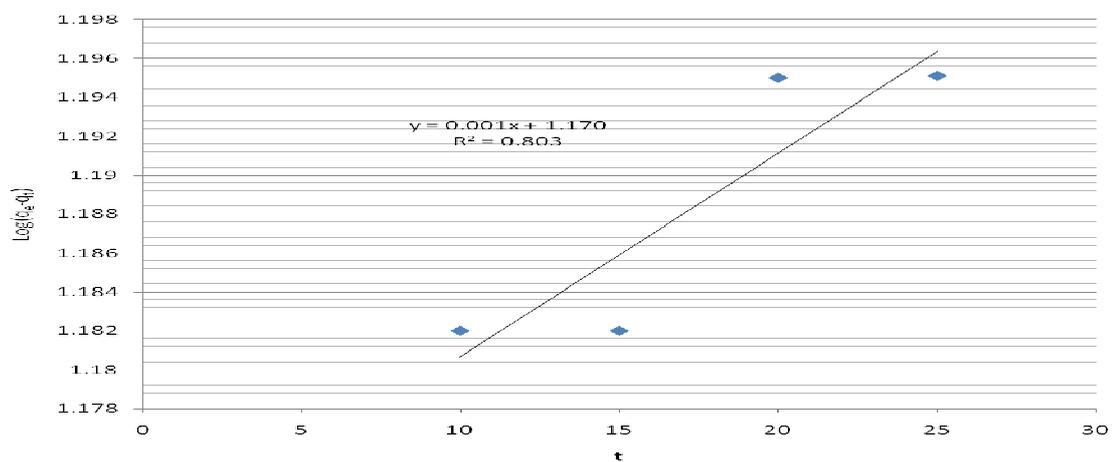


Fig.5 Langergren Kinetics plot for sample of water collected at Gold washing point

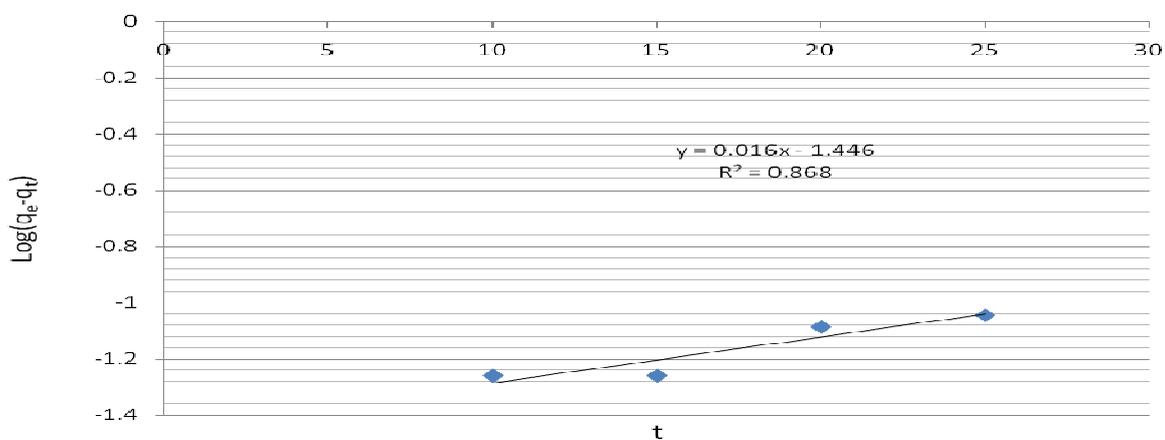


Fig.6 Langergren Kinetics plot for sample of water collected at Near-by well

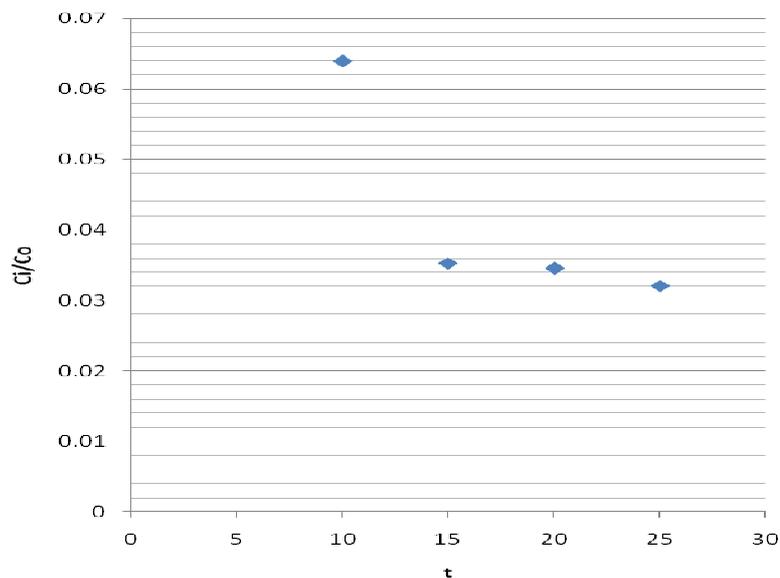


Fig.7: Concentration profile for sample collected at Gold washing point

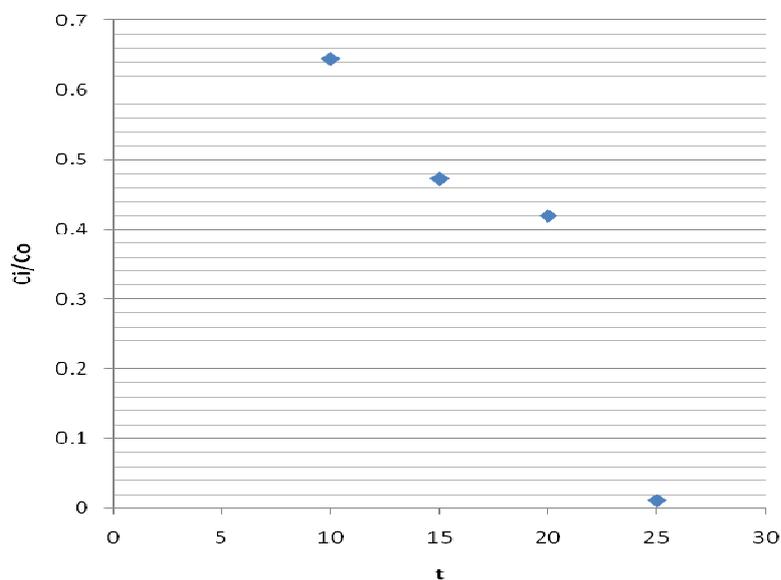


Fig.8: Concentration profile for sample collected at a near-by well