RASĀYAN J. Chem.
Vol. 10 | No. 3 |1025 - 1036 | July - September | 2017
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

OPTIMIZATION OF ZINC(II) BIOSORPTION ON TO *Boodlea struveiodes*(MARINE ALGAE) BY CENTRAL COMPOSITE DESIGN

P. Prasanna Kumar[1,2], Y. Prasanna Kumar[3] and B. Venkateswara Rao[4]
[1]Research Scholar, Dept. of Chemistry, JNTUK, Kakinada
[2]Sri Venkateswara College of Engineering & Technology, Etcherla, Srikakulam, India
[3]Visakha Institute of Engineering & Technology, Narava, Visakhapatnam, India
[4]Department of Chemistry, A.U.College of Engineering, Andhra University, Visakhapatnam, India
*E-mail: prasan.pr123@gmail.com

ABSTRACT
Heavy metal pollution is a major threat to the world as they can be toxic to all forms of life at high concentrations. They are released into the environment by a variety of industrial activities. The present study aims at removal of zinc from wastewater using low-costbiosorbent*Boodlea struveiodes*(marine algae). Batch experiments revealed that adsorption was influenced by various factors such as pH, initial metal ion concentration, the dosage of adsorbent, the size of the adsorbent and contact time. Langmuir, Freundlich and Tempkin adsorption isotherm models were used to test equilibrium data and they satisfactorily described the data. In order to analyze the effect of variables, the process parameters were set to optimum values pH 5, initial metal ion concentration 26.364 mg/l and dosage of adsorbent 3.0g were optimized with Response surface methodology through Central composite design. At optimum conditions, the maximum percentage of adsorption of Zinc by *Boodlea struveiodeswas* found to be 93.39.
Keywords: Boodlea struveiodes, equilibrium, regression coefficient, correlation, response surface methodology.

INTRODUCTION
As the industries are developing rapidly, industrial effluents pollute water bodies majorly. Industrial effluents release heavy metals into water bodies. Heavy metals damage the life style of living organisms. So it is essential to reduce the toxicity of heavy metals in the industrial wastewater. As the reason that, heavy metals can be hazardous to the human health due to their toxic nature, they tend to accumulate and can be easily introduced into the human body.[1]
Some heavy metals like Zn, Cu, Fe, and Ni at limited concentration need to maintain the metabolism of living organisms. They act as cofactors to the enzymes. Zinc at lower concentration needs to maintain physiological functions of living tissues & organize the metabolism. But, at excess concentration may be hazardous to the human body. Industrial activities are more responsible for Zinc. Zinc pollution is may be caused by automobile industry, production of protective coatings, cosmetic industry, ointments, antiseptics, paints, varnishes, rubbers, zinc fertilizers, mining, battery manufacturing, etc.,
The traditional methods used so far to remove heavy metals are ion exchange, ultra filtration, chemical precipitation, reverse osmosis etc. But there are some demerits in the traditional techniques, i.e.:
(i) incomplete metal removal, (ii) more energy is required, (iii) require reagents, (iv) release toxic sludges etc.
To avoid heavy metals from wastewater, biosorption is more useful technique as it is capable to remove heavy metals at a significant percentage. A lot of biosorbents are used so far such as agriculture waste, dried leaves, peels of fruits, fly ash, algae, rice husk etc. Biosorption has been utilized instead of accumulation. It proceeds via binding of heavy metals on cell walls of dead biomass. Metal uptake by

http://dx.doi.org/10.7324/RJC.2017.1031683

algal biomass is more efficient than chemical sorbents. In this study, low-cost and eco-friendly biosorbent *Boodlea struveiodes* (marine algae) were used to remove heavy metals from wastewater.

EXPERIMENTAL

Preparation of Zinc Solution

All the chemicals used in this study were analytical grade. All the sample bottles were cleaned and rinsed with double distilled water. 1000mg/l stock solution of Zinc was prepared by dissolving 8.80 g of $ZnSO_4.7H_2O$ in pure distilled water and diluted to get standards of different concentration.[2,3] pH of the solution was adjusted to desired value by using 0.1N HCl and 0.1N NaOH and then measured with pH meter.

Preparation of Biosorbent

Boodlea struveiodes, green marine algae were collected from the rocky seashore of Visakhapatnam. Which was washed with double distilled water for several times and then dried in a hot air oven at $60\text{-}70^0$ C temperature. After drying the biosorbent, it is subjected to grinding to get finely divided powder then sieved to various particle sizes ranging 75-112 μm.

Procedure of experimentation

Batch experiments were conducted at various conditions of variables like the concentration of the metal solution, pH of the solution, the dosage of biosorbent, agitation time and biosorbent particle size to get optimum values.[4,5]

Zinc sample solution was taken in an experimental flask with a calculated amount of adsorbent, then placed in orbital shaker for a specific time. Finally, change in concentration of the metal solution was measured by AAS (Atomic Adsorption Spectroscopy). The same experiment was repeated by varying the above parameters to optimize the variables. The percentage of biosorption was measured by the following standard equation:

$$\% \text{ adsorption} = \frac{Co - Ce}{Co} \times 100 \tag{1}$$

C_0& Ce are initial and final concentration of the metal solution.[6]

RESULTS AND DISCUSSION

Zinc removal from the sample solutions was analyzed by varying the variables such as pH, concentration, agitation time, the dosage of adsorbent and adsorbent particle size.

pH of the solution is a major factor to decide the percentage removal of metal ions from the solution[2]. Batch experiments were carried at various pH values ranging 2-10. The percentage removal of the zinc was increased at first with an increase in pH and decrease after crossing pH 5. The maximum adsorption with *Boodlea struveiodes* was taken place at pH 5. At lower pH values, there is a competitive adsorption of Zn^{+2} and H^+ was taken place. It might be the reason to get less adsorption at lower pH. At higher pH values (pH>5) metal precipitation may possible. It was the reason to decrease in % adsorption as pH increases.

Batch experiments were conducted at a set of initial metal ion concentration to analyze the effect of concentration on % adsorption. The initial metal ion concentrations used were 20, 40, 60, 80 & 100 mg/l. The % adsorption of Zinc on the biosorbent was decreased as the initial concentration is increased from 20 to 100 mg/l. The reason to decline % adsorption with increasing concentration might be that at lower concentration biosorbent providing more binding sites to adsorb metal ions but with increasing concentration, adsorption binding sites were saturated, then % adsorption was decreased.

To determine the effect of concentration of adsorbent (dosage), batch experiments were carried at various dosages ranging from 0.1 to 0.5 g. The results showed that % adsorption was increased with increase in dosage of adsorbent. It was expected that with an increase in adsorbent dosage, the available binding sites on adsorbent to adsorb Zinc ions was increased, therefore % adsorption increased. The maximum % adsorption of zinc by *Boodlea struveiodes* was 95.86 at 0.5 g of adsorbent dosage.

The effect of contact time of adsorbent with the metal solution was determined by varying the time to get equilibrium state by keeping the other factors kept constant at their optimum values. From the observed data, it was shown that % removal of metal from the solution was increased with time.[7] But this increment in % removal was more at the initial stage and less at the final stage. It might be expected that at an initial stage, more binding sites are available on biosorbent and more is the number of metal ions in the solution. Hence more is the interaction between them and adsorption occurs at a rapid rate. As the time was going on, adsorption process got a saturation point; hence the rate of adsorption was declined. After 30 min, no observable change in % removal. The maximum % adsorption was taken place at 30 min i.e. 94.89.

Biosorption experiments were conducted at various biosorbent particle sizes ranging 75 µm to 212 µm by keeping other parameters such as initial concentration of metal ion, pH, the dosage of biosorbent, contact time as constant at optimum conditions. Results showed that % adsorption was increased with a decrease in biosorbent particle size. The reason was expected that lesser is the particle size, more is the surface area of the adsorbent and more is the % adsorption.

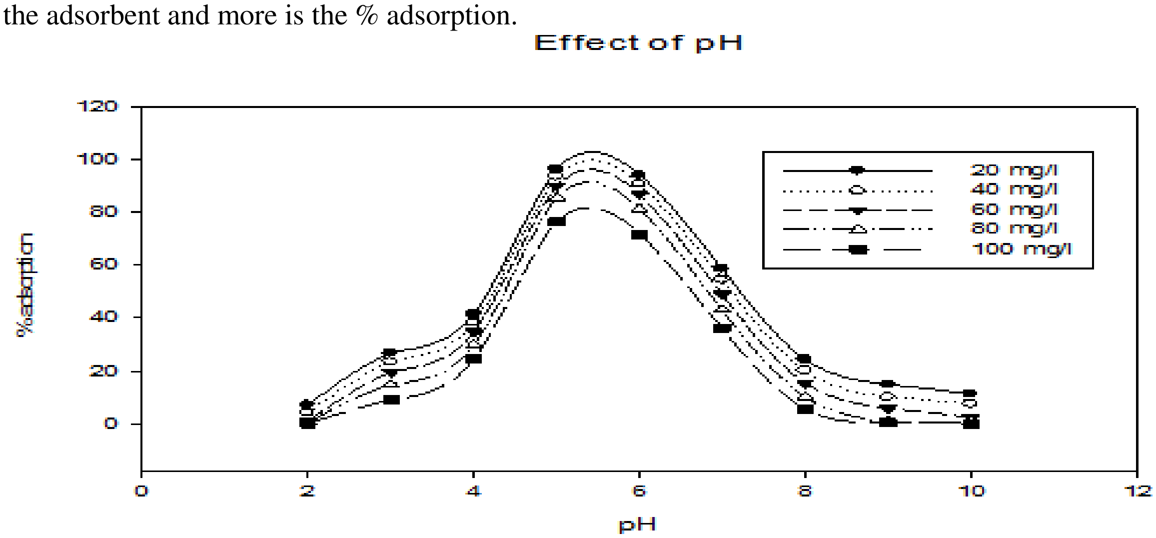

Fig.-1: Effect of pH on adsorption of Zinc onto*Boodlea struveiodes* for 0.1 g/ 30ml adsorbent concentration

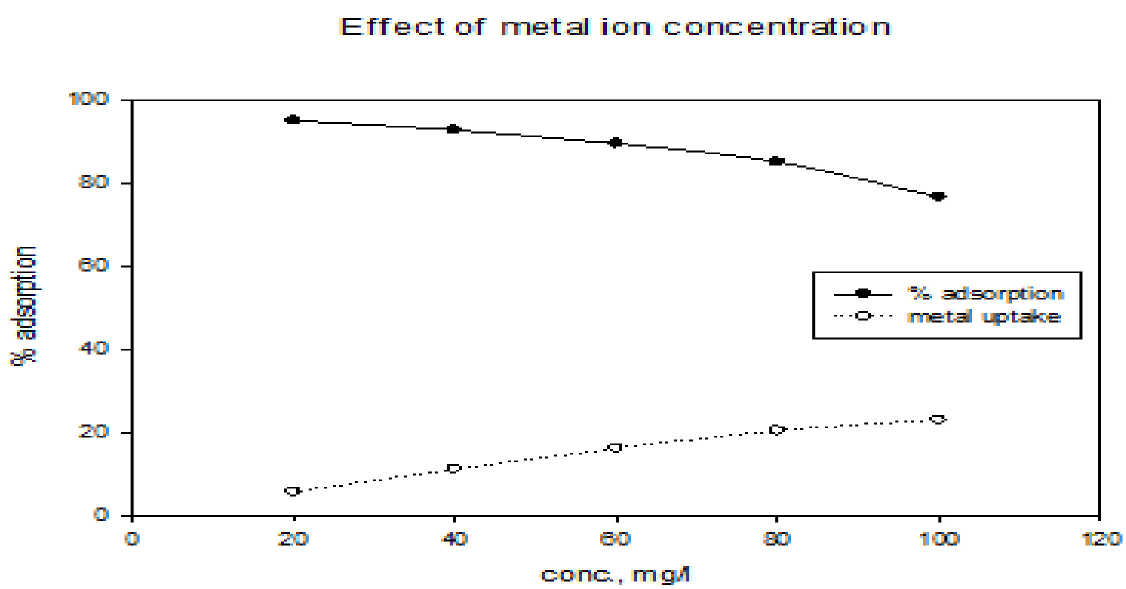

Fig.-2: Effect of metal ion concentration on adsorption of Zinc onto*Boodlea struveiodes* for 0.1 g/ 30ml adsorbent concentration

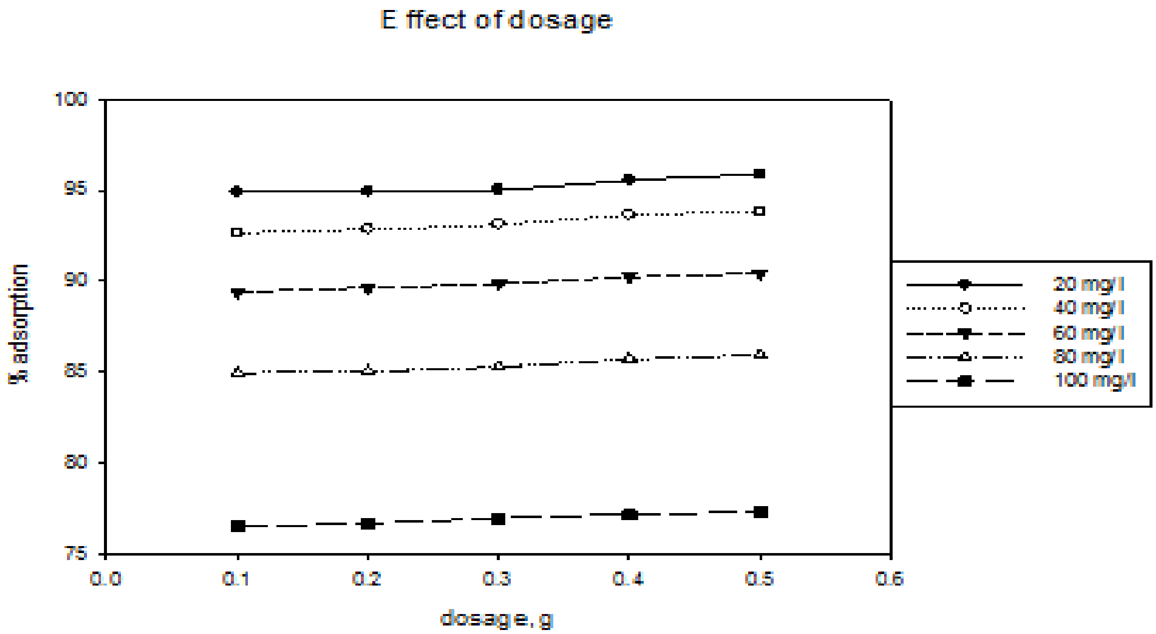

Fig.-3: Effect of dosage of adsorbent on adsorption of Zinc onto*Boodlea struveiodes* for 0.1 g/ 30ml adsorbent concentration

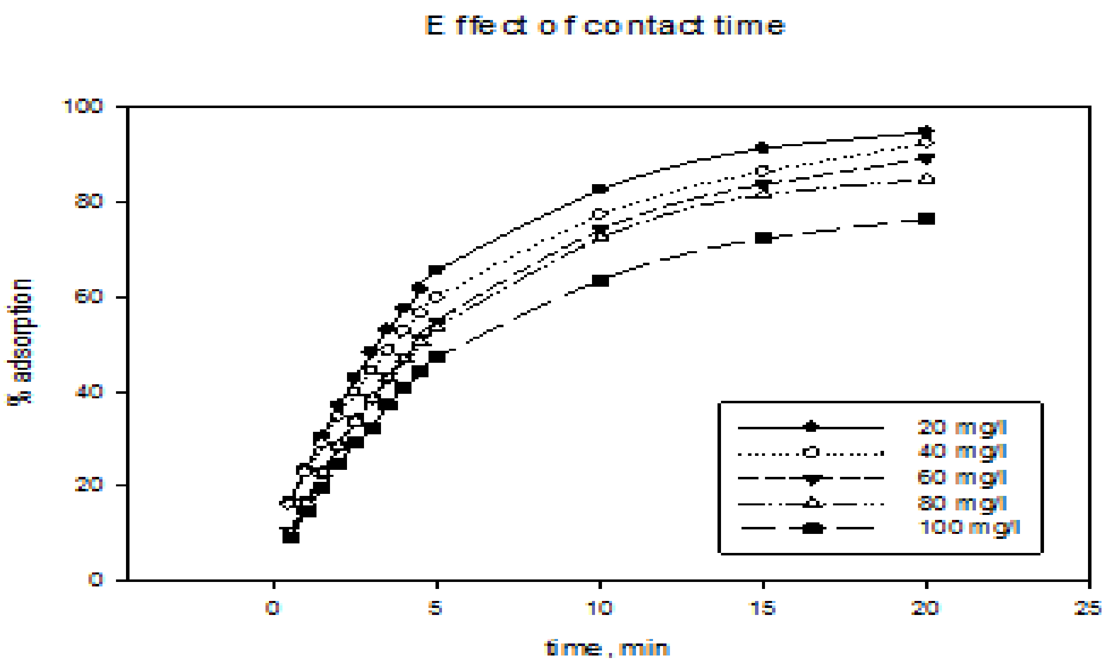

Fig.-4: Effect of contact time on adsorption of Zinc onto*Boodlea struveiodes* for 0.1 g/ 30ml adsorbent concentration

Adsorption isotherms

The process of adsorption is generally observed by the adsorption isotherms. Adsorption isotherm is a plot which relates the quantity of adsorbate adsorbed on the unit mass of adsorbent to the unadsorbed adsorbate at equilibrium state as the function of the concentration, time and pressure. Several models have been tested so far to describe the process of adsorption. In this present study, adsorption of Zinc onto *Boodlea struveiodes* was described by the Freundlich, Langmuir and Temkin adsorption isotherms.

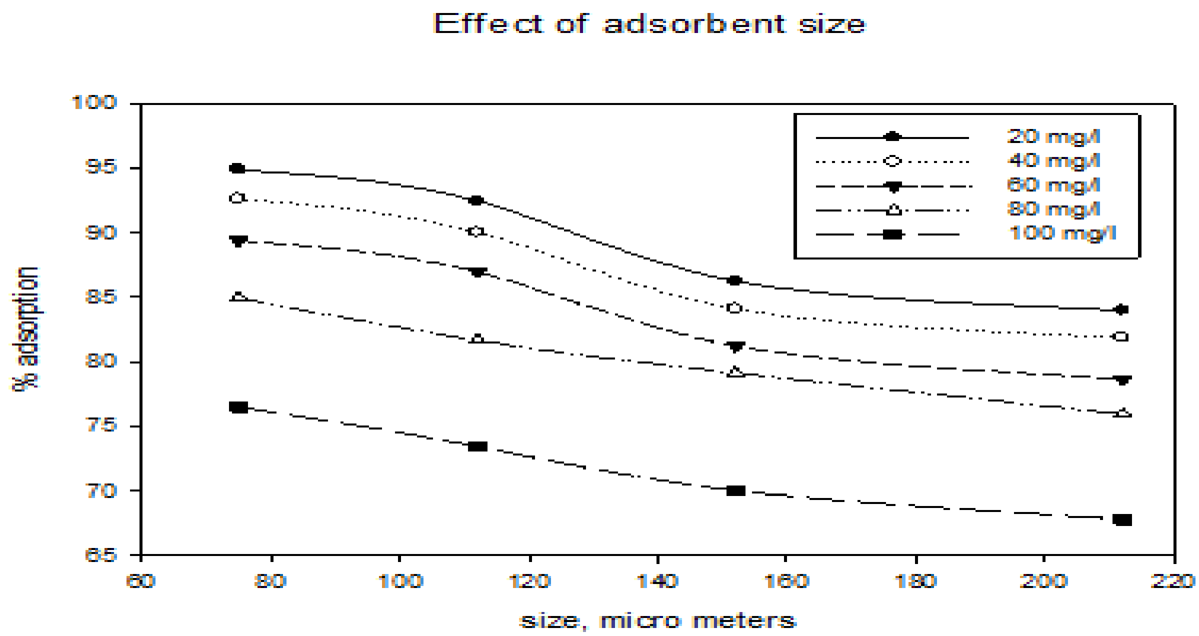

Fig.-5: Effect of adsorbent size on adsorption of Zinc onto*Boodlea struveiodes*for 0.1 g/ 30ml adsorbent concentration

Langmuir model is a semi-empirical isotherm generated from proposed kinetic mechanism. It is assumed that a dynamic equilibrium exists between adsorbed and unadsorbed metal ions. Adsorption occurs on a homogeneous surface by forming a monolayer. That is, the total surface of adsorbent is treated as uniform and all the reacting sites for adsorption are equal.
Langmuir adsorption model is represented by the equilibrium is shown below:

$$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm} \qquad (2)$$

Here Ce is equilibrium concentration;qe is the quantity of metal adsorbed at equilibrium[6] qm and b are Langmuir adsorption constants. These are measured by the plot of Ce vs Ce/qe. Langmuir model was fit for the Zinc removal by *Boodlea struveiodes*. The regression coefficient (R^2) is 0.999. qm and b values are listed in the table. R^2 values suggested that Langmuir model is satisfactorily suitable to the Zinc adsorption onto *Boodlea struveiodes*. Higher is the b value, higher is the adsorption.
Freundlich isotherm is an empirical expression indicating the isothermal variation of the amount of metal adsorbed by the unit mass of adsorbent with pressure.
Freundlich model is expressed as $qe = K_f . Ce^{1/n}$ (3)
K_f and n are Freundlich constants, which were measured by graph.

Linear form of the above equation is:

$$\ln qe = K_f + (1/n) \ln Ce \qquad (4)$$

R^2, K_f and n values suggest that Freundlich model could satisfactorily explains the adsorption of Zinc onto *Boodlea struveiodes*.
Tempkin adsorption isotherm takes the interactions between biomass and metal ions on the account. It is assumed that heat of adsorption of adsorbate on the adsorbent was decreased linearly with lowering of reacting sites.
Tempkin isotherm is characterized by the uniform distribution of binding energies.[8] Tempkin isotherm is expressed by the following equation:

$$Qe = \frac{RT}{bT} \ln A_T + \frac{RT}{bT} \ln Ce \qquad (5)$$

By plotting a graph between qe and lnCe, it gives a smart line and the constants A_T and b_T were determined by slope and intercept. Values of A_T , b_T and regression coefficient were estimated and given below:

$A_T = 1.515$, $b_T = 192.05$, $R^2 = 0.9946$

Table-1: Regression constants of Freundlich, Langmuir, and Tempkin adsorption isotherms for the biosorption of Zinc onto *Boodlea struveiodes.*

Freundlich isotherm		Langmuir isotherm		Tempkin isotherms	
R^2	0.9609	R^2	0.9995	R^2	0.9946
Kf (mg/g)	1.5703	q_m (mg/g)	26.8817	A_T	1.5150
n (l/mg)	2.2158	b (l/mg)	0.2481	b_T	192.05

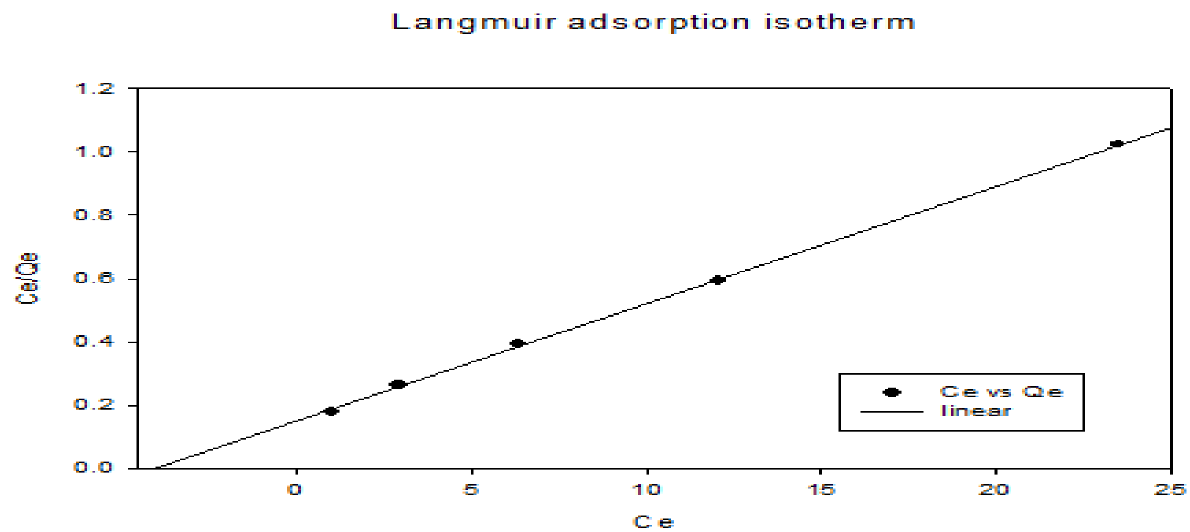

Fig.-6: Langmuir adsorption isotherm of Zinc on to *Boodlea struveiodes* for 0.1 g/ 30ml adsorbent concentration

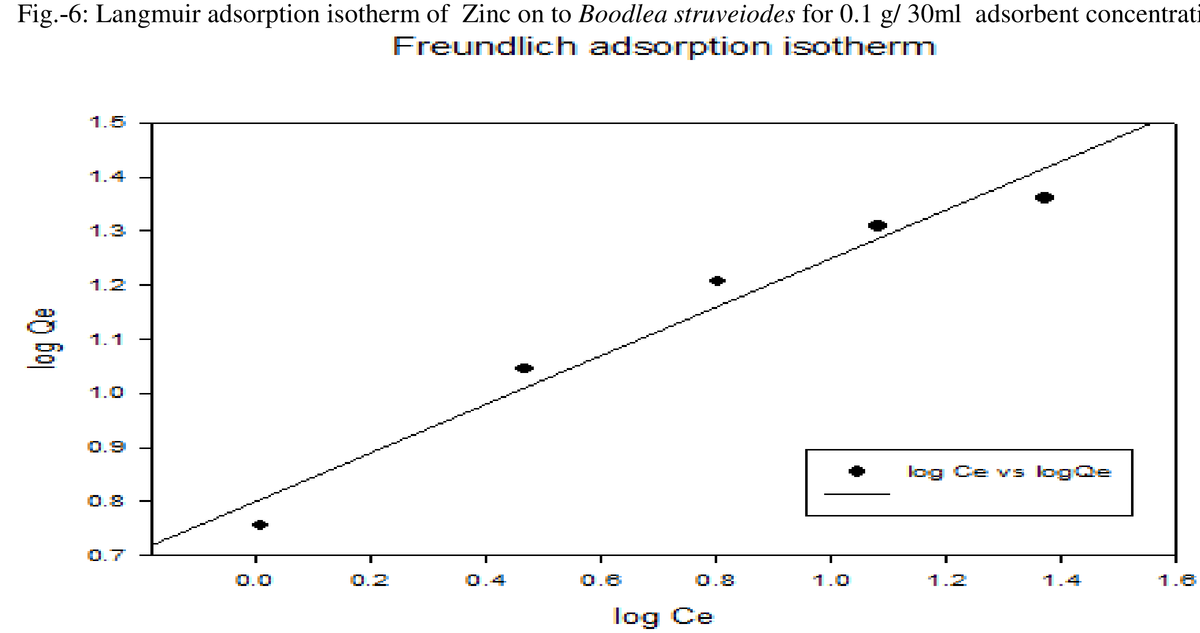

Fig.-7: Freundlich adsorption isotherm of Zinc on to *Boodlea struveiodes*for 0.1 g/ 30ml adsorbent concentration

Table-2: Kinetic constants for Zinc removal

Metal ion concentration	Pseudo first order constants		Pseudo second order constants	
	K_1	R^2	K_2R^2	
20 mg/l	0.2104	0.9969	0.0383	0.9970
40 mg/l	0.1722	0.9985	0.0183	09950
60 mg/l	0.1810	0.9992	0.0083	0.9975
80 mg/l	0.2102	0.9949	0.0069	0.9980
100 mg/l	0.1895	0.9967	0.0059	0.9964

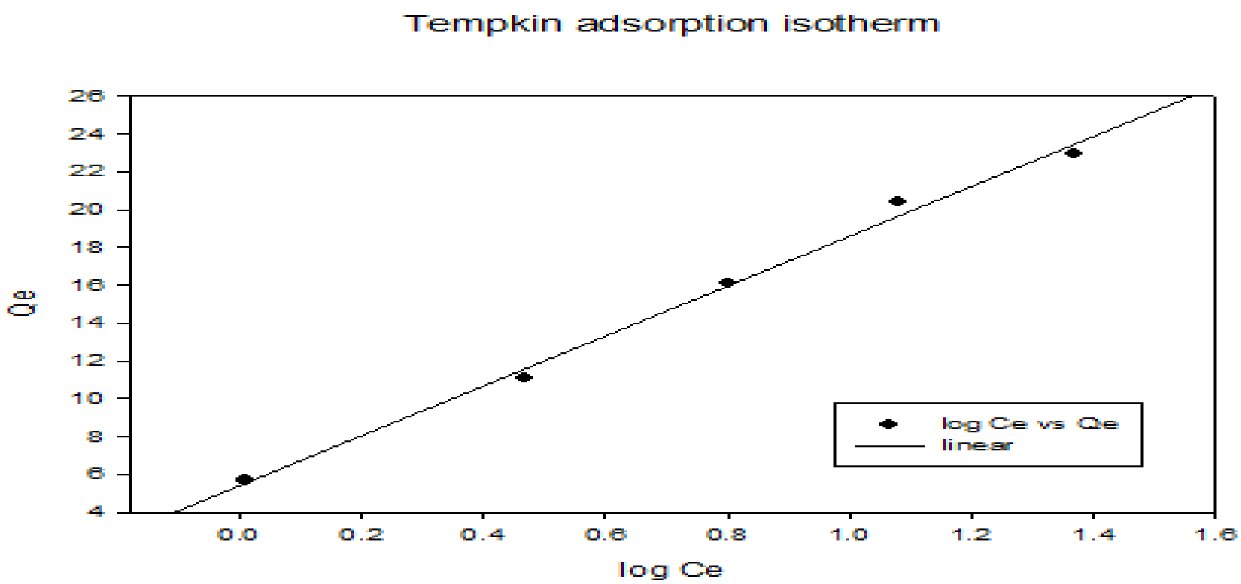

Fig.-8: Tempkin adsorption isotherm of Zinc on to *Boodlea struveiodes*for 0.1 g/ 30ml adsorbent concentration

Kinetic studies in Biosorption of Zinc onto *Boodlea struveiodes*

Kinetic studies are needed to describe the efficacy of biosorption. It is necessary to recognize the mechanism of biosorption. Kinetic studies of Zinc adsorption on the biosorbent *Boodlea struveiodes* was studied by varying biosorbent concentrations at various time intervals.

The data collected from the batch experiments of adsorption of Zinc onto *Boodlea struveiodes* was tested for the pseudo first order rate equation.

Pseudo first order rate equation is expressed as:

$$\log(qe - qt) = \log qe - \frac{K1t}{2.303} \quad (6)$$

Here qe = metal adsorbed at equilibrium, qt = metal adsorbed at a fixed time t, K1 = Pseudo first order rate constant, which was measured by the plot. The above equation is in the form of y = mx+c

The plot of t vslog(qe – qt) gave a straight line with slope - K1/2.303, from which K1 was obtained.

From the experimental data, it was observed that data fitted with a pseudo first-order rate equation with regression coefficient R^2 = 0.9969 at optimum conditions.

Pseudo second order rate equation is expressed as:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{1}{qe}t \quad (7)$$

Here K_2 is rate constant, qe equilibrium model adsorption, qt = metal adsorbed at time t

The plot of t against t/qt gives the rate constant.From the graph, it was cleared that data is also fitted with pseudo second order rate equation with regression coefficient R^2 = 0.997. The straight line in the plot indicated that fitness with experimental data.

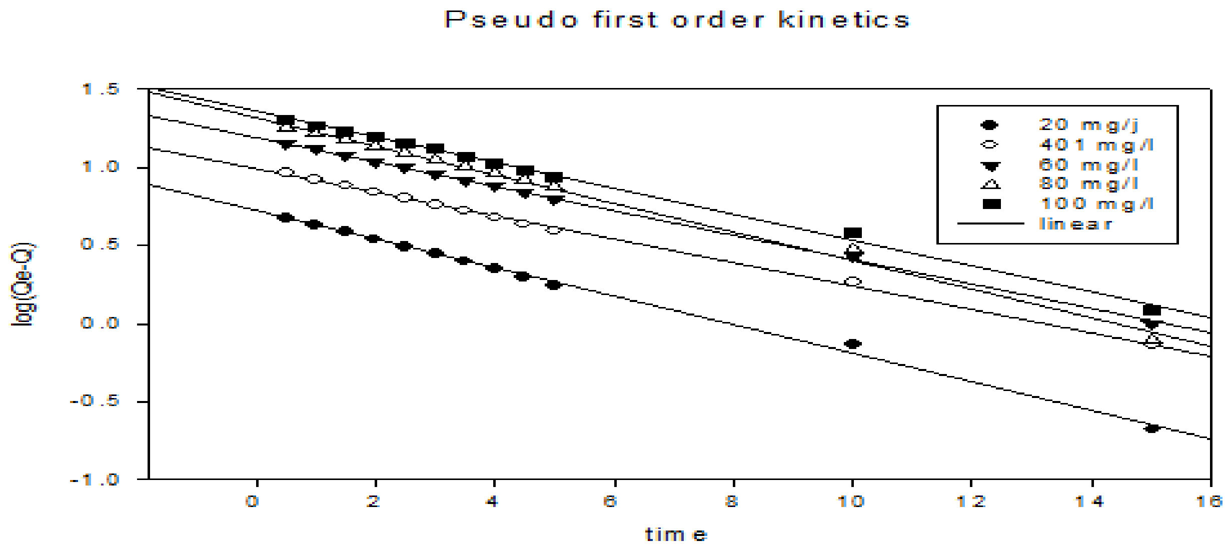

Fig.-9: Pseudo first order kinetics for Zinc on to *Boodlea struveiodes* for 0.1 g/ 30ml adsorbent concentration

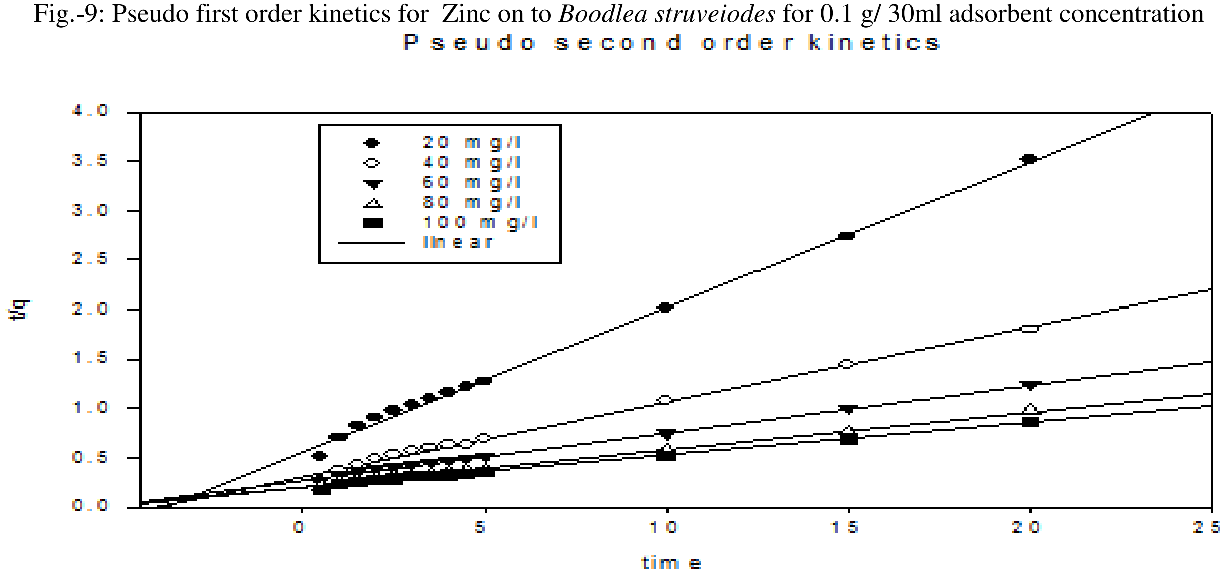

Fig.-10: Pseudo second order kinetics for Zinc on to *Boodlea struveiodes* for 0.1 g/ 30ml adsorbent concentration

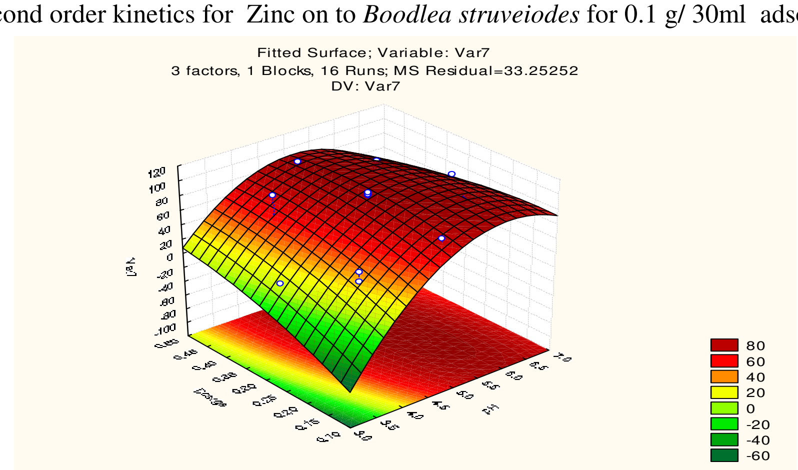

Fig.-11: Surface plot of pH vs Dosage

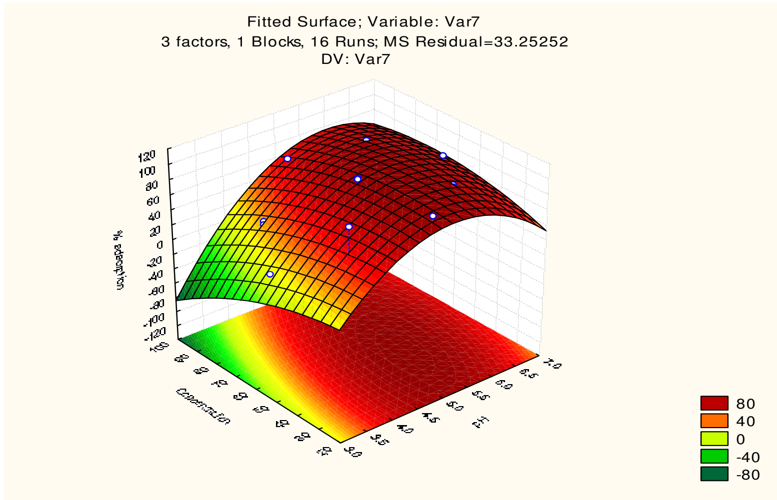

Fig.-12:Surface plot of pH vs Concentration

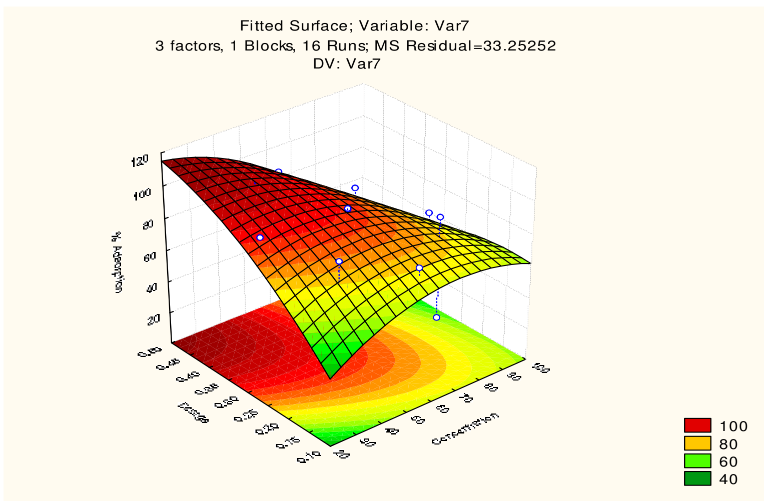

Fig.-13: Surface plot of Concentration vs Dosage

Response surface methodology and Central composite design

Response surface methodology is a technique used here to optimize % removal by relating controlled experimental variables and observed response according to desired criteria. RSM comprise a statistical & mathematical technique for the empirical model building.[9-11] Actually, it takes the response variables to the number of input variables that affect the percentage of removal.[4]

This interaction can be predicted by the following second order response surface model:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta i X i + \sum_{i=1}^{k} \beta ii X i 2 + \sum_{j=i+1}^{k} \sum_{i=1}^{k-1} \beta ij X i X j + \in ij \quad (8)$$

Here Y = measured response, β = coefficient of parameter, X_i = input variables[10]

In this study, the effect of various parameters such as pH, initial metal ion concentration, the dosage of adsorbent was studied well using CCD and RSM.[12]

The empirical model equation getting by the responses of various factors on the adsorption of Zinc on *Boodlea struveiodes* is expressed as:

$Y = -550.635 + 191.042 X_1 – 0.021 X_2 + 792.748 X_3 – 17.166 X_1^2 – 0.011 X_2^2 -300.994 X_3^2 + 0.384 X_1 X_2 – 72.475 X_1 X_3 – 3.384 X_2 X_3$ (9)

Here Y = % of adsorption of zinc on *Boodlea struveiodes* , X_1 = pH, X_2 = metal ion concentration, X_3 = dosage of adsorbent

Table-3: Coded Experimental Design for Zinc removal onto *Boodlea struveiodes*

Run	Coded values			Actual values			Experimental % adsorption
	pH	concentration	dosage	pH	concentration	dosage	
1	-1.00000	-1.00000	-1.00000	6.000000	80.00000	0.200000	87.87
2	-1.00000	-1.00000	1.00000	6.000000	40.00000	0.400000	88.33
3	-1.00000	1.00000	-1.00000	6.000000	40.00000	0.200000	85.32
4	-1.00000	1.00000	1.00000	5.000000	60.00000	0.300000	90.2
5	1.00000	-1.00000	-1.00000	5.000000	60.00000	0.131821	79.21
6	1.00000	-1.00000	1.00000	4.000000	40.00000	0.200000	38.43
7	1.00000	1.00000	-1.00000	4.000000	80.00000	0.400000	29.64
8	1.00000	1.00000	1.00000	5.000000	93.63586	0.300000	68.59
9	-1.68179	0.00000	0.00000	6.681793	60.00000	0.300000	80.57
10	1.68179	0.00000	0.00000	5.000000	60.00000	0.300000	90.89
11	0.00000	-1.68179	0.00000	4.000000	40.00000	0.400000	84.87
12	0.00000	1.68179	0.00000	6.000000	80.00000	0.400000	78.25
13	0.00000	0.00000	-1.68179	4.000000	80.00000	0.200000	24.71
14	0.00000	0.00000	1.68179	5.000000	60.00000	0.468179	90.56
15	0.00000	0.00000	0.00000	3.318207	60.00000	0.300000	9.12
16	0.00000	0.00000	0.00000	5.000000	26.36414	0.300000	93.39

Table-4: Experimental and predicted values of % Zinc adsorption

Experimental run	Observed	Predicted
1	87.87	95.43262
2	88.33	92.24129
3	85.32	83.85091
4	90.2	90.96287
5	79.21	74.58678
6	38.43	43.37137
7	29.64	34.55344
8	68.59	63.99998
9	80.57	77.17175
10	90.89	90.96287
11	84.87	80.75174
12	78.25	76.75299
13	24.71	24.24307
14	90.56	90.31216
15	9.12	7.647193
16	93.39	93.10896

Analysis of variance (ANOVA) was calculated to analyze the accessibility of the model.[13,14] The coefficients of variation have been tested to estimate the fitness of the model. F-value in the ANOVA table is the ratio of the model mean square to the appropriate error mean square. Larger is the ratio, larger is the F – value. It indicates the more significant of the model than random error. The model terms with p-value less than 0.05 is significant to the model.[15,16] ANOVA table for the removal of Zinc using *Boodlea struveiodes* was justified the model significance.

The observed values and predicted values were satisfactorily matched with regression coefficient value R^2 = 0.9827 & ms residual is 33.252. By using the CCD model optimized values are pH =5, the initial concentration of Zn^{+2} is 26.36 and dosage of *Boodlea struveiodes*biosorbentare 0.3 gm. The maximum optimized % adsorption of Zinc on *Boodlea struveiodes* was 93.39.

Table-5: Analysis of regression coefficients for Zinc removal

Term symbol	Regr. Coeff.	Std.Err.	t	p
const	-550.635	79.2002	-6.95245	0.000439
X_1	191.042	20.8852	9.14725	0.000096
X_1^2	-17.166	1.8946	-9.06077	0.000101
X_2	-0.021	0.8261	-0.02524	0.980685
X_2^2	-0.011	0.0047	-2.31559	0.059809
X_3	792.748	165.2198	4.79814	0.003006
X_3^2	-300.994	189.4566	-1.58872	0.163223
X_1 X_2	0.384	0.1019	3.76576	0.009335
X_1 X_3	-72.475	20.3877	-3.55485	0.012002
X_2 X_3	-3.384	1.0194	-3.31941	0.016016

Table-6: ANOVA table for Zinc removal

Source	Sum of squares	Degrees of freedom	Mean square	Factor(F)	Probability(p)
X_1	5834.75	1	5834.749	175.4679	0.000011
X_2	2729.95	1	2729.947	82.0975	0.000101
X_3	1022.82	1	1022.821	30.7592	0.001451
X_1^2	178.30	1	178.298	5.3619	0.059809
X_2^2	298.50	1	298.503	8.9769	0.024128
X_3^2	83.93	1	83.931	2.5240	0.163223
X_1 X_2	471.55	1	471.552	14.1809	0.009335
X_1 X_3	420.21	1	420.210	12.6369	0.012002
X_2 X_3	366.39	1	366.392	11.0185	0.016016
Error	199.52	6	33.253		
Total SS	11575.14	15			

ANOVA; Var.:Var7; R-sqr = 0.98276; Adj: 0.95691, 3 factors, 1 Blocks, 16 Runs; MS Residual=33.25252, DV: Var7

CONCLUSION

Adsorption studies on Zinc onto *Boodlea struveiodes* were carried out by evaluating the percentage of adsorption at different optimized conditions. Batch experiments were conducted by considering pH, initial metal ion concentration, the dosage of adsorbent, the particle size of the adsorbent and contact time as variables which were affected the adsorption process. The analysis of theoretical data and experimental data shown that the maximum % adsorption taken place at pH 5. The kinetic studies revealed that adsorption of Zinc onto *Boodlea struveiodes* was better described by pseudo first order as well as second order kinetics. It was further found that the experimental data were well represented by Langmuir, Freundlich and Tempkin adsorption isotherms with higher correlation coefficients. The objective of this study was to optimize the process conditions for maximum adsorption using RSM through CCD for the removal of Zinc using *Boodlea struveiodes*. The maximum % adsorption of Zinc was 93.39 at optimum conditions of pH 5, initial metal ion concentration 26.36 mg/l and dosage of adsorbent 3.0 g. Regression coefficient R^2 value 0.9827 indicated that high correlation between observed and predicted value of the response.

REFERENCES

1. M. Malakootian, A. Almasi, H. Hossaini, *Int. J. Environ. Sci. Tech*, **5(2)**, 217 (2008).
2. Bahia Meroufel, Mohamed Amine Zenasni, Andre Merlin, Beatrice George., *Journal of Environmental Protection*, **6**, 735 (2015).

3. D. Sheikha, I. Ashour and F. A. Abu Al-Rub, *The Journal of Engineering Research*, **5(1),** 20 (2008).
4. E. Cicek, C. Cojocaru, *Nukleonika*, **53**, S121 (2008).
5. Sunil Rajopriya, Balpreet Kaur, *International Journal Engineering Science Invention*, **3**, 2319(2014).
6. O. S. Amuda, A. A. Giwa, I. A. Bello, *Biochemical Engineering Journal*, **36**, 174 (2007).
7. Zurina Z. Abidin, M. A. Mohd Salleh, M.Y. Harun, N. Abu Bakar, *Journal of Scientific & Industrial Research*, **73**, 191 (2014).
8. M. I. Tempkin, V. Pyzhev, *Actaphys. Chem.*, **12**, 327 (1940).
9. J. Aravind, P. Kanmani, G. Sudha, R. Balan, *Global J. Environ Sci. Manage*, **2(1)**, 61(2016).
10. B. A. Oyejola, J. C. Nwanya, *International Journal of Statistics and Applications*, **5(1)**, 21(2015).
11. Sauntak Kamsonlian and Bipin Shukla, *Research Journal of Chemical Sciences*, **3(7)**, 31 (2013).
12. B. S. Kruthi, M. R. Rajani, *International Journal of Technical Research and Applications*, **3**,169(2015).
13. D. Krishna, K. Siva Krishna and R. Padma Sree, *International Journal of Applied Science and Engineering*, **11(2)**, 213(2013).
14. D. Ozturk, Tekin Sahan,Erkan Disli and Nahit Aktas,Hacettepe, *J. Biol. & Chem.*,**42 (2)**, 183(2014)
15. Zaharaddeen N. Garba, Idris Bello, Ahmad Galadima, Aisha Y. Lawal, , *Karbala International Journal of Modern Science,* **2**, 20(2016).
16. Z. Z. Chowdary, Sharifuddin M. Zain, Rashid. A. Khan, *Research Journal of Applied Sciences Engineering and Technology* **4(5)**, 458 (2012).

[RJC-1683/2017]