



REMOVAL OF ZINC (II) IONS FROM AQUEOUS SOLUTION USING MSASA TREE (*BRACHYSTEGLIA SPICIFORMIS*) LEAF POWDER: EQUILIBRIUM STUDIES

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ABSTRACT

*The efficiency of using *Brachystegia spiciformis* leaf powder to remove zinc (II) ions from aqueous solution was studied. The influence of various process parameters like pH, contact time, biomass dose and initial metal ion concentration was investigated using batch experiments. The biosorbent was characterized by infrared spectroscopy and surface area analyzer. The obtained optimum conditions for highest metal uptake was at solution pH 6, contact time of 120 mins and biomass dosage of 2.0 g. The increase in initial zinc ions concentration led to an increase in uptake by the biomass. The equilibrium sorption data for the metal system was modelled and found to fit better to the Langmuir than to the Freundlich isotherm. The Freundlich constant K_f , n value and the correlation coefficient were 0.041 [$\text{mg/g}(\text{L/mg})^n$], 1.235 (g/L) and 0.9569 respectively. The Langmuir maximum adsorption capacity Q_{max} , b and R^2 values were found to be 1.85 mg/g, 0.0152 L/g and 0.9902 respectively.*

Keywords: *Brachystegia spiciformis*, Biosorption, Zn (II) ions, Adsorption equilibrium isotherms.

INTRODUCTION

The last century witnessed accelerated and intensified industrialization and urbanization activities which led to degradation and contamination of our aquatic environment with different serious pollutants (Bradl, 2005). Waste water contaminated with heavy metals is one of the most common environmental problem due to their toxicity since they are non-biodegradable. Heavy metals have a tendency of accumulating inside the human body when they are incorporated through the food chain (Wang and Chen, 2009). Industrial operations units like metallurgy, steel production, paint

and pigment industry, copper smelting, mining, electroplating and galvanizing units significantly contribute to heavy metal pollution including zinc in natural water streams (Hasan *et al.*, 2008). Soluble zinc acid salts in large doses (about 10 g), have caused internal organ damage and death (Gupta and Sharma, 2003).

Various conventional remedial technologies like reverse osmosis, electro-coagulation and flocculation, solvent extraction, hydroxide precipitation and membrane separation have been adopted to remove heavy metals across liquid phases (Petrik, 2004; Abu Al-Rub *et al.*, 2006b). These afore-mentioned techniques are all generally expensive and might possibly generate by-products dangerous to human health (Sabriye *et al.*, 2005). For these reasons, alternative technologies that are cheap, efficient and practical at low metal concentrations are being explored. Biosorption has been emerging as the most prominent alternative technology for this purpose (Matheickal and Yu, 1999). Recent studies have shown that heavy metals can be removed using plant materials such as palm pressed fibers, coconut husk, water fern, peat moss, duck weed, lignocellulosic substrate extracted from wheat bran and fungi (Fagundes-Klen *et al.*, 2007). In particular, recent studies have also revealed the removal of zinc (II) ions from aqueous solution using *Reynoutria japonica* leaves (Melcakova and Ruzovic, 2010), palm tree leaves (Abu Al-Rub, 2006a) and *erythrina variegata* leaves (Venkateswarlu *et al.*, 2008). *Brachystegia spiciformis* remain in abundance as an indigenous plant in Southern Africa. This study was aimed at utilizing *Brachystegia spiciformis* leaves as a cheap method for Zn (II) ions removal from aqueous solution. The effect of process parameters and the application of adsorption isotherms were also demonstrated.

MATERIALS AND METHODS

Biosorbent Sampling and Preparation

Mature *Brachystegia spiciformis* leaves were collected from Midlands State University grounds, Gweru, Zimbabwe. The sample was collected in clean polythene bags, washed with distilled water repeatedly to remove dust and soluble impurities, stored in a shade at room temperature and then sun dried until crisp. It was then ground and passed through a 300 μm particle size sieve. The resulting powder was washed with distilled water several times to remove colour and turbidity, oven dried (Cycilo DHG-9070A) at 70°C to constant mass, then put in air tight bottles and stored in a desiccator for further use.

Characterization of Biosorbent

FT-IR spectroscopy was used to identify the functional groups in the *Brachystegia spiciformis* biosorbent. FT-IR spectra of the biosorbent before and after biosorption of Zn (II) were recorded in the range 4000-400 cm^{-1} using a Digilab Merlin 2000 model FT-IR spectrometer with KBr discs (Sigma). Surface area analysis was done using (Brunauer Emmett Teller (BET) (Micromeritics ASAP 2020).

Sorption Equilibrium Experiments

Stock solution (1000 mg/L) of Zn (II) was prepared by dissolving 4.439 g of $ZnSO_4 \cdot 7H_2O$ in deionized water. Synthetic solutions of different Zn (II) concentrations for batch experiments and calibration curve were prepared by appropriate dilutions of this stock solution. Batch experiments were carried out using 100 mL of Zn (II) solution of known concentrations in 250 mL conical flasks at a specified pH, contact time and adsorbent dosage. In each case the mixture was agitated on a shaker (Vasal-401 208 Rajendra Electrical) at a speed of 120 rpm at room temperature for a specified amount of time which was sufficient for the zinc uptake process to reach equilibrium. The pH of the solution was adjusted using either 0.1 M HNO_3 or 0.1 M NaOH solutions. A pH meter (Az-8601) was used to measure the pH of the biosorbent and that of various solutions. Optimization studies were performed at room temperature at different pH (2, 4, 6, 8, 10 and 12), sorbent amount (0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g and 3.0 g) initial Zn (II) concentration (20, 40, 60, 80, 100, 120 and 140 mg/L) and contact time (30, 60, 90, 120, 150 and 180 mins) to obtain the equilibrium data. All experiments were performed in replicates and the results mean was reported with reproducibility within at most 5%. After attainment of equilibrium, the samples were filtered through Whatman No. 1 filter paper and the residual Zn (II) concentration in the filtrate was estimated using the Flame Atomic Absorption Spectrometer (FAAS) (Shimadzu, 50B, Japan) at wave length of 213.9 nm. The amount of zinc removed per unit mass of *Brachystegia spiciformis* leaves was calculated as follows;

$$Q_e = \frac{(C_o - C_e) V}{M} \dots\dots\dots (1)$$

Where, Q_e is the amount of Zn (II) adsorbed by biomass (mg/g), C_o and C_e are the initial and equilibrium concentrations of Zn (II) (mg/L), V the volume of solution (L), and M is the mass of *Brachystegia spiciformis* leaves (g).

The equilibrium data obtained from the effect of initial zinc metal ion concentration on biosorption was used to test the applicability of Langmuir and Freundlich isotherm models.

RESULTS AND DISCUSSION

Characterization of *Brachystegia Spiciformis* Leaf Powder

FT-IR analysis of *Brachystegia spiciformis* leaf powder

The FT-IR spectra of *Brachystegia spiciformis* indicated the presence of hydroxyl, amine carboxyl and carbonyl groups which are important adsorption sites (Figure. 1). A peak at 3400 cm^{-1} indicated the presence of OH and NH groups. The band at 2920 cm^{-1} indicates C-H stretching vibration of methyl, methylene and methoxy groups. Peaks at 1640 cm^{-1} , 1400 cm^{-1} and 1040 cm^{-1} indicate the presence of carbonyl, ionic carboxylic groups and stretching vibrations of C-OH alcohols respectively. After biosorption the peak at 3400 cm^{-1} lost intensity due to the participation of OH and NH groups in sorption. The shift of the carbonyl group from 1640 cm^{-1} to about 1600 cm^{-1} indicated its involvement in sorption (Gnanasambandam and Protor, 2008). The change in

intensity of the peaks at 1400 cm^{-1} and 1040 cm^{-1} after sorption also reveal the involvement of ionic carboxyl groups and C-OH alcohols respectively. Similar FT-IR results were also reported for the biosorption of metals on orange peel biomass (Feng *et al.*, 2009).

Surface Analysis

Surface area, pore volume and pore diameter of the biosorbent were determined with BET (N_2 /BET method). The sorbent material showed an average single point surface area of $2.1\text{ m}^2\text{g}^{-1}$. The natural pH of the biosorbent was found to be 5.2. The physical properties of the biosorbent are shown in Table 1.

BATCH EQUILIBRIUM STUDIES

Effect of PH

Biosorption processes are strongly pH dependent and different species may have different pH optima, possibly due to the different solution chemistry of the species (Pagnanelli *et al.*, 2003). The influence of pH on the adsorption of Zn (II) ions was studied within the range of 2.0-12 as shown in Figure. 2. The results showed that the uptake of metals increases with an increase in solution pH up to pH 6. Q_e was initially low at pH 2 due to protonation of the biomass active sites by H^+ ions and this led to the overall surface charge on the cells to be positive, and thus the approach of positively charged zinc metal ions was limited. At pH values around 6, there is a net negative charge on the cell wall components, which promoted reaction with metal ions. After pH 6, biosorption capacity decreased because of the presence of hydroxyl ions which resulted in precipitation of the metal ions to form $\text{Zn}(\text{OH})_2$ (Bailey *et al.*, 1999).

Effect of Contact Time

The contact time is an important parameter when designing efficient biosorption units. The investigation showed a general increase in the adsorption of the zinc metal ions with an increase in contact time up to 120 minutes (Figure.3). However, the adsorption reached equilibrium in 120 minutes. The higher sorption rate in the first 60 minutes may be a result of an increased number of vacant sites available on the adsorbent surface. With the progressive occupation of these sites, the process became slower resulting in a decrease in the sorption capacity after 120 minutes since there were no more vacant sites for the metal ions to occupy (Bishnoi *et al.*, 2007).

Effect of Adsorbent Dosage

The effect of adsorbent dosage was investigated by varying the biomass from 0.5 to 3.0 g at pH 6. (Figure. 4). The fraction of the zinc metal ions removed from the aqueous phase increased with an increase in the dosage from 0.5 to about 2.0 g because the numbers of active sites available for metal biosorption were more as the dosage increased. There was no significant change beyond the dose of 2.0 g possibly because of the overlap of biosorbent sites, electrostatic interactions and poor mixing at high biomass concentrations (Aksu, 2001).

Effect of Initial Zinc Concentration

It was observed that the biosorption capacity of the zinc metal ions to the surface of biomass increased as initial metal concentration was increased from 20 to 100 mg/g (Figure. 5). The reason for this could be the increased migration of zinc (II) ions into the vacant sites of the sorbent at high initial zinc (II) ions (Michalak *et al.*, 2007). Beyond 100 mg/g the absorption uptake remained constant. This might have been due to the agglomeration of adsorbent particles at higher concentration leading to a decrease in the total surface area of the adsorbent particles available for adsorption. The results correlate with the observations by (Melcakova and Ruzovic, 2010) in the biosorption of zinc (II) ions by *Reynoutria japonica* leaves.

Adsorption Equilibrium Isotherms

The adsorption isotherms indicate how the adsorption molecules distribute between the solid phase and the liquid phase when the adsorption process reaches an equilibrium state. The analysis of the adsorption data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose (Hameed *et al.*, 2007). The commonly used Langmuir and Freundlich isotherms were tested in order to establish the most appropriate correlations for the equilibrium data in the design of adsorption system. The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface and can be linearized as;

$$\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \dots\dots\dots (2)$$

Where Q_e is the zinc ions adsorbed in mg/g, b is the Langmuir constant related to energy of sorption in L/mg, Q_{max} is the maximum sorption capacity corresponding to complete monolayer coverage in mg/g and C_e is the equilibrium solute concentration in mg/L. A plot of C_e/Q_e against C_e from the linearized equation gave a straight line as shown in Figure. 6. The Langmuir parameters for the biosorption of zinc on *Brachystegia spiciformis* leaves were found from the slopes and intercepts of the straight line shown in Figure. 6 and are listed in Table 2. The correlation coefficient of the linear regression ($R^2 = 0.9902$) indicate that the Langmuir model could describe the biosorption of zinc leaves. The separation factor (R_L) value of 0.32 obtained satisfies the range ($0 < R_L < 1$) indicating favourable biosorption (Ong *et al.*, 2010). The value of b found was 0.0152 which is < 0.1 implying low surface energy in the system, thus indicating a probable stronger bonding between Zn^{2+} and the sorbent (Sajidu *et al.*, 2006). The maximum adsorption capacity Q_{max} was found to be 1.85 mg/g and was comparable to other biosorbents in literature. The Q_{max} values for the removal of zinc for other biosorbents used previously by other researchers were lower than that obtained in this study [(cork biomass, 0.34 mg/g (Natalia *et al.*, 2004); hazelnut shells, 1.78 mg/g (Cimino *et al.*, 2000)]. The Q_{max} values for zinc uptake by various adsorbents are shown in Table 3.

The empirical Freundlich isotherm model is suitable for a highly heterogeneous surface. This can be linearized as;

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots(3)$$

Where Q_e is the amount of zinc uptake by *Brachystegia spiciformis* biomass (mg/g), C_e is equilibrium adsorbate concentration in mg/L, K_f is the adsorbent capacity measure and n is the adsorption intensity. Figure 7 shows Freundlich isotherm model with the correlation coefficient ($R^2 = 0.9569$) being lower than that obtained for the Langmuir isotherm. The values of K_f (0.041) and n (1.235) were calculated from the intercept and slope respectively of the plot of $\log Q_e$ against $\log C_e$. The value of K_f is very low indicating low sorption in this model. The obtained n , K_f and R^2 values indicate that the sorption process is less heterogeneous and thus the Langmuir model is more applicable in this case. The Langmuir and Freundlich isotherm parameters are shown in Table 2.

CONCLUSION

This study showed the practical feasibility of utilization *Brachystegia spiciformis* leaf powder for removal of zinc ions from aqueous solution. Biosorption of zinc has been shown to depend upon optimum pH of 6, contact time of 120 minutes and optimum adsorbent dosage of 2 g. The FT-IR analysis showed the involvement of hydroxyl, carbonyl, amine and carboxyl groups in the uptake of zinc. The uptake of zinc showed an increase with an increase in initial metal concentration. The Langmuir isotherm model described the sorption of zinc onto *Brachystegia spiciformis*. The maximum adsorption capacity was found to be of 1.85 mg/g according to the Langmuir isotherm indicating good sorption capacity of the biosorbent.

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TABLES

Table-1. Physical properties of *Brachystegia spiciformis*

Property	Magnitude
Single point surface area (m ² /g)	2.1
Total pore volume (cm ³ /g)	0.049
Adsorption average pore diameter (Å)	44.61
pH	5.2

Table-2. Langmuir and Freundlich parameters for biosorption of zinc ions by *Brachystegia spiciformis*

Adsorption Isotherm	Parameter	Value
Langmuir	Q _{max} (mg/g)	1.85
	b (L/g)	0.0152
	R _L	0.32
	R ²	0.9909
Freundlich	K _f (mg/g)(L/mg) ⁿ	0.041
	n (g/L)	1.235
	R ²	0.9569

Table-3. Zinc uptake capacities by various adsorbents

Biosorbent	Q_{max} (mg/g)	Reference
Hazelnut shells	1.78	(Cimino <i>et al.</i> , 2000)
Fungus <i>mucor rouxii</i>	7.75	(Guangyu and Thiruvengkatachari, 2003)
Cork biomass	0.34	(Natalia <i>et al.</i> , 2004)
<i>Erythrina variegata</i> leaves	12.7	(Venkateswarlu <i>et al.</i> , 2008)
<i>Brachystegia spiciformis</i>	1.85	(Present study)

FIGURES

Figure-1. FT-IR spectrum of *Brachystegia spiciformis* before and after biosorption

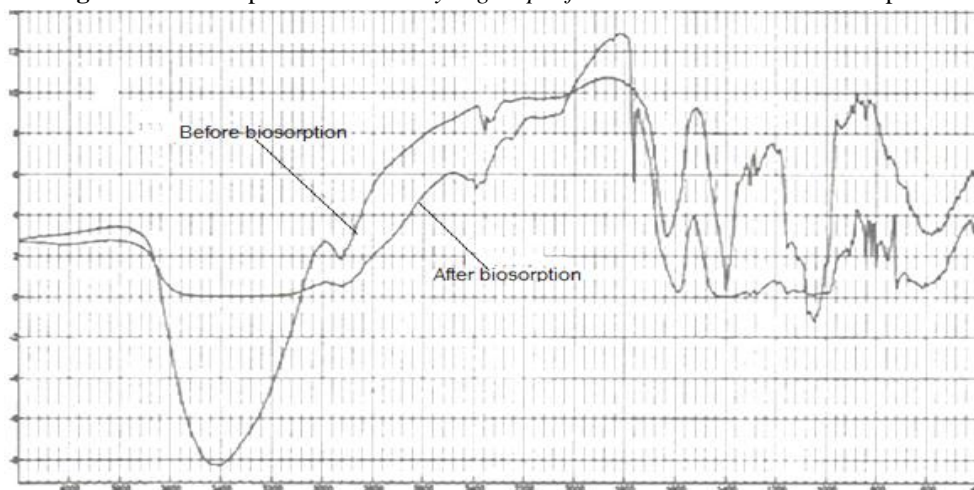


Figure-2. Effect of pH on biosorption of zinc (II) ions

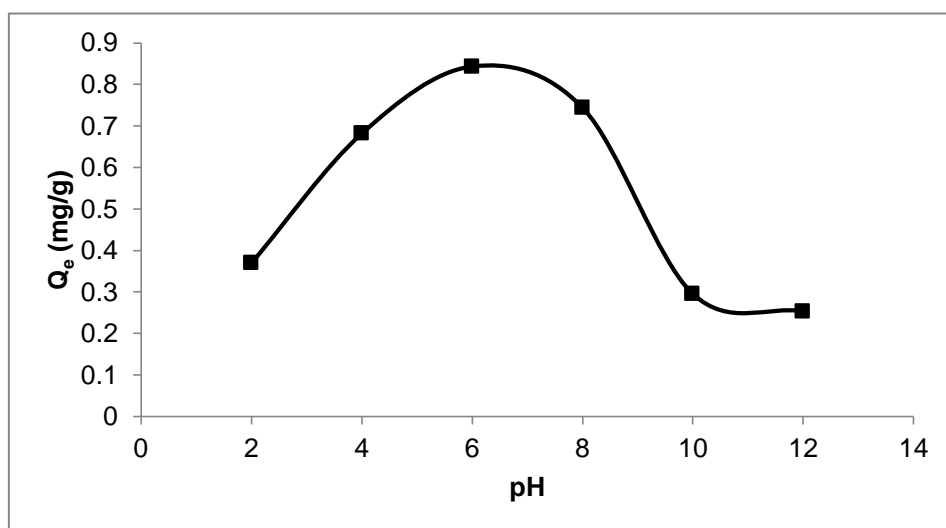


Figure-3. Effect of contact time on biosorption of zinc (II) ions

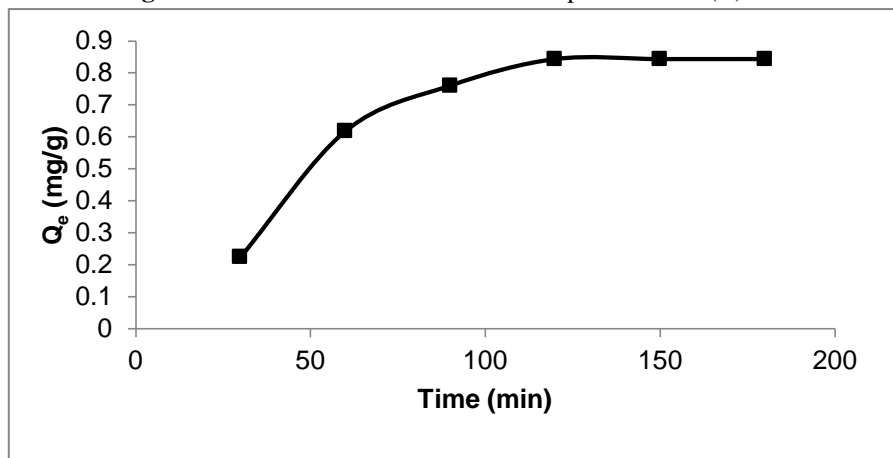


Figure-4. Effect of adsorbent dosage on biosorption of zinc (II) ions

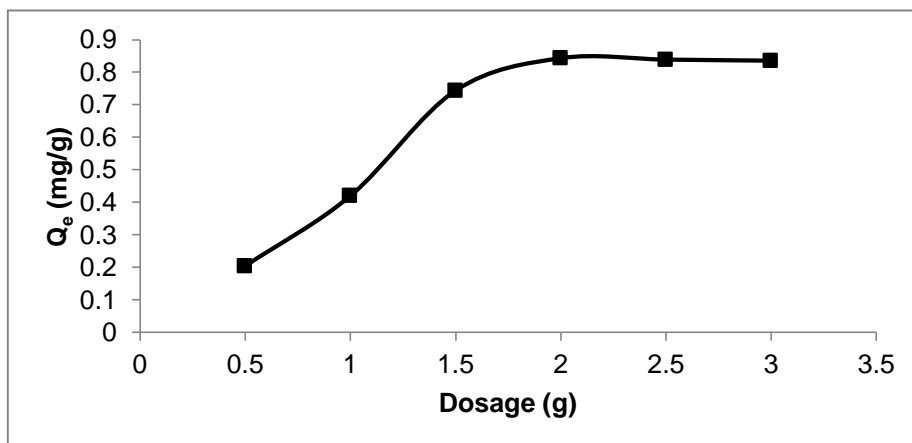


Figure-5. Effect of initial zinc (II) ions concentration on biosorption capacity

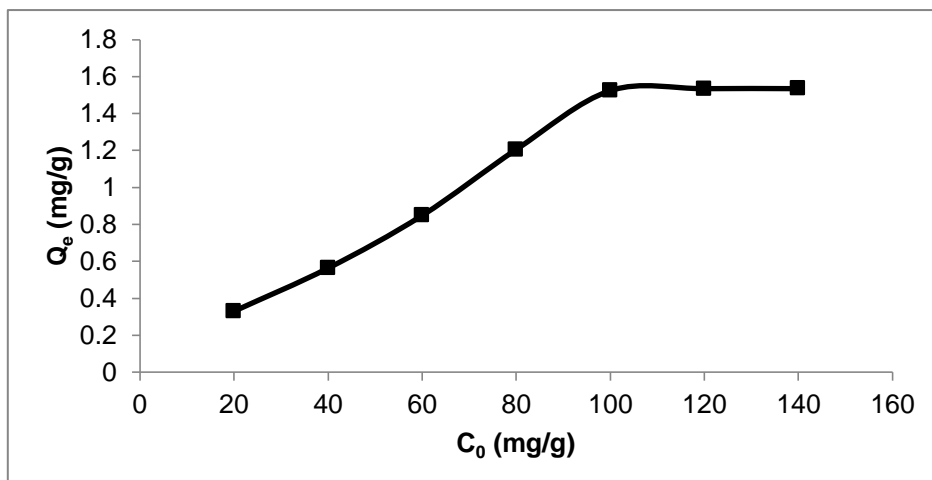


Figure-6. Langmuir isotherm for biosorption of zinc (II) ions

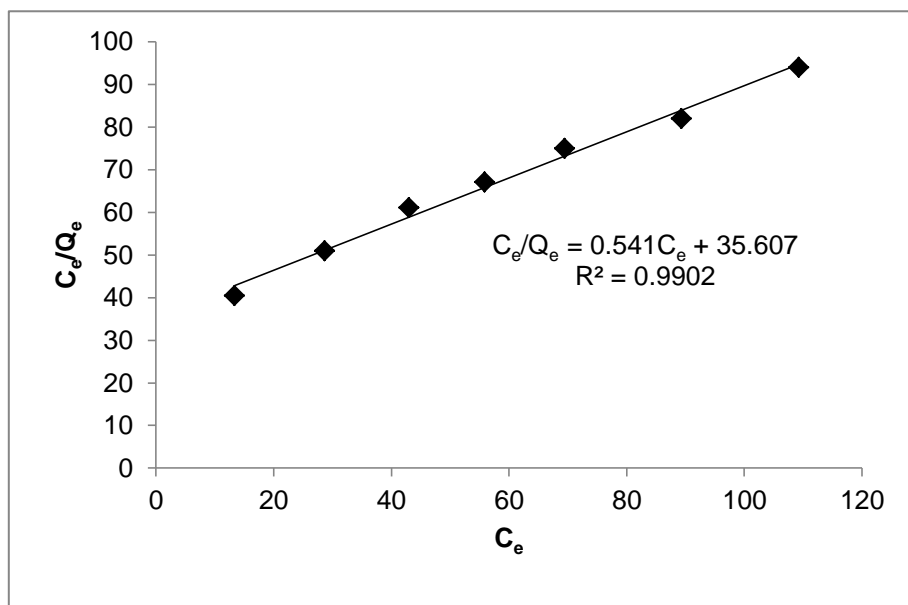


Figure-7. Freundlich isotherm for biosorption of zinc (II) ions

