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APPLICATION OF ALGAE BIOMASS AS A POTENTIAL BIOSORBENT FOR THE REMOVAL OF Pb(II) IONS FROM AQUEOUS SOLUTIONS

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ABSTRACT

Presently heavy metal pollution has become a serious global environmental problem. The industrial activities and technological development lead to a discharge of significant amount of heavy metal ions including Pb(II) in their effluent. The long term exposure of Pb(II) cause nervous system problems, increase in blood pressure, anaemia. Therefore, it is a matter of great concern to eliminate heavy metals including lead from waste water before discharging it into the water bodies. In the present research feasibility of algae biomass as an adsorbent for the removal of lead ions from aqueous solution has been investigated. Batch studies have been conducted to explore the effects of various parameters such as pH, contact time, adsorbent dose and metal ion concentration on the adsorption of lead by algae biomass. It has been observed from the result that the maximum adsorption percentage of Pb(II) was 97.7% at 4 pH and found to decreased with the increase of metal ion concentration. The equilibrium time required for maximum adsorption was 90 minutes. The adsorption data was best fitted Langmuir adsorption model as indicated by highest value of R^2*= 0.9918. The experimental data was found to obey pseudo second order model perfectly. The obtained results concluded that algae biomass can be employed effectively for the removal of Pb(II) ions from waste water at commercial level.*

Key words: Adsorption, Algae biomass, Langmuir, Freundlich, Pseudo second order etc.

1.INTRODUCTION

Heavy metal is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3 and has atomic numbers above 20[1]. The toxicity of heavy metals to marine life and consequently to man has been established for many years. Lead pollution particularly results from battery manufacturing, automobile exhaust fumes and metal finishing industries [2]. Lead being one of the three most toxic heavy metals, has long-term potential negative impacts on anemia, encephalopathy, hepatitis and nephritic syndrome [3]. The removal and recovery of heavy metals from wastewater is important for the environmental protection and human health. There is a wide range of treatment methods such as membrane filtration, adsorption, ion exchange, reverse osmosis, chemical precipitation, or solvent extraction, which have classically been employed for stripping toxic metals from wastewaters. However, these methods have disadvantages, like incomplete metal removal, high reagent or energy requirements, and generation of toxic sludge or other heavy metal-containing waste products [4]. In recent years, the need of safe and economical methods for the elimination of heavy metals from contaminated water have deviated the interest of researchers towards the development of low cost alternative swaste water treatment technologies [5]. Biosorption utilizes the ability of certain materials to accumulate heavy metals from aqueous solutions by either metabolically mediated or physico-chemical pathways of uptake [6]. The most prominent features of biosorption are the use of low cost and highly efficient biomass materials to adsorb heavy metals from aqueous solutions present even at very low concentrations [7].

II. METHODOLOGY

2.1 Collection and Preparation of adsorbent

Green algae (Chlorophyta) used in this study were collected locally from pond near Ambedkar colony Aligarh (UP), India in the month of October. The collected algae were washed several times with double distilled water to eliminate the extra salts and impurities present in it. Then it is kept for sun drying for 5-7 days. After drying it was grounded to obtain fine powder of algae. The powder was then sieved through 150µ size ASTM mesh. Finally, obtained powder was stored in air tight container to use as adsorbent for the removal of ions from aqueous solutions.

2.2 Adsorbate solution

A required amount of $Pb(NO_3)_2$ was dissolved in 1 litre double distilled water to prepare the stock solution of lead of 1000mg/. This stock solution was used to prepare solutions required for other batch operations. The pH of solutions was adjusted by adding 0.1 M NaOH and HCl.

2.3 Determination of point of zero charge

The point of zero charge (pH_{pzc}) of algae biomass was determined by solid addition method with DDW and 0.1 N KNO_3 solutions [8]. The 50 ml DDW (Double distilled water) was transferred into a series of conical flasks and the initial pH (pH_i) of these solutions were roughly adjusted between 2 to 10 by adding either 0.1 N HCl or 0.1 N NaOH solutions. The initial pH (pH_i) of these solutions was than measured accurately by using pH meter. After that 0.5 gm of adsorbent was added into each flask and allowed to equilibrate for 24 hours with intermittent manual shaking. After attaining equilibrium solution was filtered and the final pH (pH_f) of the supernatant liquid was then noted. The difference between initial and final values ($\Delta pH = pH_i - pH_f$) were plotted against pH_i, the point of intersection of resulting curve with abscissa at which ΔpH is zero, gave the point of zero charge (pH_{pzc}). The same procedure was repeated using 0.1 N KNO_3 solutions.

2.4 Batch Studies

The adsorption properties of green algae were investigated as a function of adsorbent dose, initial pH, initial metal ion concentration and contact time. Adsorption isotherms and kinetics studies were carried out by batch process in which 0.5 gm of adsorbent was weighed and placed in series of 100ml standard conical flask containing 50ml of Pb(II) solution of desired concentration. This solution was shaken in a rotary shaker for about 30 min and kept for 24 hours to attain equilibrium with intermittent manual shaking. All the operations were conducted at constant temperature and with 50 ml solutions of 50 mg/L metal ion concentration except during the study of effect of concentration in which 5 to 200 mg/L metal ion concentration solutions were used. The solutions were filtered to separate the adsorbent from supernatant liquid. The residual concentration of metal ions was determined by Atomic Absorption Spectrophotometer model GBC 902 using air Acetylene flame. The removal percentage (R%) of metal ions and adsorption capacity or amount of metal ions adsorbed per unit mass of adsorbent (q_e) were calculated for each run by the following expression

$$R\% = \frac{(Ci - Ce)}{Ci} \text{ X } 100 \qquad q_e = \frac{(Ci - Ce)}{m} \text{ X V}$$

where, C_i is the initial concentration of metal ions in the solution, C_e is the final concentration of metal ions in the solution, V is the volume of the solution and m is the mass of the adsorbent (in gram)

III. RESULTS AND DISCUSSION

3.1 Batch Studies

3.1.1 Effect of pH

The pH of the solution is an improtant controlling parameter in the uptake of Pb(II) ions. The effect of pH of solution containing Pb(II) ions on adsorption by algae biomass is shown in fig.1. It was found that Pb(II) uptake by algae biomass is strongly affected by pH of the solution. The amount of Pb(II) adsorbed was found to increase from 18.2% to 97.7% on increasing pH from 1 to 4 and then decrease slowly up to 87.96% at pH 10. The variation in the adsorption of pb(II) with respect to pH can be explained by considering the initial pH (pH_i), final pH or equilibrium pH (pH_f) and speciation of metal ions in the solution . At pH 1, Pb^{2+} ions compete with H^+ ions for binding sites of adsorbent, therefore the adsorption of Pb(II) ions was less (18.2%) at low pH 1. When the initial pH of the solution was raised upto 4 the adsorption percentage increases quickly up to maximum of 97.7%, possibly due to little less competition of pb^{2+} ions and H^+ ions. Further increase in pH of the solution up to pH 8 results slightly decrease in the adsorption of Pb(II) ions (92.46%). A similar trend was observed when pH was increased to 10 (87.96%). The decrease in the adsorption of Pb(II) at pH >4 can be explained on the basis of Pb(II) speciation at different pH values. The chemical species of Pb(II) formed at different pH values are Pb^{2+} at pH=2-4, $Pb(OH)^+$ at pH=4-6, $Pb(OH)_2$ at pH=6-10 and $Pb(OH)_3^-$ at pH=10-12 [9]; [10]. The speciation suggested that majority of the copper is adsorbed in pH range 4-6 in the form of Pb^{2+} ions and lead hydroxide species due to micro precipitation as indicated by the equation

$$Pb^{2+} + H^+ + OH^- \rightarrow Pb(OH)^+ + H^+$$

$$Pb^{2+} + 2H_2O \rightarrow Pb(OH)_2 + 2H^+$$

Moreover, the point of zero charge (P_{ZC}) has an important influence on adsorption processes. The surface of adsorbent was positive when pH < P_{ZC}, neutral when pH = P_{ZC} and negative at pH > P_{ZC} [11]. The data plotted in fig. 8 indicated that the pH_{zpc} value of algae biomass was 5.6 showing that the surface was negatively charged above this pH and hence fairly large amount of Pb(II) ions (97.7 % at pH 4) were adsorbed.

3.1.2 Effect of dose

The effect of dose of algae on biosorption of Pb(II) are shown in fig.2. It was found that adsorption percentage (R%) increased from 12.2 to 99.6 % and adsorption capacity (q_e) decreased from 3.05 to 1.66 mg/g on increasing adsorbent dose from 0.1 to 1.5 g. The increase in adsorption percentage may be due to the fact that increase in dose results increase in number of active sites available for biosorption. The biosorption capacity

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decreases may be due to fact that at lower biosorbent dose almost all the biosorption sites are saturated by the Pb(II) ions but as the dose increased, the biosorption sites would be excessive for the biosorption reaction. Since the concentration Pb(II) ions as well as the volume of the solution are constant, the amount of Pb(II) adsorbed per unit of mass algae biomass was decreased. [12].The maximum adsopriton capacity (4.835 mg/g) of algae biomass for the removal of Pb(II) ions was found at adsorbent dose of 0.5 g. Therefore, 0.5 g adsorbent dose was taken as optimum dose in other experiments.

3.1.3 Effect of contact time

The effect of contact time on the adsorption of Pb(II) ions at concentration of 50 mg/L was studied by varying contact time 5 to 120 minutes and shown in fig.3. The biosorption percentage was found to increase with increase in contact time and reaches maximum (97.7%) in 90 minutes and hence, attained equilibrium. The increase in adsorption percentage of Pb(II) ions by algae biomass with the increase of contact time may due to the fact that at initial period less number of sites was occupied by metal ions but as the contact time of metal ions with adsorbent surface was increase the active sites captured by Pb(II) ions also increased and the process become slower and attained equilibrium with 90 minutes.

3.1.4 Effect of concentration

Adsorption of Pb(II) by algae biomass is highly dependent on the initial concentration of metal ions. The adsorption of lead was carried out at different initial Pb(II) ions concentration ranging from 5 mg/L to 200 mg/L. It was observed that increase of initial lead ions concentration decreases the percentage removal of lead ions from 100 % at 5 mg/Lto 45.54 % at 200 mg/L as shown in fig. 4. It may be due to the fact that adsorbent has a limited number of active sites, which become saturated at a certain concentration [13].

It can be observed from the fig. 4 that adsorption capacity q_e, increased with increase in initial concentration of lead ions from 0.5 mg/g at 5 mg/L to 9.108 mg/g at 200 mg/L which may be due to the fact that increased concentration gradient between the bulk solution and adsorbent surface resulted from lowering down the resistance to mass transfer of Pb(II) from aqueous to solid phase and hence increased adsorption capacity of adsorbent [14], [15].

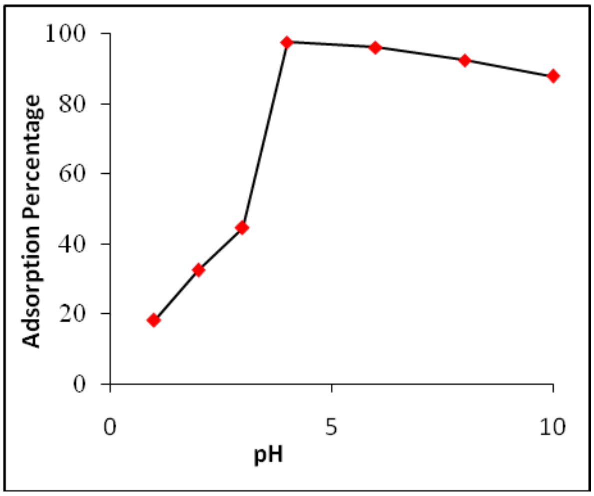

Fig.1 Effect of pH

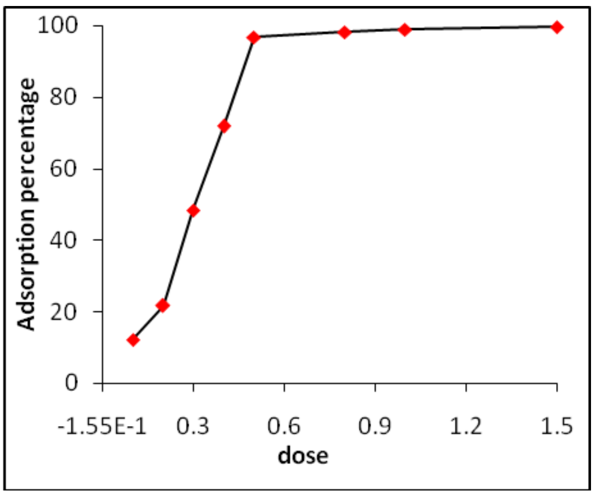

Fig. 2 Effect of dose

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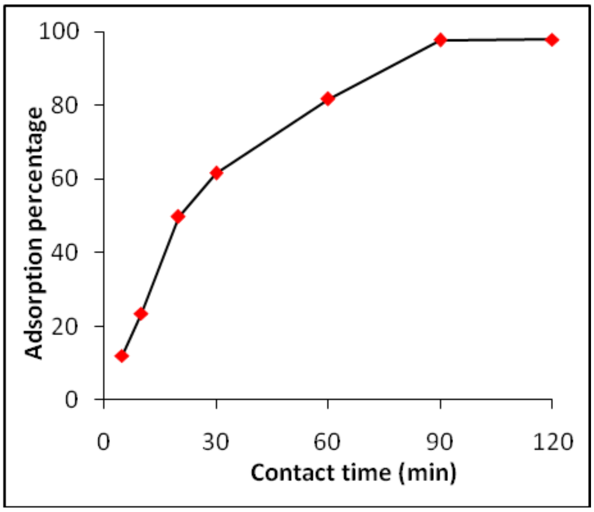


Fig. 3 Effect of contact time

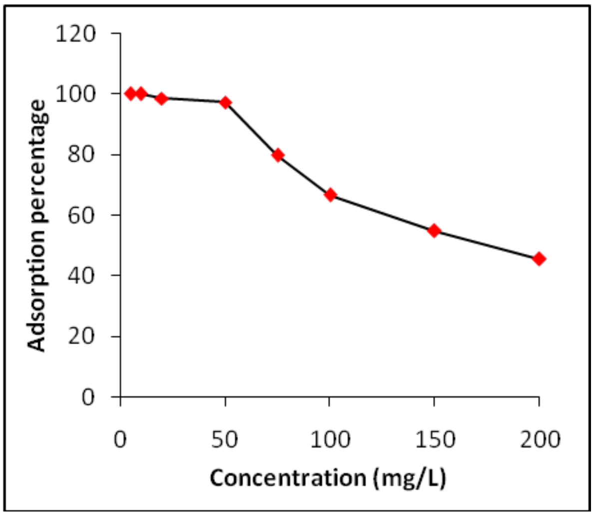


Fig. 4 Effect of concentration

3.2 ADSORPTION ISOTHERMS

The equilibrium sorption of Pb(II) ions was carried out by contacting 0.5g of algae biomass with 50 ml solutions of Pb(II) ions of concentrations ranging from 10 – 200 mg/L in 100 ml conical flasks with intermittent shaking for 90 minutes on the rotary shaker. The adsorption behaviour of Pb(II) ions by algae biomass was studied by analysing obtained data with the Langmuir, Freundlich andTemkinadsorption isotherm models.

Langmuir model is commonly used for liquid phase adsorption which assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions [16]. The Langmuir isotherm is expressed as follows:

$$\frac{1}{q_e} = 1/q_m \times 1/b \times 1/C_e \times 1/q_m$$

Where, q_e is the amount of metal ions adsorbed per unit mass of the adsorbent (mg/g) at equilibrium, C_e is the concentration of metal ions solution (mg/L) at equilibrium, q_m is the quantity of metal ions required for a single monolayer on the unit mass of adsorbent (mg/g), b is a Langmuir constant related to the bonding energy of adsorption and monolayer adsorption capacity of adsorbent (mg/g), respectively. A linear plot of $1/q_e$ vs $1/C_e$ shows that adsorption of metal ions follows the Langmuir model. The values of q_m and b were calculated from the intercept and slope of the plots shown in fig. 5.

The linear form of the Freundlich adsorption isotherm [17] is expressed as:

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

Where, C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed per unit weight of the adsorbent (mg/g), K_f is a Freundlich constant which indicates the relative adsorption capacity of the adsorbent related to bonding energy and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The values of K_f and n were calculated from slope and intercepts of plot log q_e vs log C_e shown in fig. 6.

Temkin isotherm assumes that heat of adsorption on the surface of the adsorbent decrease linearly with coverage due to adsorbent-adsorbate interactions [18]; [19]. The linear form of Temkin equation can be represented as

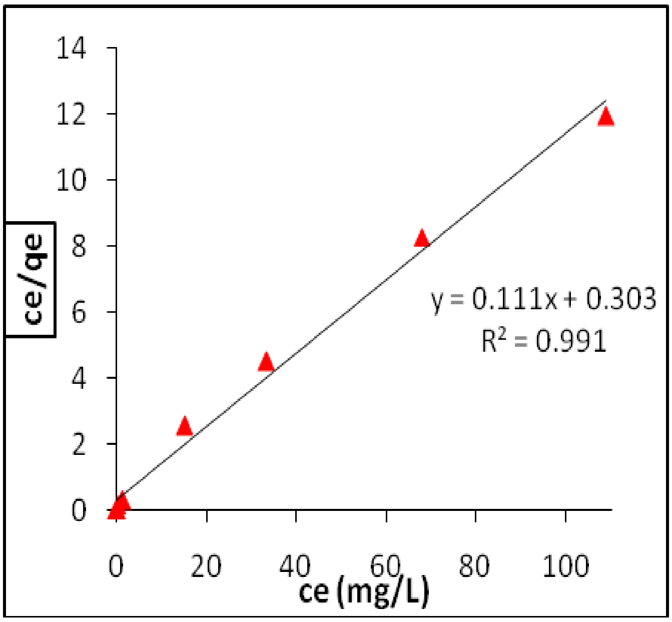
$$q_e = RT/b \times InA + (RT/b) \times InC_e \quad \text{or} \quad q_e = B\ InA + B\ InC_e$$

where, B = (RT/b), R is universal gas constant, T is the absolute temperature and b is a constant. C_e is the concentration of solution (mg/L) at equilibrium and q_e is the amount of metal adsorbed (mg/g) on the surface of adsorbent. The quantities A (g/L) and B are Temkin constants related to the adsorption potential and heat of adsorption, respectively. The values of A and B can be calculated from slopes and intercepts of the plot of q_e vs In C_e shown in fig. 7.

The obtained experimental data has been evaluated with Langmuir, Freundlich and Temkin isotherm models to indicate how molecules of adsorbate are partitioned between the adsorbent and liquid phase at equilibrium as a function of adsorbate concentration. Adsorption of Pb(II) ions was carried out at concentration ranging from 5 to 200 mg/L at pH 4 for 90 minutes of equilibrium time. The value of R^2 and other parameters of adsorption isotherms were obtained from their graphs shown in fig. 5, 6 and 7 mentioned in Table 3. The values obtained from these models and values of correlation coefficients (R^2) i.e 0.1392, 0.7045, 0.8107 and for the Langmuir, Fruendlich, Temkin and D-R isotherms, respectively indicated that adsorption of Pb(II) on algae biomass favoured Langmuir isotherm the most which showed that the adsorbent algae biomass has homogeneous surface and Pb(II) ions were adsorbed on it by forming monolayer. The monolayer adsorption capacity of bone algae biomass for Pb(II) ions calculated from Langmuir plot of $1/q_e$ vs $1/C_e$ was found to be 3.695 mg/g. The essential characteristic of the Langmuir isotherm parameters can be used to predict the affinity between the adsorbent and adsorbate using separation factor or dimensionless equilibrium parameters, R_L which is expressed as:

$$R_L = \frac{1}{1 + b\ C_i}$$

Where, b is the Langmuir constant and C_i is the concentration of Cd(II) ions. The value of R_L provided important information about the nature of adsorption process. The value of R_L indicated whether the process of adsorption is to be irreversible (R_L=0), favourable (0< R_L<1), linear (R_L=1). The value of R_L was found 0.1392 for Pb(II) ions of concentration ranging from 10-200 mg/L which indicated that the adsorption of Pb(II) ions on bone china pottery waste is favourable. The values of K_F, 1/n and R^2 obtained from the graph of log q_e vs log C_e for Freundlich isotherm shown in fig. 6 are listed in table .1. The value of n was found to be 2.923 which is greater than 1 indicated that the adsorption of Pb(II) ions on algae biomass occurred through chemisorption process. Moreover, the values of $K_F \approx 1.958$ indicated good adsorption capacity of adsorbent. Furthermore, the obtained data also revealed the better applicability of the Temkin isotherm model than Fruendlich which indicated that the heat of adsorption of lead on fired ceramic was decreased with coverage due to adsorbate-adsorbent interactions. The higher value of R^2 for Temkin isotherm indicate that Pb(II) ions gets adsorbed on the surface algae biomass with uniform heat of adsorption.



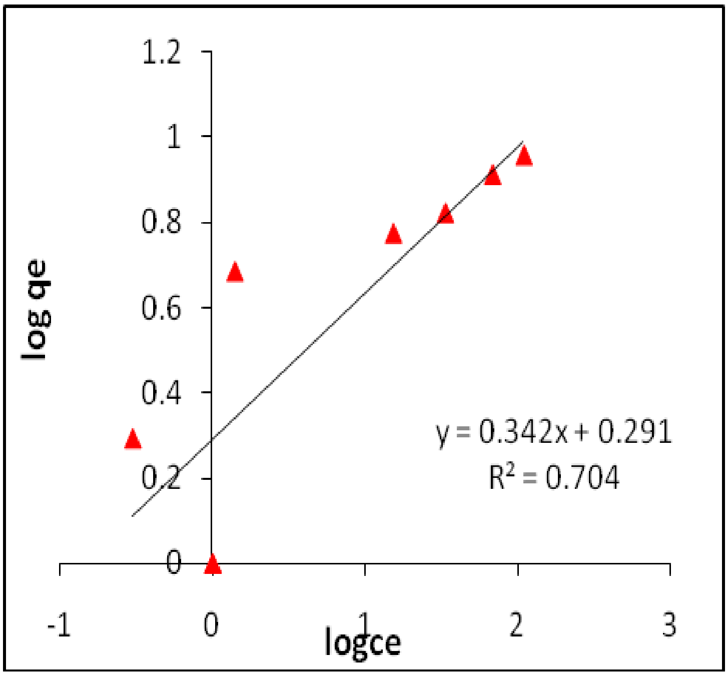


Fig.5 Langmuir adsorption isotherm Fig.6 Freundlich adsorption isotherm

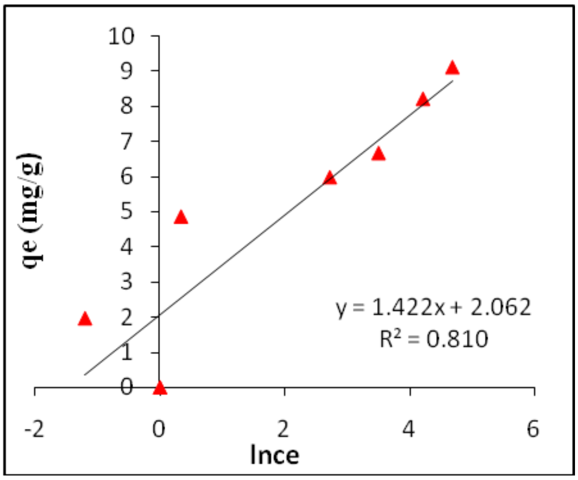


Fig.7 Temkin adsorption isotherm

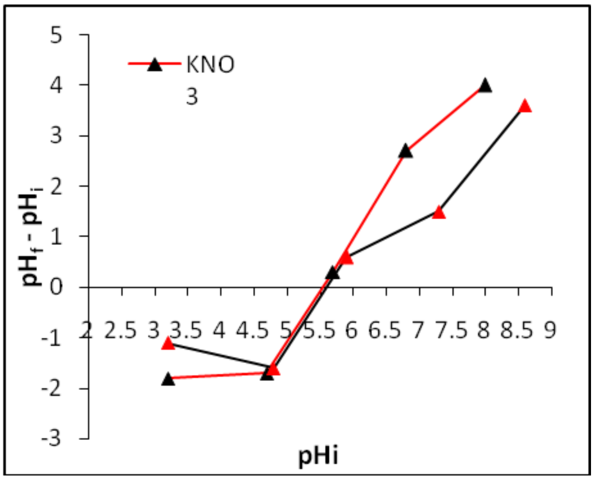


Fig.8Point of zero charge

Table: 1 Langmuir, Freundlich and Temkin isotherm constants for the adsorption of Pb(II) onto algae biomass

Metal	Langmuir isotherm				Freundlich isotherm				Temkin isotherm		
Pb^{2+}	q_m	b	R^2	R_L	1/n	n	K_F	R^2	A	B	R^2
	8.976	0.367	0.991	0.139	0.342	2.923	1.958	0.704	4.264	1.422	0.810

3.3 ADSORPTION KINETICS

The equilibrium kinetics of Pb(II) ions uptake was carried out by contacting 0.5g of algae biomass with 50 ml solutions of Pb(II) ions of concentrations 50 mg/L in 100 ml conical flasks with intermittent shaking ranging from 5 minutes to 120 minutes. The kinetic data was analysed by using the pseudo first-order kinetic model express by Lagergren [20] and pseudo second order [21].

The pseudo first-order kinetic equation given by Lagergren was widely used for the adsorption of liquid/solid system on the basis of solid capacity is represented as:

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

where, k_1 is the Lagergren rate constant for adsorption (min^{-1}),q_e is the amount of metal adsorbed at equilibrium (mg/g), q_t is the amount of metal adsorbed (mg/g) at any time t. The values of k_1 and q_e were calculated from the slope and intercept of the plot of log (q_e - q_t) vs time, t shown in fig. 9

The equation of pseudo second order model is expressed as:

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

where, k_2 is the equilibrium rate constant of second order kinetics model (g/mg/min), q_e is the Amount of metal adsorbed at equilibrium (mg/g), q_t is the amount of metal adsorbed (mg/g) at any time t. The time, t was plotted against t/q_t. The values of k_2 and q_e was determined from the slope and intercepts of graph plotted shown in fig. 10.

Table .2 Pseudo-first order, Pseudo-second order and Inter-particle diffusion model constants

Metal	Pseudo-first order	Pseudo-second order

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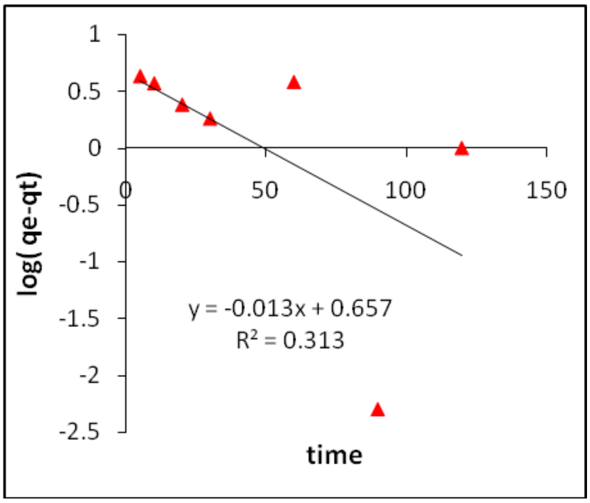
Pb^{2+}	q_e	K_1	R^2	q_e	K_2	R^2
	4.547	0.027	0.313	7.272	8.156	0.990

The evaluation of kinetic models is an important aspect for designing and optimization of water and wastewater treatment process as it relates the adsorbate uptake rate with bulk concentration .In order to investigate the mechanism of adsorption of Pb(II) on fired ceramic, the kinetic data was analysed using the Lagergren first order, pseudo second order kinetic model and intra-particle diffusion model. The graphs plotted for the models mentioned above are shown in fig. 9.10, and 11.The values of R^2 and other parameters for pseudo first order ($R^2 \approx 0.0272$) and pseudo second order ($R^2 \approx 0.9905$) indicated that adsorption of Pb(II) ions by algae biomass was best described by pseudo second order kinetic model. From Table.2 values indicated the applicability of pseudo second order model implies that adsorption of Pb(II) on algae biomass is a chemisorption process which involves the formation of single layer of Pb(II) ions on the surface of adsorbent by chemisorption and may be followed by additional layer of physically adsorbed Pb(II) ions.



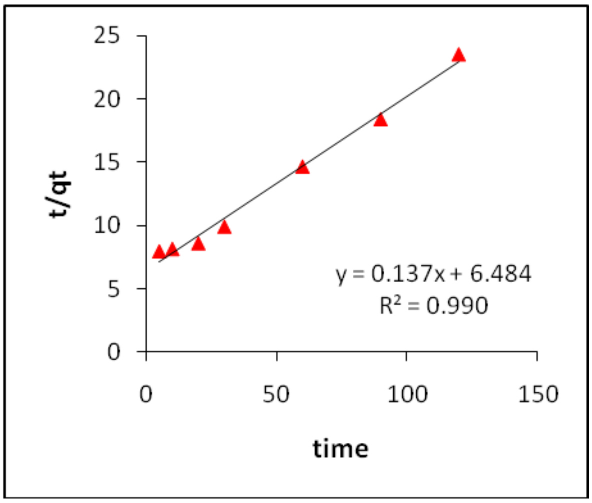


Fig.9 Pseudo- first order model fig.10 Pseudo second order model

IV. CONCLUSION

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The studies found that the algae biomass is a potential adsorbent for the removal of the Pb(II) ions from aqueous solution. The maximum adsorption of Pb(II) by algae biomass was found to be 97.7% within 90 minutes of contact time at pH 4-6 . The experimental data is best fitted to langmuir isotherm as indicated by the highest value of correlation coefficient (R^2 = 0.9918). The kinetics studies showed that the adsorption of Pb(II) ions on algae biomass was perfectly described by pseudo second order kinetic model. It may be concluded from the above results that algae biomass can be commercially employed as a potential biosorbent for the removal of Pb(II) ions from aqueous solution since its is available free of cost in bulk.

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