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EQUILIBRIUM AND KINETIC STUDIES ON BIOSORPTION OF ZINC ONTO *Gallus Domesticus* SHELL POWDER

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ABSTRACT

Biosorption is potentially an attractive technology for treatment of wastewater for retaining heavy metals from dilute solutions. Studies carried through the environmental biotechnology have shown that many biosorbents present in the nature have great capacity for removal of heavy metals. The paper presents the results of studies carried out on sorption of zinc ions from aqueous solutions by *Gallus Domesticus shell* powder as a low-cost sorbent. It was found that crushed *Gallus Domesticus* shell posse's relatively high sorption capacity, when comparing with other sorbents that was evaluated as 46.05 mg/g. The biosorption experiments were performed under various conditions such as different initial concentrations, pH, biosorbent concentration and biosorbent particle size. It was found that the equilibrium of the process was reached after 60 min. About 0.1g of *Gallus Domesticus* shell powder was found to be enough to remove 86.50% of zinc for 20 mg/l of metal ion concentration from 30 ml aqueous solution. The optimum pH value was found to be 6. The pseudo first order and pseudo second order kinetic models were used to describe the kinetic data. The dynamic data fitted with the pseudo second order kinetic model for zinc. The experimental equilibrium data were adjusted by the biosorption isotherms from Langmuir, Freundlich, Redlich & Peterson and Temkin models, and their equilibrium parameters were determined. The best-adjusted model to the experimental equilibrium data for egg shell powder was the Freundlich model followed by Langmuir model.

Keywords: zinc, biosorption, egg shells, adsorption isotherm, kinetic studies.

1. INTRODUCTION

It has been shown that the release of toxic substances and their dispersal in the environment may cause tragic effects on exposed populations. Over the fast few decades the huge increase in the use of heavy metals has resulted in an increased flux of metallic substances in aquatic environment. The most important characteristics of these metals are that they are non-degradable and therefore persistent. Furthermore, most of the metal ions are toxic to living organisms. Therefore, in order to have a pollution-free environment, the toxic materials should be removed from wastewater before its disposal [1]. The source of environmental pollution with heavy metals is mainly industry, i.e. metallurgical, electroplating, metal finishing industries, tanneries, chemical manufacturing [2]. Heavy metals such as lead, mercury, arsenic, copper, zinc and cadmium are highly toxic when adsorbed into the body [3]. Zinc is one of the most important metals often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants and not biodegradable and travels through the food chain via bioaccumulation. Therefore there is significant interest regarding zinc removal from wastewaters [4] and its toxicity for humans at levels of 100-500 mg/day [5]. World Health Organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/l [6].

Removal of toxic heavy metals from industrial wastewater has been practiced for several decades, the conventional physico-chemical removal methods, such as chemical precipitation, electro plating, membrane separation, evaporation or resin ionic exchange, are usually expensive and sometimes, not effective. Recently, heavy metal ions removal from industrial waste streams became particularly difficult due to implementation of more restrict law regulations that control the concentration of pollutants in effluents discharged into waters and soils on the level lower than 1 mg/kg [7]. Traditional methods of metal ions removal became inefficient in the removal of metal ions below this concentration. Therefore, there is the need to search for other methods that would be efficient at low concentration of pollutants [7]. Such a possibility offers biosorption, based on living or non living microorganisms or plants could be such an alternative method of treatment. Biosorption can be defined as the ability of biological materials to accumulate heavy metals through metabolically mediated or physico-chemical pathways of uptake [4]. It has distinct advantages over conventional methods of treatments, such as this process does not produce chemical sludge, hence no secondary pollution, more efficient and easy to operate.

The effectiveness of biosorption for the removal of heavy metals has been shown in a number of studies. However, only when the cost of the biosorption process can complete with the existing technologies will it be accepted commercially. Kuyucak indicated that the cost of biomass production played an important role in determining the overall cost of a biosorption process [8]. Therefore, low cost biomass becomes a crucial factor when considering practical application of biosorption. It leads to a search for biological sorbents among waste materials from food and agricultural industry. These materials can be considered as low-cost sorbents [7].

In the present paper it is proposed to apply hen egg shells as low-cost biological sorbent of zinc. In USA annually 120,000 tones of waste egg shells is generated and disposed in landfills [9]. The egg shell (which is almost entirely disposed of as waste) is currently used as source of calcium in animal feeds and human health supplements (i.e. for osteoporosis) [10]. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, adsorbent concentration and adsorbent size were evaluated. The equilibrium adsorption data were evaluated by Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm models.

2. MATERIALS AND METHODS

2.1. Biosorbent

The biosorbent used in the present paper is hen egg shell powder. Eggs are one of the first multifunctional food products, with various important gradients. They are well known for their whipping, gelling and emulsification properties in addition to their high quality protein [47]. The shell accounts for about 9-12 % by its total weight depending on egg size. It comprises about 94% $CaCO_3$ with small amounts of $MgCO_3$, calcium phosphate and other organic matter including protein [45]. Most good quality egg shells from commercial layers contain approximately 2.2 grams of calcium in the form of $CaCO_3$ weighing 5.5 grams [10]. The average eggshell contains about 0.3 % phosphorous and 0.3 % magnesium and traces of sodium, potassium, zinc, manganese, iron and copper [46].

Hen egg shells powder contains high levels of calcium and strontium. Levels of potentially toxic lead, aluminium, cadmium and mercury are very low. The levels of selenium, copper, chromium and strontium in an egg shells can vary significantly depending on the feed and environment. The protein fraction of egg shells powder contains high levels of Glycine and Arginine, and small amounts of Calcitonin and Progesterone hormones. Shell thickens depends upon the amounts of Mg and Ca; high levels of Mg, combined with low levels of Calcium increase shell deformity [47].

2.2 Preparation of biosorbent

Hen egg shells were collected from Andhra University College of Engineering hostels, Andhra University campus of Visakhapatnam, Andhra Pradesh, India. Shells were washed with deionized water several times to remove dirt particles. The dried egg shells powders of 75-212 μm particle size were used as biosorbent without any pretreatment for zinc adsorption.

2.3. Chemical

Analytical grades of $ZnSO_4\ 7H_2O$, HCl and NaOH were purchased from Merck, India. Zinc ions were prepared by dissolving its corresponding sulphate salt in distilled water. The pH of solutions was adjusted with 0.1 N HCl and NaOH.

All the experiments were repeated five times and the average values have been reported. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

2.4. Biosorption experiments

Biosorption experiments were performed in a rotary shaker at 180 rpm using 250 ml Erlenmeyer flasks containing 30 ml of different zinc concentrations. After one hour of contact (according to the preliminary sorption dynamics tests), with 0.1 g egg shell powder biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with whatman filter paper. The amount of metal adsorbed by eggshell powder was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q = \left(C_o - C_f\right) \times \frac{V}{M} \tag{1}$$

Where Q is the metal uptake (mg/g); C_o and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (ml); and M is the mass of biosorbent (g). The pH of the solution was adjusted by using 0.1 N HCl and 0.1 N NaOH.

The Langmuir [21] sorption model was chosen for the estimation of maximum zinc sorption by the biosorbent. The Langmuir isotherm can be expressed as,

$$Q = \frac{Q_{\max} b C_f}{1 + b C_f} \tag{2}$$

Where

$Q_{\max}$ Indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant b (L/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{Q} = \frac{1}{Q_{\max}} + \frac{1}{b Q_{\max} C_f} \tag{3}$$

The Freundlich [22] model is represented by the equation,

$$Q = K C_f^{1/n} \tag{4}$$

Where

K (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent and n is the Freundlich exponent related to adsorption intensity (dimensionless). For fitting the experimental data, the Freundlich model was linearized as follows,

$$\ln Q = \ln K + \frac{1}{n} \ln C_f \tag{5}$$

The Redlich-Peterson [23] model is represented by the equation,

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{6}$$

Where A (L/g) and B (L/mg) are the Redlich-Peterson isotherm constants and g is the Redlich Peterson isotherm exponent, which lies between 0 and 1. The linearized form of equation is given by:

$$\ln\left(\frac{AC_e}{q_e} - 1\right) = g\ln(C_e) + \ln(B) \tag{7}$$

Redlich-Peterson isotherm equation contains three unknown parameters A, B and g. Therefore a minimization procedure is adopted to maximize the coefficient of determination, between the theoretical data for q_e predicted from the linearized form of Redlich-Peterson isotherm equation and the experimental data.

The Temkin [24] isotherm has generally been applied in the following form,

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{8}$$

Where

A_T (L/mg) and b_T are Temkin isotherm constants.

2.5. Biosorption kinetics

The kinetics studies were carried out by conducting batch biosorption experiments with different initial zinc concentrations. Samples were taken at different time periods and analyzed for their zinc concentration.

3. RESULTS AND DISCUSSIONS

3.1. The effect of contact time

The data obtained from the biosorption of zinc ions on the egg shell powder showed that a contact time of 60 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and unadsorbed zinc concentrations at the end of 60 min are given as the equilibrium values (q_e, mg/g; C_{eq}, mg/l), respectively (Figure-1). And the other adsorption experiments were conducted at this contact time of 60 min.

3.2. Effect of pH

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls. Thus pH is an important process parameter on biosorption of metal ions from aqueous solutions since it is responsible for protonation of metal binding sites, Calcium Carbonate solubility and metal speciation in the solution [7].

It was found that Zn (II) uptake by eggshells was a function of solution pH. As shown in Figure-2, the uptake of zinc increased with the increase in pH from 2.0 to 6.0. Similar results were also reported in literature for different biomass systems [13-17]. The effect of pH can be explained by ion-exchange mechanism of sorption in which the important role is played by Carbonate groups that have cation- exchange properties. At lower pH values zinc removal was inhibited, possibly as a result of the competition between hydrogen and zinc ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as Carbonate groups in egg shells would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface.

In this study, these zinc cations at around pH 6 would be expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for zinc adsorption was found as 6 and the other adsorption experiments were performed at this pH value.

3.3. Effect of metal ion concentration

Figure-3 shows the effect of metal ion concentration on the adsorption of zinc by egg shell powder. The data shows that the metal uptake increases and the percentage adsorption of zinc decreases with increase in metal ion concentration. This increase (5.19 to 23.49 mg/g) is a result of increase in the driving forces i.e. concentration gradient. However, the percentage adsorption of zinc ions on egg shell powder was decreased from 86.50 to 78.29%. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of zinc displays an opposite trend. At lower concentrations, all zinc ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher zinc ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

3.4. Effect of adsorbent size

The effect of different adsorbent particle sizes on percentage removal of zinc is investigated and showed in Figure-4. It reveals that the adsorption of zinc on *egg* *shell* powder decrease from 86.50 to 76.85 % with the increased particle size from 75 to 212 µm at an initial concentration of 20 mg/l. The smallest size obtained was 75 µm due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity.

3.5. Effect of adsorbent concentration

Figure-5 shows the effect of adsorbent concentration on the % removal at equilibrium conditions. It was observed that the amount of zinc adsorbed varied with varying adsorbent concentration. The amount of zinc adsorbed increases with an increase in adsorbent concentration from 0.1 to 0.5 g. The percentage zinc removal was increased from 86.50 to 94.85% for an increase in biomass concentration from 0.1 to 0.5 g at initial concentration of 20 mg/l. The increase in the adsorption of the amount of solute is obvious due to increasing biomass surface area. Similar trend was also observed for zinc removal using pyrolusite as adsorbent [48].

4. BIOSORPTION EQUILIBRIUM

The equilibrium biosorption of zinc on the egg shell powder as a function of the initial concentration of zinc is shown in Figures 6 to 10. There was a gradual increase of adsorption for zinc ions until equilibrium was attained. The Langmuir, Freundlich models are often used to describe equilibrium sorption isotherms and Redlich-Peterson and Temkin models are also applied to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm constants are given in Table-1.

It was found that the adsorption of zinc on the egg shell powder was correlated well with the Freundlich equation and Langmuir equation as compared to Redlich-Peterson and Temkin equations under the concentration range studied. Examination of the Redlich-Peterson and Temkin data shows that these two isotherms are not modeled as well across the concentration range studied.

5. KINETICS OF ADSORPTION

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig.11 shows the plot between amount adsorbed, q_e (mg/g) versus time, t (min) for different initial solute concentrations. From the figure it was observed that q_e value increased with increase in initial zinc concentration. The adsorption rate within the first 15 minutes was observed to be very high and thereafter the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after equilibrium. The saturation time was found to be 60 min based on the initial metal concentration. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first order and pseudo-second order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows:

The Pseudo-first order equation

The pseudo-first order equation of Lagergren [40] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{9}$$

Where

q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo-first order sorption, (1/min). After integration and applying boundary conditions, $q_t = o$ to $q_t = q_t$ at $t = 0$ to $t = t$; the integrated form of equation (9) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \tag{10}$$

The equation applicable to experimental results generally differs from a true first order equation in two ways [41]:

- the parameter $k_1(q_e - q_t)$ does not represent the number of available sites; and
- the parameter $\log(q_e)$ is an adjustable parameter which is often not found equal to the intercept of a plot of $\log(q_e - q_t)$ against t, whereas in a true first order sorption reaction $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t.

In order to fit equation (10) to experimental data, the equilibrium sorption capacity, (q_e), must be known. In many cases (q_e) is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount [42]. In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, on treat (q_e) as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, (q_e), in order to analyse the pseudo-first order model kinetics. In over 50% of literature references, based on analyzing sorption kinetics, the authors did not measure an equilibrium isotherm.

The pseudo first order rate constant k_1 can be obtained from the slope of plot between $\log(q_e - q)$ versus time, t. Figure-12 shows the Lagergren pseudo-first order kinetic plot for the adsorption of zinc onto egg shell powder. The pseudo first order rate constant k_1 values were calculated from the slope of Figure-12. The calculated k_1 values and their corresponding linear regression correlation coefficient values are shown in Table-2. The linear regression correlation coefficient value R_1^2 found 0.9680, which shows that this model can not be applied to predict the adsorption kinetic model.

The Pseudo second order equation

If the rate of sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{11}$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g) and k is the rate constant of pseudo-second order sorption, (g/mg min). For the boundary conditions $q_t = o$ to $q_t = q_t$ at $t = 0$ to $t = t$; the integrated form of equation (11) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{12}$$

This is the integrated rate law for a pseudo-second order reaction. Equation (12) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}} \tag{13}$$

This has linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{14}$$

Where t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t. Equation (14) does not have the problem of assigning as effective q_e. If pseudo-second order kinetics is applicable, the plot of t/q_t against t of equation (14) should give a linear relationship, from which q_e and k can be determined from the slope and intercept of the plot (Figure-13) and there is no need to know any parameter beforehand.

The pseudo-second order rate constant k_2, the calculated q_e value and the corresponding linear regression correlation coefficient value R_2^2 are given in Table.2. At all initial zinc concentrations, the linear regression correlation coefficient R_2^2 values were higher. The higher R_2^2 values confirm that the adsorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the adsorption is due to chemisorptions.

A comparison of the maximum capacity $Q_{\max}$ of egg shell powder with those of some other adsorbents reported in literature is given in Table-3. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

6. CONCLUSIONS

The present study shows that the egg shell powder was an effective biosorbent for the adsorption of zinc ions from aqueous solution. The biosorption capacity of egg shell powder was superior due to the higher content of carbonate groups. The effects of process parameters like pH, metal ion concentration, adsorbent concentration and adsorbent size on process equilibrium were studied. The uptake of zinc ions by egg shell powder was increased by increasing the metal ion concentration and the adsorbent concentration and decreased by increasing the adsorbent size. The uptake was also increased by increasing pH up to 6. The adsorption isotherms could be well fitted by the Freundlich equation followed by Langmuir equation. The biosorption process could be best described by the second-order equation.

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Table-1. Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm constants and correlation coefficients.

Langmuir	$Q(mg/g)$	46.05
	$b(L/mg)$	0.0446
	R^2	0.9676
Freundlich	$K_f(mg/g)$	2.61
	n	0.7136
	R^2	0.9981
Redlich-Peterson	$A\ (L/g)$	1.2391
	$B\ (L/mg)$	41.85
	g	-1.5846
	R^2	0.3123
Temkin	$A_T\ (L/mg)$	0.5960
	b_T	297.1100
	R^2	0.9613

Table-2. Kinetic constants for zinc onto *Gallus Domesticus* shell powder

Initial concentration mg/L	**Pseudo-first order**			**Pseudo-second order**		
	Rate constant k_1	Amount of zinc adsorbed on adsorbent q_e, (mg/g)	Correlation coefficient R_1^2	Rate constant k_2	Amount of zinc adsorbed on adsorbent q_e, (mg/g)	Correlation coefficient R_2^2
20	0.0865	2.5901	0.9048	0.0840	5.2918	0.9997

Table-3. Maximum adsorption capacities for zinc adsorption to different adsorbents.

Adsorbent material	**Adsorption capacity** (mg/g)	**pH**	**Reference**
Volcanic ash soil(VAS)	5.5	3	1
Biosolids(dry & unground)	36.66	4	4
Activated carbon	31.11	4.5	6
Pseudomonas putida CZ1(living) (non-living)	27.4 17.7	5	11
Carrot residue(CR)	29.61	4.5	12
Sheep manure waste(SMW)	32	4	14
Cassava(Manihot esculenta cranz) (untreated) (treated with acid)	43.4 58.1	7.1	15
Aerobic granules	164.5	4	16
Aspergillus niger 405	4.70	4-6	17
Myriophyllum spicatum	15.59	5-6	18
Mucor rouxii	4.89	4.5	19
Fly ash	7.87	6	20
Crushed concrete fines	33	5.5	26
Marine green macroalga Caulerpa lentillifera	1.17×10^{-5}	5-6	27
Coir	8.6	5.5	28
Papaya wood	0.64	5	33
Fontinalis antipyretica	14.7	5.0	30
Streptoverticillium cinnamoneum	21.3	5.5	32
Penicillium digitatum	9.7	5.5	33
Citrobacter strain MCMB-181	23.62	6.5	36
Sargassum sp.	24.35	4.5	37
Animal bones	11.55	5.0	38
Botrytis Cinerea biomass	12.98	5-6	39
Egg shell powder	46.05	6	(present study)

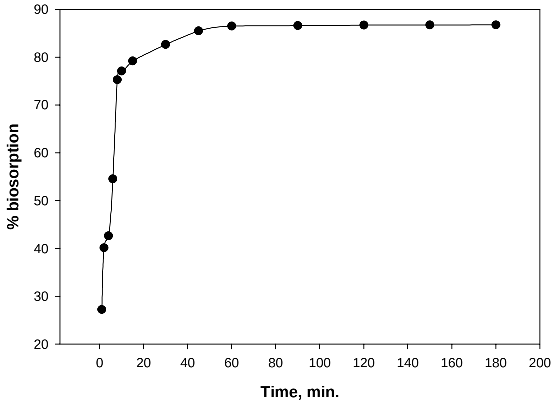

Fig.1. Effect of cotact time on biosorption of zinc by *eggshell* powder for 20 mg/L metal and 0.1 g/30 mL of biosorbent concentration.

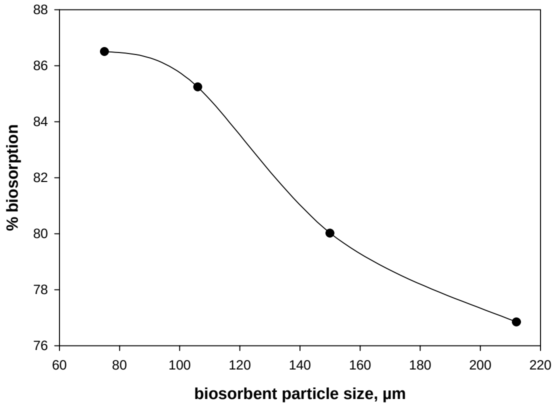

Fig.4. Effect of *eggshell* particle size on biosorption of Zinc fo 20 mg/L of metal and 0.1 g/30 mL of biosorbent concent

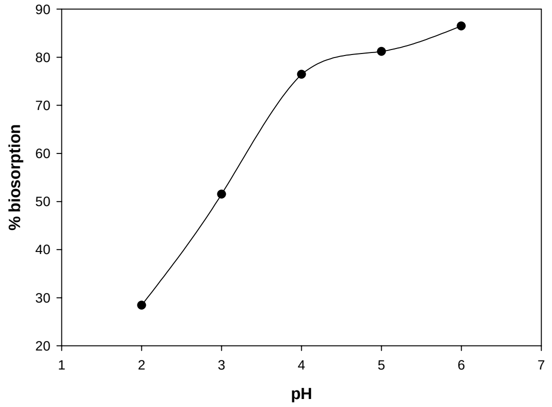

Fig.2. Effect of pH on zinc biosorption by *eggshell* powder for 20 mg/L metal and 0.1 g/30 mL biosorbent concen

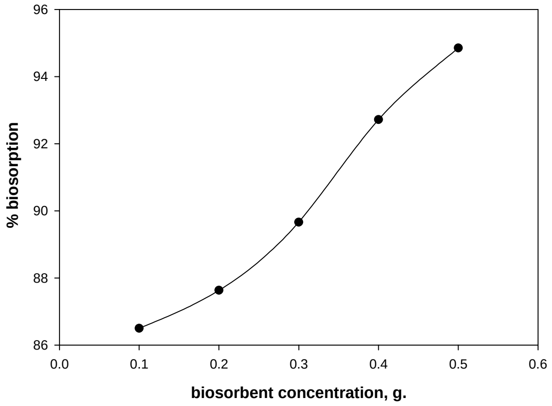

Fig.5. Effect of eggshell powder dosage on biosorption of Zinc for 20 mg/L of metal concentration.

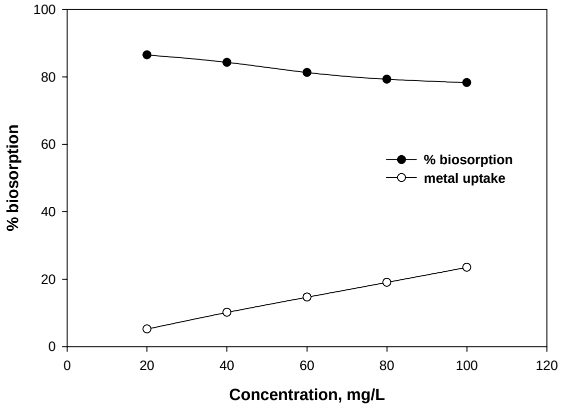

Fig.3. Effect of metal concentration on the biosorption of zinc by *eggshell* powder at 0.1 g/ 30 mL of biosorbent concentratio

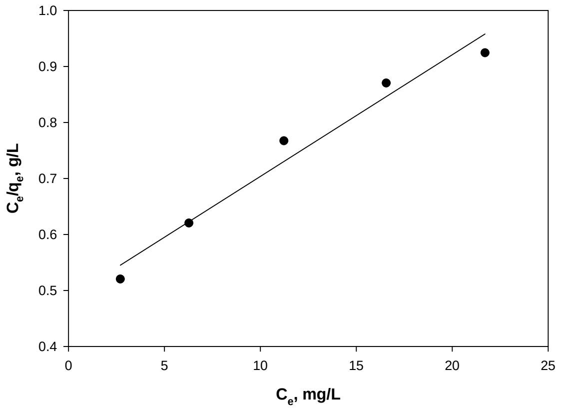

Fig.6. Langmuir adsorption isotherm for zinc at 0.1 g/ 30 L of biosorbent concentration.

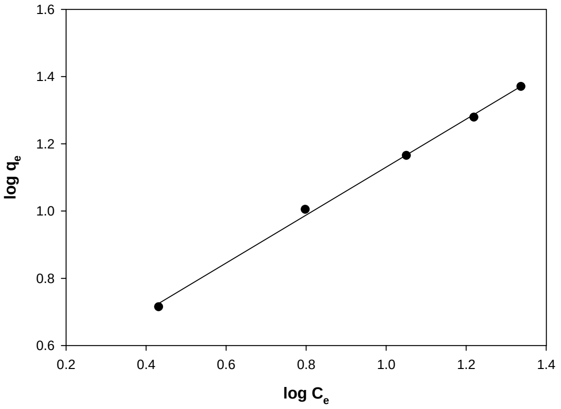

Fig.7. Freundlich adsorption isotherm for zinc at 0.1 g/ 30 mL of biosorbent concentration.

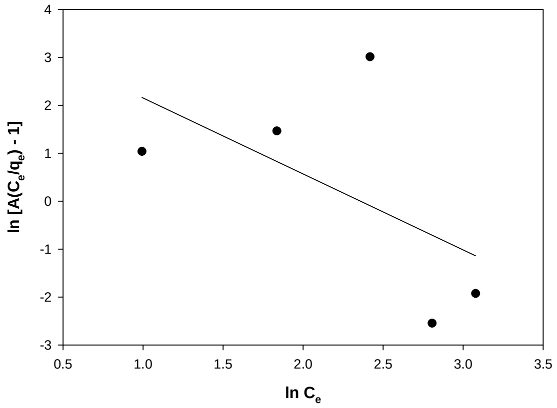

Fig.8. Redlich-Peterson adsorption isotherm for zinc at 0.1 g/ 30 mL biosorbent concentration.

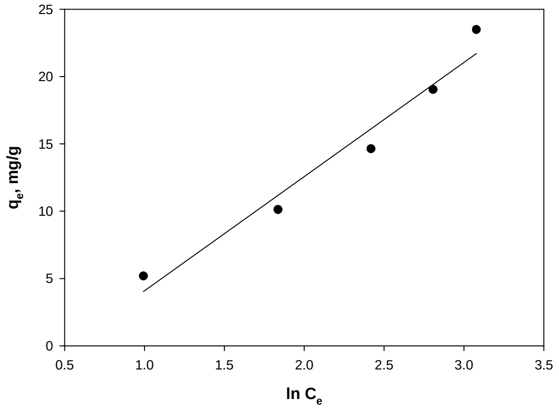

Fig.9. Temkin adsorption isotherm for zinc at 0.1 g/ 30 mL biosorbent concentration.

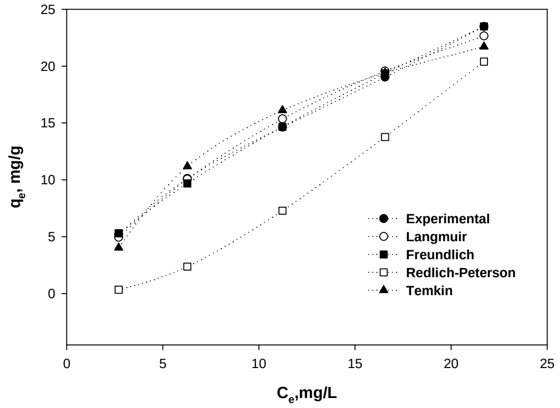

Fig.10. Equilibrium curves for zinc on to *eggshell* powder.

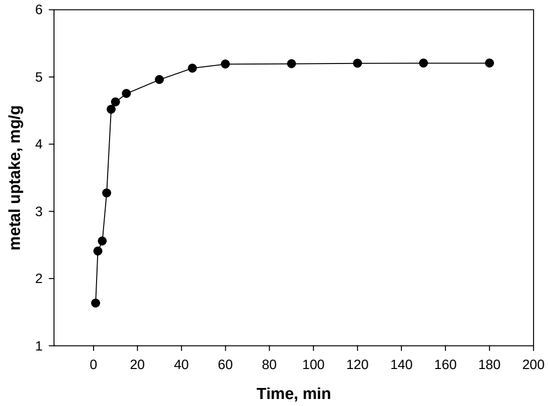

Fig.11. Effect of contact time on zinc uptake by *eggshell* powder.

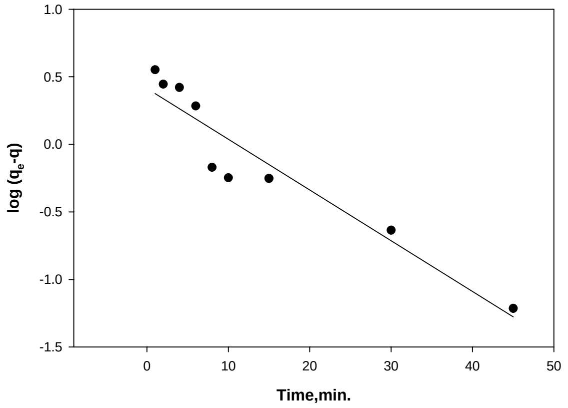

Fig.12. Pseudo first order adsorption of zinc by *eggshell* powder for 20 of metal and 0.1 g/ 30 mL of biomsorbent concentration.

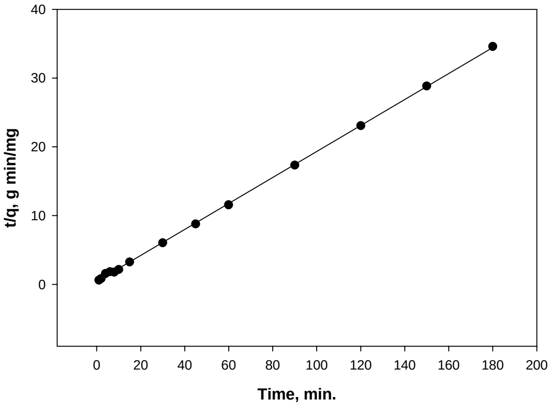

Fig.13. Pseudo-second-order adsorption of zinc by *eggshell* powder for 20 mg/L of metal and 0.1 g/ 30 mL of biosorbent concentration.