MODELING EQUILIBRIUM AND KINETICS OF ZINC UPTAKE FROM AQUEOUS SOLUTION USING COCONUT SHELL

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ABSTRACT

In the current work coconut shell is used as an alternate cost effective adsorbent to determine its application for the removal of Zn(II) ions from aqueous solutions. The adsorbent was analysed for moisture content, volatile content and pore volume to get an idea of physical properties associated with coconut shell. Batch studies were conducted to determine the optimum pH & adsorbent dose, and to study the effect of metal ion concentration, contact time and temperature so as to design an efficient and optimum condition for maximum removal of Zn(II) ions. The equilibrium data obtained was fitted to various equilibrium models like Langmuir, Freundlich, Temkin & D-R isotherm to find out the nature and the behaviour of adsorption process. Kinetic models like Pseudo first order, Pseudo second order and Intra-particle diffusion were also employed so as to relate the adsorbate uptake rate with bulk concentration. It was found that adsorption of Zn(II) ions on coconut shell was pH-dependent with maximum adsorption (81.6 %) occurring at pH 6. It was found that 0.3 g of dose of coconut shell was found to be optimum for the removal of Zn(II) ions from wastewater with an adsorption capacity (q_e) of 4.78 mg/g. For equilibrium studies it was observed that equilibrium data was best fitted to the Langmuir model with correlation coefficient (R^2) value 0.9936 and monolayer adsorption capacity (q_m) was found to be 7.9554 mg/g indicating the surface of adsorbent to be homogeneous. For kinetic models, it was observed that pseudo first order model best depicted the adsorption process. The above obtained results clearly indicated that the coconut shell has high potential for removing Zn(II) from metal loaded wastewater.

Keywords: Adsorption, Batch Studies, Coconut Shell (CS), Kinetics, Isotherms etc.

I. INTRODUCTION

Water pollution raises a great concern now-a-days since water constitutes a basic necessity in life and thus, is essential to all living things. Among other issues, water contaminations by heavy metals are more pronounced than other pollutants especially when heavy metals are exposed to the natural ecosystem. ‘Heavy metals’ refers to any elements with the atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 [1]. Pollution through heavy metals from the effluents is one of the most serious environmental problems [2]. These metals cannot be degraded or destroyed [3]. The risks of exposure, for instance, may contribute to adverse effects on central nervous system, pulmonary kidney functions and chromosomes [4]. Zinc is widely used metal and there are many sources of zinc pollutions. Generally, any process or container using zinc may contaminate the products such as food, water, drink etc. although zinc is essential to human life is potentially toxic like other heavy metals [5]. Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes. Removal of heavy metals from industrial wastewaters can be accomplished through various treatment including chemical precipitation, coagulation, ion exchange, solvent extraction, foam flotation, membrane operationsand conventional adsorption [6-7]. Adsorption on low cost absorbent for removal of toxic metals from waste water has been investigated extensively [8]. The use of coconut shell as an absorbent material showed strong potential due to its high content of lignin and cellulose [9]. In the same contest this study was conducted to utilize coconut shell for the removal of Zn(II) ions from aqueous solution.

II. METHODOLOGY

2.1 Collection and Preparation of adsorbent

Coconuts were purchased from the fruit seller and brought to laboratory. First coconuts have been washed thoroughly with tape water to remove dirt and other adhering impurities and kept in sunlight for drying. The coconut shell was then removed, crushed and grinded into fine particles. These particles were sieved through 300µ size ASTM sieve to get particles of uniform diameter. The obtained particles were again dried in oven at about 50 °C and stored in an air tight container to be utilized as adsorbent in the removal of Zn(II) ions from aqueous solutions.

2.2 Adsorbate solution

Stock solution of 1000 mg/L for Zn(II) ions was prepared by dissolving required amount of zinc sulphate salt in double distilled water in a 1000 ml standard flask. This stock solution was used to prepare the working solutions of desired concentrations for different experiments. The pH value of the solutions was adjusted by adding 0.1 mol/L NaOHor 0.1 mol/L HCl.

2.3 Determination of point of zero charge

The point of zero surface charge of the coconut shell was determined by the solid addition method [10]. A series of five 100 ml conical flasks was taken of containing 40 ml of 0.1N KNO_3 each. The initial pH (pH_i) of the solutions in each flask was roughly adjusted to 2, 4, 6, 8 and 10, respectively, by adding either 0.1N HCl or 0.1N NaOH. The total volume of the solution in each flask was adjusted exactly to 50 ml by adding KNO_3 of the same strength. Initial pH (pH_i) of the solution was then accurately noted with the help of pH meter. 0.5 g sorbent was then added to each flask and then allowed to equilibrate for 24 hours with intermittent manual shaking. The final pH (pH_f) of the supernatant liquid was noted. A graph of the difference between initial pH (pH_i) and final pH (pH_f) values ($\Delta pH = pH_i - pH_f$) was plotted against pH_i. The point of intersection of the resulting curve with abscissa at which $\Delta pH = 0$, gave Zero point charge (pH_{zpc}) Fig. 5.

2.4 Batch adsorption studies

Batch studies have been conducted at room temperature in which an accurately weighed (0.5 gm) of adsorbent, coconut shell was placed in 100 ml stoppered conical flask containing known volume (50 ml) of metal ions solution of known concentration (50 mg/L). This solution was shaken in a rotary shaker for about 30 min and kept for 2 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.

III. RESULTS AND DISCUSSION

3.1 Adsorption studies

3.1.1 Effect of pH

Effect of pH solution containing Zn(II) ions on adsorption of zinc by coconut shell is shown in Fig. 1. It has been observed that Zn(II) uptake by coconut shell is strongly affected by pH of the solution. The amount of Zn(II) adsorbed was found to increases from 14.2 % to 81.6 % on increasing pH from 1 to 6 and then decrease slowly up to 76.2 % at pH 10. The variation in the adsorption of Zn (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, Zn^{2+} ions compete with H^+ ions for binding sites of adsorbent, therefore the adsorption of Zn(II)ions was less (14.2%) at low pH. When the initial pH of the solution raises up to 6 the adsorption percentage increases quickly up to maximum of 81.6 %, possibly due to little less competition of Zn^{2+} ions and H^+ ions. Further increase in pH of the solution up to pH 8 results slightly decreases in the adsorption of Zn (II) ions (80.5%).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}. The data plotted in fig.5 indicated that the P_{ZC} value of coconut shell was 5.3, showing that the surface was negatively charged above this pH and hence fairly large amount of Zn (II) ions (81.6 % at pH 6) were adsorbed.

3.1.2 Effect of contact time

The effect of interaction time of Zn(II) ions with the surface of coconut shell on adsorption of Zn(II) ions is shown in Fig 2.The contact time reached to equilibrium was found to be dependent on initial concentration of Zn (II) up to 50 mg/L and then became independent at higher concentration. This may be due to the fact that vacant sites of adsorbent adsorbed Zn(II) ions rapidly at lower concentration but at higher concentration adsorption of copper occurred by slower process (diffusion) into the inner sites of adsorbent. The equilibrium time for the maximum removal of Zn (II) ions from aqueous solution was found to be 90 minutes at concentration 50 mg/L. But at higher concentration it will require more contact time for the maximum removal of Zn (II) ions.

3.1.3 Effect of concentration

The influence of initial Zn(II) concentration on adsorption of Zn(II) on coconut shell is shown in fig. 3. It was found that adsorption capacity of coconut shell as usual increases with an increase in initial Zn (II) ions concentration. It may be due to the fact that increase in concentration gradient between the bulk solution and adsorbent surface lower the resistance to mass transfer of Zn(II) ions from liquid to solid phase. The maximum adsorption capacity of coconut shell at equilibrium was found to be 0.5, 1, 2, 4.08, 4.73, 5.48, 7.05, and 8.34 mg/g at initial Zn(II) ions concentration of 5, 10, 20, 50, 75, 100, 150 and 200 mg/L, respectively. It is also evident from the fig 4 that adsorption percentage of Zn(II) ions decreases from 100 to 41.7% with the increase of initial concentration of copper from 5 mg/L to 200 mg/L. It may be due to the saturation of active sites of adsorbent at certain metal ions concentration.

3.1.4 Effect of adsorbent dose

The effect of dose of coconut shell on adsorption capacity and percentage adsorption of Zu(II) is shown in Fig. 4. The adsorption percent increased while adsorption capacity, q_e (mg/g) decreased when adsorbent dose increased from 0.1 to 1.5 g. The adsorption percentage increases up to 95% at 1.5 g of adsorbent dose. This might be due to the increase in the number of sites available for adsorption [16]. The adsorption capacity decreases from 4.7 mg/g to 1.59 mg/g on increasing adsorbent dose from 0.1 g to 1.5 g. The decrease in adsorption capacity with increasing adsorbent dose might be due to the fact that at lower adsorbent dose almost all the adsorption sites are saturated by the Zn(II) ions but at higher adsorbent dose, the adsorption sites would be excessive for the adsorption reaction since the concentration Zn(II) ions as well as the volume of the solution are constant. Thus, amount of Zn(II) adsorbed per unit mass of adsorbent was decreased [17].

3.2 Adsorption isotherms studies

Adsorption of Zn(II) ions on coconut shell was carried out at concentration ranging from 5 to 200 mg/L at pH 6 for 90 minutes of equilibrium time and obtained data was anaylsed with Langmuir, Freundlich, Temkin and Dubinin-Redushkeuich adsorption isotherms. The graphs plotted for these isotherms are shown in Fig. 6, 7, 8 and 9. The value of R^2 and other parameters of adsorption isotherms indicated that adsorption of Zn(II) onto coconut shell was best fitted to Langmuir isotherm model (R^2 = 0.9936) and the obtained value of monolayer adsorption capacity q_m was 7.955 mg/g. Moreover the higher value of correlation coefficient for Freundlich (R^2=0.925), and Temkin (R^2=0.9445) listed in table 1, indicated that adsorption of Zn(II) ions on coconut shell occurs on heterogeneous surface of coconut shell by formation of monolayer followed by multilayer of Zn(II) ions with uniform heat of adsorption [20], [21].

The essential characteristic of the Langmuir isotherm is expressed in terms of a dimensionless constant separation factors or equilibrium parameter, R_L.

$$R_L = 1/(1 + b\,C_o)$$

Where, b is the Langmuir constant, C_o is the initial concentration.

The value of R_L between 0 and 1 indicates favourable adsorption of adsorbate on adsorbent. R_L for Zn(II) ions adsorption on coconut shell is 0.15 which concluded that adsorption process is favourable.

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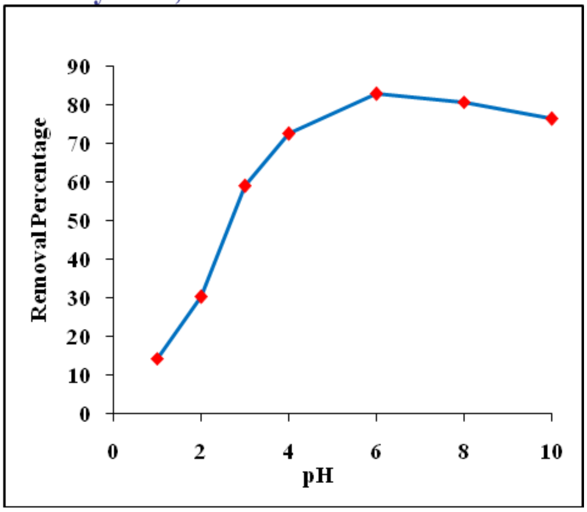


Fig. 1 Effect of pH

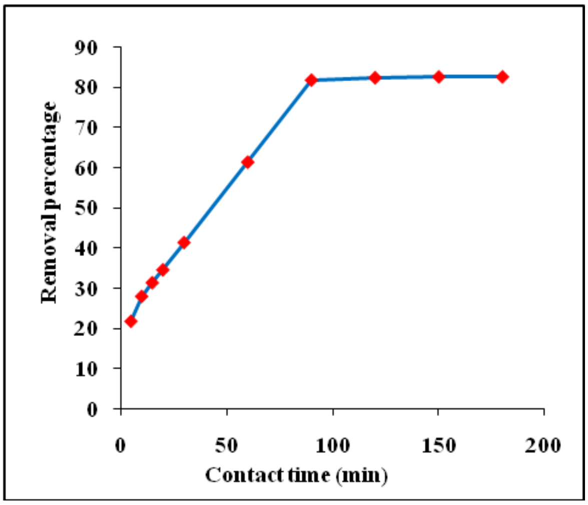


Fig. 2 Effect of contact time

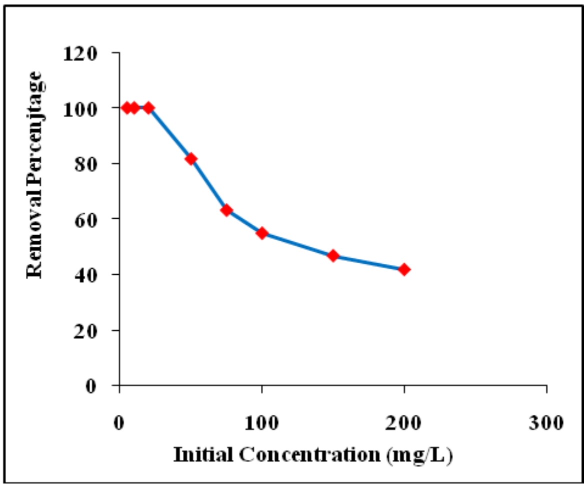


Fig. 3 Effect of concentration

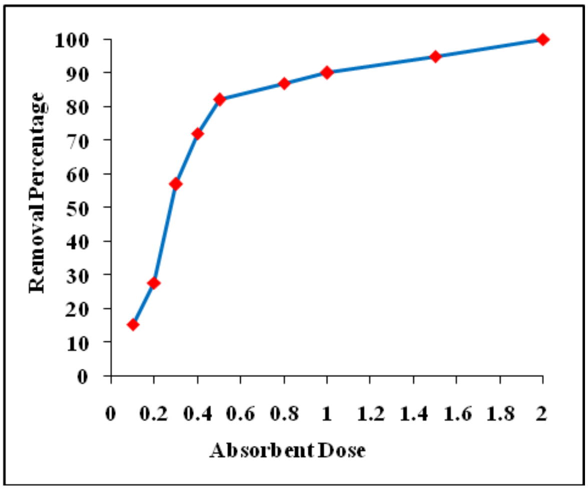


Fig. 4 Effect of absorbent dose

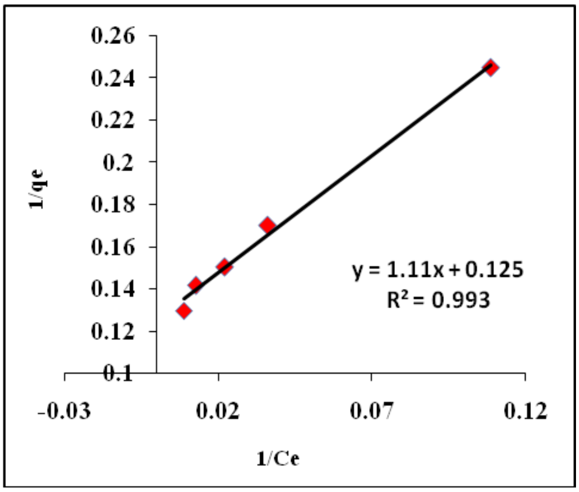


Fig. 6 Langmuir isotherm plot

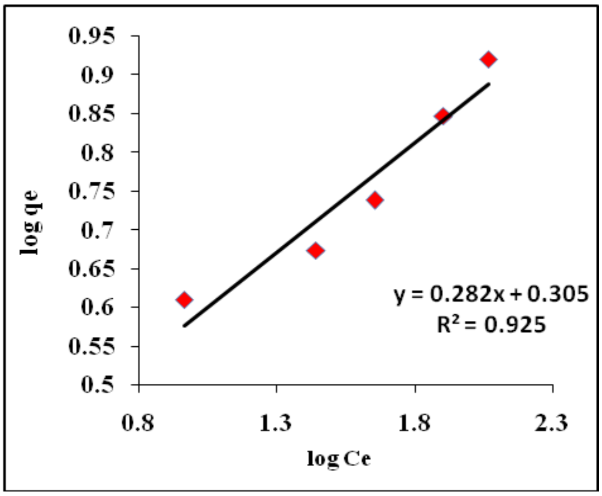
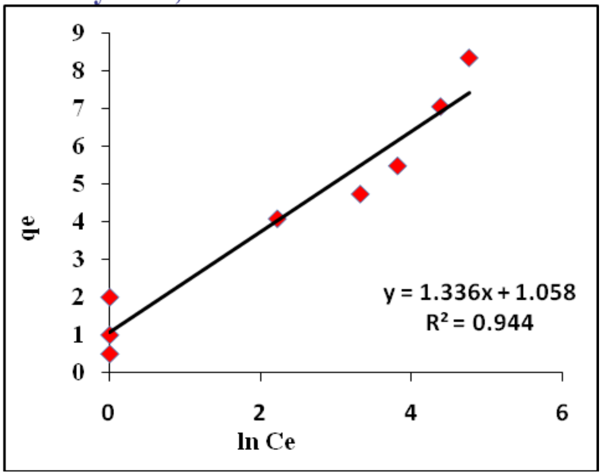


Fig. 7Fruendlich isotherm plot



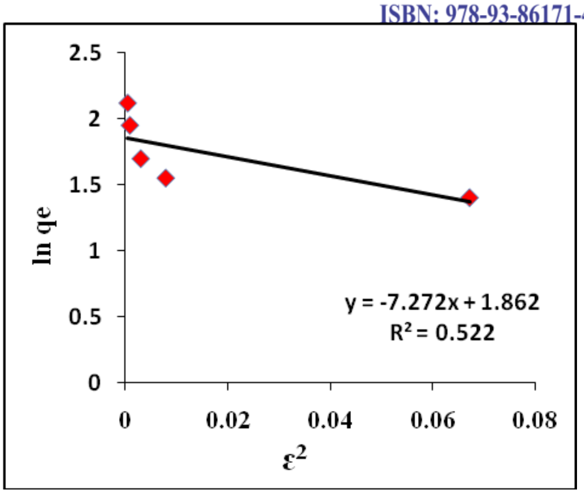


Fig. 8Temkin isotherm plot **Fig. 9Dubinin-Radushkevich isotherm plot**

Table: 1 Langmuir, Freundlich, Temkin& D-R isotherm constants

Metal	Langmuir isotherm				Freundlich isotherm			
Zn^{+2}	q_m	b	R^2	R_L	1/n	n	K_F	R^2
	7.9554	0.113	0.993	0.15	0.2821	3.5448	2.02	0.925
	Temkin isotherm				D-R isotherm			
	A	B		R^2	q_m	β	R^2	
	3.535	1.0585		0.9445	6.441	7.2724	0.5223	

3.3 Kinetic Studies

The values of correlation coefficient, R^2 and other kinetic parameters are mentioned in table 2. It had been observed from plots shown in fig. 10, 11 and 12that values of R^2 for pseudo first order ($R^2 \approx 0.9863$), pseudo second order ($R^2 \approx 0.9827$) and intra particle diffusion ($R^2 \approx 0.9374$) that adsorption of Zn(II) ions by coconut shell was best described by pseudo first order kinetic model which showed that adsorption occurs chemically having correlation coefficient value ($R^2 \approx 0.9863$) and involves valency forces through ion sharing or exchange of electron between the adsorbent and ion adsorbed on it. Also the Pseudo-second order model showed very close correlation coefficient value ($R^2 \approx 0.9827$) to pseudo-first order model which suggests that Zn(II) ions adsorption occurs in a monolayer fashion and which relies on the assumption that chemisorptions or chemical adsorption is rate limiting step. Zn(II) ions react chemically with the specific binding sites on the surface of adsorbent.

Table: 2 Pseudo first, Pseudo second order & Intra-particle Diffusion constants

Metal	Pseudo- First Order Model			Pseudo- Second Order Model		
Zn^{+2}	q_e	k_1	R^2	q_e	k_2	R^2
	5.667	0.0193	0.9863	8.130	0.00421	0.9827
	Intra-Particle Diffusion					
	K_d	I			R^2	

	0.5169	0.7508	0.9374

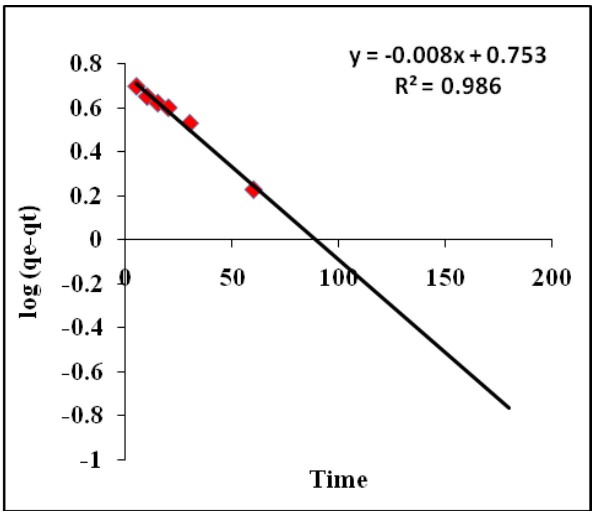


Fig. 10 Pseudo First Order

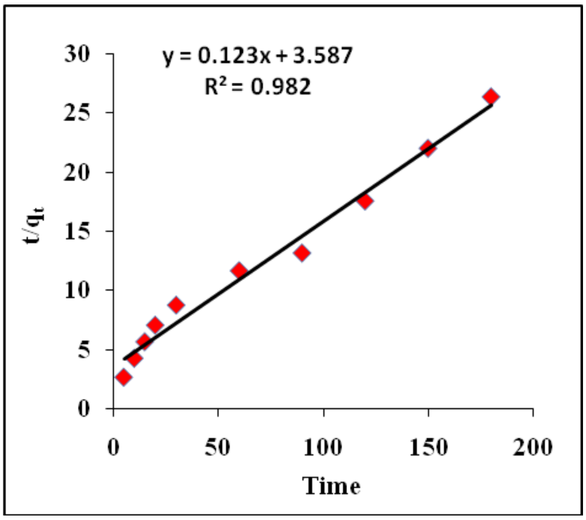


Fig. 11 Pseudo Second Order

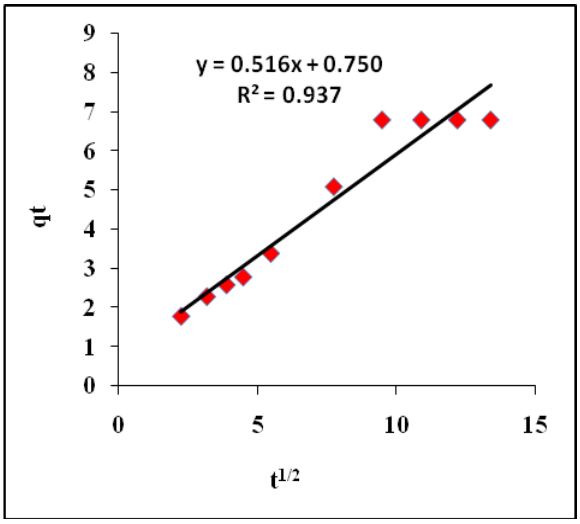


Fig. 12 Intra Particle Diffusion

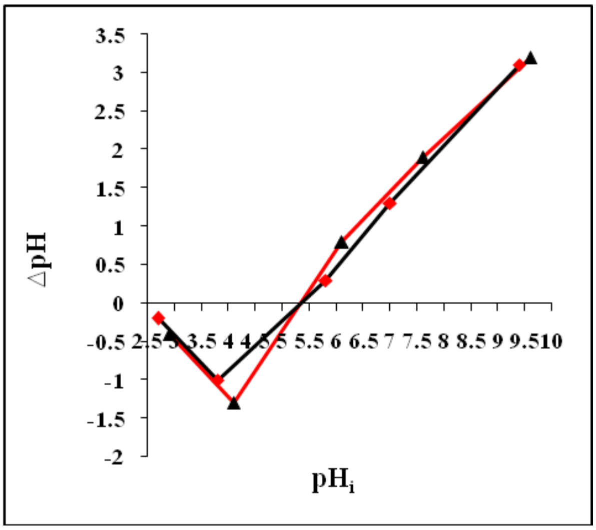


Fig. 5 Point of zero charge (pHzpc)

IV. CONCLUSION

In this study a simple and cost effective treatment procedure was adopted for the removal of heavy metals through adsorption on coconut shell. Adsorption is a strong choice for removal of heavy metals from wastewater. From batch adsorption studies it was found that maximum removal of zinc takes place at pH 6 with removal efficiency of 81.6%. Also the 0.3 g of coconut shell was found to be optimum dose for Zn(II) ions having maximum adsorption capacity of 4.78 mg/g. The effect of contact time showed that the adsorption process increases steadily for 20 minutes and then it reaches for saturation limit at 90 minutes. The equilibrium sorption data fitted best into the Langmuir isotherm model. The correlation coefficient for Langmuir isotherm was found to be 0.9936 showing monolayer adsorption capacity, q_m was 7.955 mg/g and the value of b and R_L was found to be 0.1132 and 0.15 respectively. Kinetic studies showed that the experimental data obeyed better by Pseudo first order model as compared to Pseudo second order model and Intra-particle diffusion. The R^2 value obtained from pseudo first order model was found to be 0.9863 and obtained adsorption capacity value

(q_e) to be 5.667 mg/g and K_1 value to be 0.0193. The Pseudo Second Order showed the correlation coefficient to be 0.9827 and the value of q_e and K_2 was 8.13 mg/g and 0.00421. The above results clearly indicated that the coconut shell has high potential for removal of Zn(II) ions from Zn(II) loaded wastewater.

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