

EQUILIBRIUM ISOTHERM ANALYSIS OF THE BIOSORPTION OF Zn^{2+} IONS BY ACID TREATED ZEA MAYS LEAF POWDER

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ABSTRACT

The potential of Zea Mays leaf powder for the removal of Zn^{2+} ions from waste waters was investigated using the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherms. Batch biosorption studies were carried out in stopper Erlenmeyer flasks to optimize pH, contact time and biomass dosage at a solution temperature of 27 ± 2 °C, a flask agitation rate of 200 rpm and initial concentration of Zn^{2+} ions of 100 mg/L. Adsorption isotherm experiments were conducted by varying metal ion initial concentration in the range from 10 to 100 mg/L under optimum conditions of pH 5, 120 minute contact time, a dosage of 1g/L at constant temperature and agitation rate of 27 ± 2 °C and 200 rpm respectively. The equilibrium data showed good fit to all the adsorption isotherms with $R^2 \geq 0.98$. High maximum sorption capacities were obtained from Langmuir (74.0741 mg/g) and D-R (13.2779 mg/g) isotherms. The Langmuir dimensionless separation factor (R_L) depicted sorption favorability with all its values falling between 0 and 1 for all initial concentrations investigated. The Freundlich adsorption intensity parameter fell in the range $1 < n < 10$ showing easy-separation beneficial biosorption. The magnitude and sign of the mean biosorption energy ($E_D = 22.9419$ kJ/mol) suggested the sorption process to be physisorption and endothermic in nature. The equilibrium sorption study showed that Zea Mays leaf powder can be effectively used for the biosorption of Zn^{2+} ions from waste waters.

KEYWORDS: Biosorption, Dubinin-Radushkevich isotherm, waste waters, Zea mays, zinc.

I. INTRODUCTION

Industrial activities have contributed to the increase of toxic heavy metals in plants and animals that survive or live in water [1]. Among the various metal ions present in waste waters from mining operations, electronics, electroplating and municipalities, zinc is one of the most prevalent heavy metal [2]. Zinc is not biodegradable and it travels through the food chain and it bioaccumulates causing zinc-induced copper deficiency [3]. Acute adverse effects of high zinc intake include nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches.

Removal of heavy metal ions from waste waters is usually achieved by physico-chemical processes such as precipitation, coagulation, ion exchange, chemical oxidation and reduction, membrane processes and evaporation recovery [3]. However these techniques have disadvantages such as less efficiency, are expensive, sensitive operating conditions, low removal of the metal ions less than 100 mg/L and the production of toxic secondary sludge [4]. Such drawbacks led to the discovery of biosorption that has several advantages over the conventional treatment methods. The advantages include: low cost, high efficiency, ready availability, high uptake capacity, minimization of sludge and regeneration of the sorbent [5].

A variety of biomaterials have been tested on the removal of heavy metal ions from wastewaters [1-4]. Among these sorbents, parts of the *Zea mays* plant have been extensively investigated for their potential to remove both dyes and heavy metal ions [4], [6], [7]. Untreated *Zea mays* leaf powder was investigated for its potential to remove zinc ions from waste waters [8] and a maximum sorption capacity of 2.805 mg/g was achieved. There is need for biomass treatment to reduce fouling and

desorb inorganic and organic materials adsorbed during plant growth [9] that may interact with metal ions. The treatment cleans up the surface and opens up the biosorbent pores and hence the biosorption capacity of the sorbent is enhanced. In addition to surface clean up, biomass treatment chemically modifies the sorption sites [10]. The preliminary investigation on the best chemical to treat the biomass involved the use of alkalis, inorganic and organic acids. Hydrochloric acid produced the highest sorption capacity and nitric acid oxidized the biomass from grey to brown-red color and it produced the least sorption capacity.

Zimbabwe, a southern African country, has an agro-based economy with *Zea Mays* (ZM) as its staple food. The country requires an estimated 2 million tones of ZM grain every year that is produced under both commercial and subsistence farming [11]. Large amounts of *Zea Mays* plants are produced yearly and a small fraction of these is used as/or to make stock feeds after harvest. The majority of the maize stalks and leaves are burnt during land preparation for winter crop (wheat) production.

The study focused on the use of the most abundant *Zea Mays* leaf powder, treated with 0.1 M HCl, in the removal of Zn^{2+} ions from simulated waste waters under sorption conditions of pH, contact time and adsorbent dosage at constant temperature, flask agitation rate and volume of synthetic effluent. The effect of initial concentration was investigated under optimum conditions and the equilibrium data obtained was analyzed using the Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms. The *Zea mays* leaf powder proved to be a good biosorbent of Zn^{2+} ions with the sorption process being endothermic and physisorption in nature.

1.1 Related work

The removal of Zn^{2+} ions from waste waters by adsorption onto plant waste products has received overwhelming attention. Sunflower stalks and carrot residues have been employed and the Langmuir maximum sorption capacities were found to be 30.70 and 29.90 mg/g respectively [7]. Mahamadi and Nharingo [9] investigated the removal of zinc ions using *Eichhornia crassipes* root powder and found the sorption capacity to be 12.5 mg/g.

The various parts of the *Zea mays* plant have been investigated for their potential to clean waste waters of heavy metal ions. Bioremediation of Zn^{2+} ions from aqueous solution using unmodified and EDTA-modified maize cobs was performed and maximum sorption capacities of 57.47 and -5.59 mg/g respectively were reported [12]. The use of maize stalks resulted in maximum sorption capacity of 30.30 mg/g. The removal of Zn^{2+} ions from solution was also studied employing natural (untreated) maize leaf powder and very low maximum sorption capacity of 2.8 mg/g was reported [8]. Sorption enhancement of the maize leaf powder may be achieved through chemical treatment, hence the need to explore possible chemical treatment methods.

II. MATERIALS AND METHODS

2.1 Biomass preparation and treatment.

The *Zea Mays* leaves were harvested from a farm near City of Gweru, Zimbabwe. The leaves were washed with tap water and were rinsed three times with deionized water. They were oven dried at 80 °C to constant mass. The leaves were crushed and ground to a powder and acid treated with 1000 mL of 0.1 M HCl for 24 hours at room temperature over a reciprocated shaker (HY-4) set at 200 rpm. The biomass was rinsed with deionized water until a pH of 7 was attained [13]. It was dried in an oven (N75C Genlab) at 60°C for three days and was stored in polyethene containers. This Acid Treated *Zea Mays* (ATZM) leaf powder was used for all sorption experiments.

2.2 Optimization of adsorption parameters

The batch experiments were carried out in stopper Erlenmeyer flasks at constant solution volume of 50 mL, a temperature of 27 ± 2 °C and a flask agitation rate of 200 rpm. All the experiments were contacted in triplicates and averages were used in data analysis. The sorbent was separated from the solution by vacuum filtration at appropriate time intervals. The initial and residual Zn^{2+} ion concentrations were determined by a Shimadzu Flame Atomic Absorption Spectrometer (AA-6800).

2.2.1 Effect of pH

The effect of pH on the biosorption of Zn^{2+} onto ATZM leaf powder was investigated over the pH range from 2 to 7. All pH adjustments were done using 0.1 M HCl and NaOH as appropriate. A volume of 50 mL of pH adjusted 100 mg/L of Zn^{2+} ion solution was agitated with 0.1 g of ATZM leaf powder for 12 hours. The samples were then vacuum filtered and analyzed for residual Zn^{2+} concentration using Flame Atomic Spectrophotometer (FAAS).

2.2.2 Effect of contact time

The effect of contact time on the biosorption of Zn^{2+} onto ATZM leaf powder was evaluated from 15 to 180 minutes. A series of Erlenmeyer flasks containing 50 mL of 100 mg/L Zn^{2+} solution contacted with 0.1 g of ATZM leaf powder at pH 5, were placed on a shaker at 200 rpm. Triplicate analysis of residual zinc ion was done at 15 minute intervals for the time range given.

2.2.3 Effect of biomass dosage

Varying doses of ATZM leaf powder in the range from 0.1 to 1 g were contacted with 50 mL of 100 mg/L of Zn^{2+} ion solution at pH 5. The mixture was agitated on a reciprocated shaker at 200 rpm at a temperature of 27 ± 2 °C for 120 minutes.

2.3 Adsorption equilibrium studies.

Equilibrium studies were performed with different initial concentrations of Zn^{2+} ions ranging from 10 to 100 mg/L at optimum experimental conditions. ATZM leaf powder (0.5 g) was added to 50 mL of Zn^{2+} ions of different initial concentrations at a pH of 5 and a temperature of 27 ± 2 °C. The flasks were placed on a shaker at 200 rpm for 120 minutes. The analyses of both initial and residual Zn^{2+} ion concentrations were done by FAAS [14].

2.4 Zn^{2+} ion analysis by FAAS.

The concentration of Zn^{2+} ions before and after biosorption was determined by a Shimadzu AA-6800 Flame Atomic Absorption Spectrometer. Spectroscopic grade, $Zn(NO_3)_2$, standards were used to calibrate the instrument over the linear dynamic range of 2 to 8 mg/L. The minimum acceptable correlation of determination was 0.997 in all instrument calibrations [10]. Triplicate analysis of the sample was done after appropriate sample dilution.

2.5 Calculations.

Linear regression analysis was used to test the fitness of equilibrium data to the equilibrium isotherm models. All plots with $R^2 > 0.970$ were regarded as linear and therefore revealed fitness of the data to the model [15].

The amount of metal ion adsorbed at equilibrium, Q_e , was calculated using the mass balance equation 1.

$$Q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

Where C_0 and C_e are initial and equilibrium metal ion concentrations (mg/L) and m is the mass of the sorbent (g).

The rate of adsorption was estimated using equation 2 below:

$$\text{Rate of adsorption} = \frac{Q_{t_2} - Q_{t_1}}{t_2 - t_1} \quad (2)$$

Where Q_t is the metal ion adsorbed after the biomass is exposed to the synthetic effluent for time, t minutes.

III. RESULTS AND DISCUSSION

3.1 Effect of pH

The influence of pH on the biosorption capacity of zinc is shown in Fig 1. Solution pH affects metal species distribution. At low pH, Zn^{2+} (aq) species dominate while at high pH $Zn(OH)_2$ (s) dominates. The amount of Zn^{2+} ions sorbed (Q_e) increased with increase in pH up to an optimum pH of 5. At low pH, the surface of the biomass would be protonated and would therefore repel Zn^{2+} ions [16]. H_3O^+ dominates the competition against Zn^{2+} ions for the sorption sites on the biomass surface and hence the sorption of Zn^{2+} is minimal at low pHs. Increasing the pH resulted in increasing the number of

negatively charged sites and decreasing the number of positively charged sites on the biomass that favored the electrostatic attraction of the Zn^{2+} ions [17]. After pH 6, the observed increase in Zn^{2+} removal was attributed to the precipitation of $Zn(OH)_2$ [18] that may be mistaken as having been removed by the sorption process.

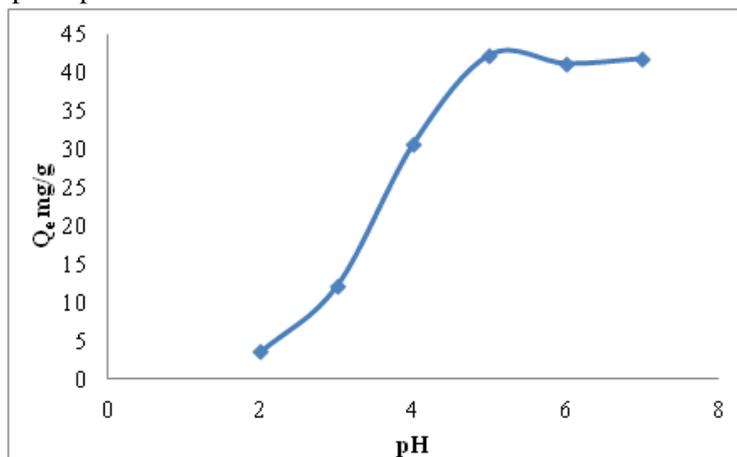


Fig 1. Effects of pH on zinc sorption onto ATZM leaf powder.

3.2 Effect of contact time

The effect of contact time on the biosorption of Zn^{2+} ions by ATZM leaf powder is shown in Fig 2. The trend shows that the amount of metal ion sorbed (Q_e) increases with contact time. Sorption rate was very high for the first 30 minutes ($0.809 \text{ mgg}^{-1}\text{min}^{-1}$); it fell drastically from 45 to 105 minutes ($0.193 \text{ mgg}^{-1}\text{min}^{-1}$) and was around zero from 120 minutes onwards.

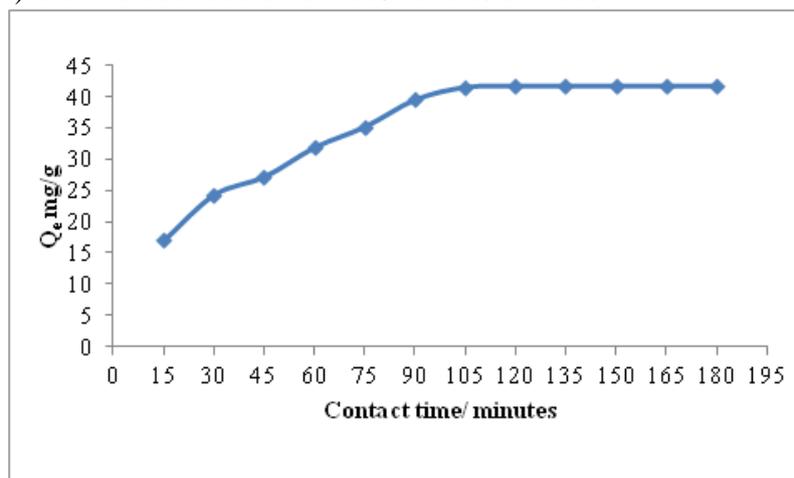


Fig 2. Effect of contact time on zinc sorption onto ATZM leaf powder.

The high sorption rate at the initial stage of the sorption process was attributed to higher concentration gradient between Zn^{2+} ions in solution (100 mg/L) and those on the sorbent surface (almost zero). The number of vacant sites on ATZM surface gradually decreased with contact time leading to decreasing concentration gradients and hence rates of sorption of the Zn^{2+} ions until equilibrium was achieved [19].

3.3 Effect of biosorbent dosage

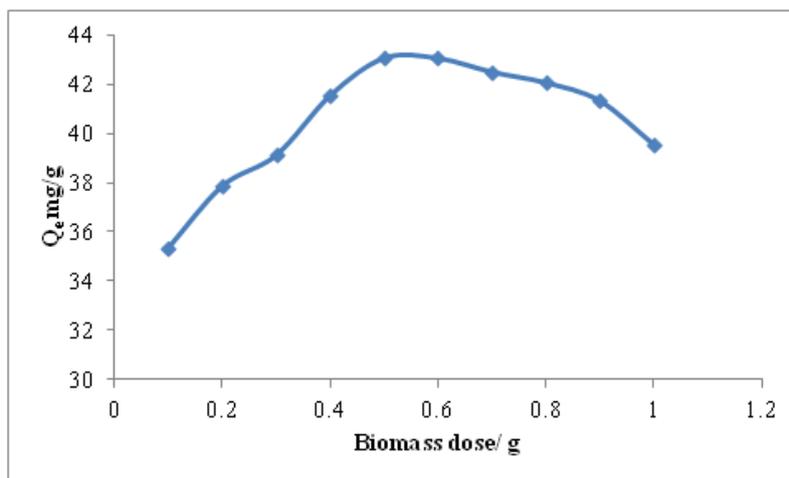


Fig 3. Effect of adsorbent dosage on zinc sorption onto ATZM leaf powder.

As shown in Fig 3, the uptake of Zn²⁺ ions increased with an increase in biosorbent dosage up to the optimum dosage of 0.5 g. During initial stages of sorption, the biosorbent dosage offered limited surface area and its addition would increase the surface area on which sorption occurred. This inevitably increased the sorption process. After the optimum biosorbent dosage of 0.5 g, the biomass was in excess and the concentration Zn²⁺ ions became limiting hence some sorption sites remained unoccupied. Further increase in dosage resulted in reduction in Zn²⁺ ion uptake. As the dosage increases, the mass of Zn²⁺ ions adsorbed per unit weight of the biosorbent decreases giving rise to decrease in Q_e values [20].

3.4 Effect of initial metal ion concentration

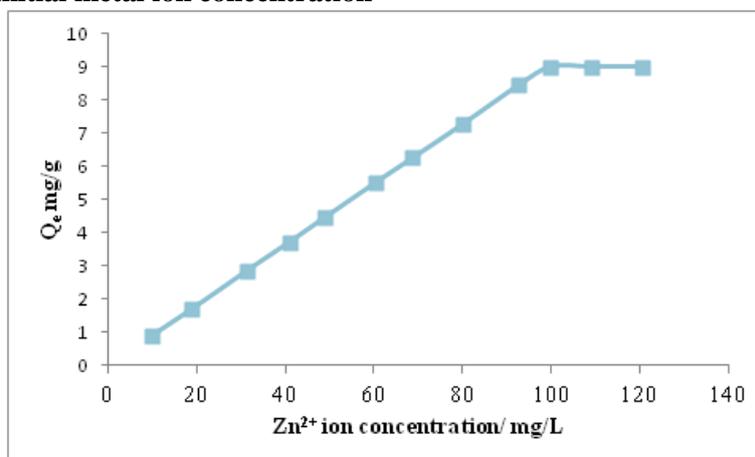


Fig 4. Effect of initial zinc concentration on its sorption onto ATZM leaf powder.

The effect of initial zinc ion concentration on Q_e is shown in Fig 4. The initial metal ion concentration was varied from 10 to 120 mg/L under optimum conditions. As the concentration increased the amount of metal ion sorbed increased up to 100 mg/L after which it became constant. Increasing the initial concentration increased the sorption gradient (Zn²⁺ in solution and those on the biomass surface) and hence Q_e increased. The initial zinc ion concentration provides the driving force to overcome mass transfer resistance between the two phases. It also promotes the interaction between adsorbent and sorbate [21]. After the initial concentration of 100 mg/L, biomass saturation occurred and the biomass became limiting. Further increase in initial Zn²⁺ ion concentration would not increase Q_e since all available sites were utilized.

IV. ADSORPTION ISOTHERM PARAMETERS

Equilibrium studies were carried out with varying initial concentrations of Zn²⁺ ions in the range from 10 to 100 mg/L under optimized conditions of pH (5), contact time (120 minutes) and biosorbent

dosage (0.5 g). The equilibrium data obtained was fitted to Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms.

4.1 Langmuir adsorption isotherm.

The adsorption isotherm assumes the existence of monolayer coverage of adsorbate on the structurally homogeneous surface of the adsorbent. All the sorption sites are assumed to be identical and energetically equivalent [21]. The general and linearized forms of the Langmuir adsorption isotherms are expressed in equation (3) and (4) respectively:

$$Q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{3}$$

$$\frac{1}{Q_e} = \frac{1}{Q_o b C_e} + \frac{1}{Q_o} \tag{4}$$

Where Q_e is the metal ion adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L) b and Q_o are the constants related to the energy of adsorption and the maximum adsorption capacity respectively, [22], [23]. The values of Q_o and b were calculated from the intercept and slope of the linear plot of $1/Q_e$ against $1/C_e$. The equilibrium data was fully described by the Langmuir adsorption isotherm as shown in Fig 5.

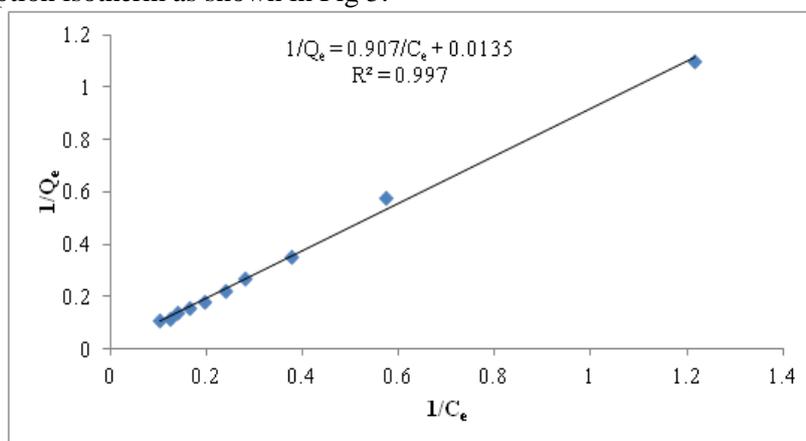


Fig 5. Langmuir plot for the adsorption of zinc onto ATZM leaf powder.

Table 1. Adsorption isotherm parameters for zinc sorption onto ATZM leaf powder.

<i>Langmuir</i>			<i>Freundlich</i>			<i>Dubinin-Radushkevich</i>			
Q_o	b	R^2	K_f	$1/n$	R^2	Q_D	B_D	E_D	R^2
74.0741	0.0149	0.9970	1.0852	0.9673	0.9962	13.2779	9.5×10^{-4}	22.9419	0.9800

Table 1 shows the adsorption isotherm parameters. A low b value on the Langmuir adsorption parameters indicated the low affinity of the sorbent for the sorbate [9]. The biomass exhibited a high adsorption capacity, implying that the biomass can be successfully used for the removal of Zn^{2+} ions from aqueous solution with a minimum number of adsorption cycles. The essential characteristics of the Langmuir isotherm may be expressed in terms of the separation factor, R_L that is calculated using the relationship shown in equation 5:

$$R_L = \frac{1}{1 + b C_o} \tag{5}$$

Where b is the Langmuir equilibrium constant related to the energy of adsorption and C_o is the initial metal ion concentration. The value of R_L lying between 0 and 1 shows favorable adsorption, $R_L > 1$ unfavorable adsorption, $R_L = 1$ adsorbate and adsorbent exhibit a linear relationship and when $R_L = 0$ chemisorption predominates and is irreversible [24]. Fig 6 shows the plot of the separation factor against initial concentration of Zn^{2+} ions.

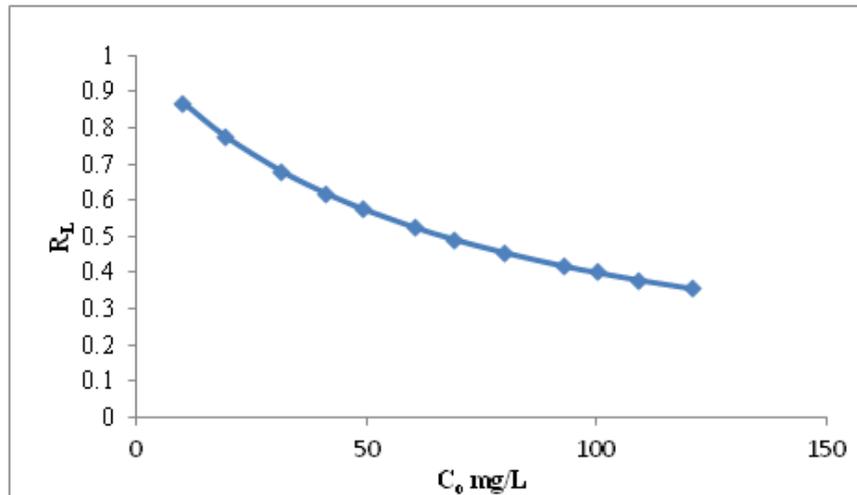


Fig 6. Separation factor for the sorption of zinc onto ATZM leaf powder.

The R_L values in Fig 6 showed that adsorption was more favorable at higher initial concentrations than at low concentration. The result pointed to a physisorption mechanism of adsorption. A similar trend was obtained by many researchers [9, 19, 24, 25].

4.2 Freundlich adsorption isotherm

This adsorption isotherm assumes that the adsorption occurs on amorphous surface that is heterogeneous and there is exponential distribution of active sites and their energies [26]. The logarithmic form of the Freundlich adsorption isotherm is expressed in equation 6 below [15].

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

Where Q_e and C_e have similar meaning to those in the Langmuir adsorption isotherm while K_f and $1/n$ are the adsorption capacity and adsorption intensity respectively. K_f and $1/n$ were obtained from the intercept and gradient of the linear plot of $\ln Q_e$ against $\ln C_e$ shown in Fig 7.

The Freundlich adsorption parameters are shown in Table 1. The R^2 value confirmed the fitness of the data to this model [27]. The adsorption intensity parameter ($1/n$), was within the range $1 < n < 10$ that shows that there was easy separation beneficial biosorption and therefore must be capitalized.

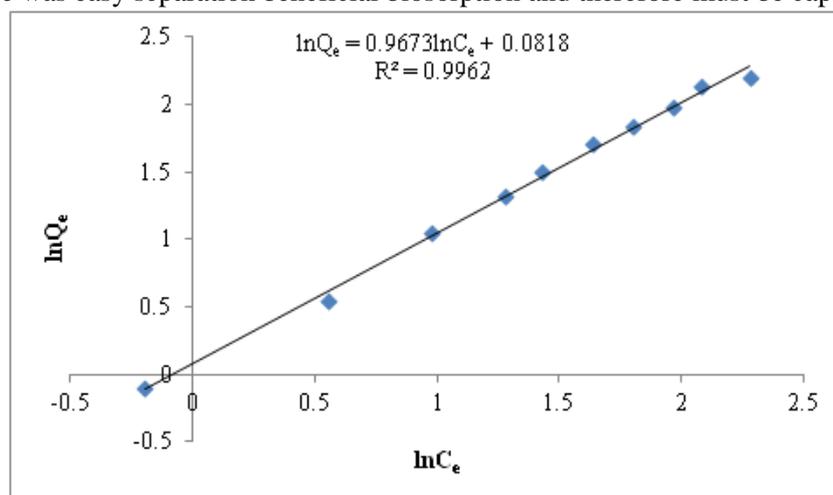


Fig 7. Freundlich plot for the sorption of zinc onto ATZM leaf powder.

The adsorption capacity (Table 1) was larger than those for Ni^{2+} (0.85 mg/g) and Cr^{3+} (0.41 mg/g) during their sorption onto fungal pellets [28] but was comparable to that of As (1.128 mg/g) onto palm bark (PB) biomass [29].

4.3 Dubinin-Radushkevich adsorption isotherm.

In order to estimate the characteristic porosity of the ATZM leaf powder and the apparent energy of adsorption, the Dubinin-Radushkevich adsorption isotherm was used to fit the equilibrium data. The general equation is represented by [30]:

$$Q_e = Q_D (-B_D [RT \ln(1 + 1/C_e)]^2) \quad (7)$$

The linear form of the equation is presented as in 8:

$$\ln Q_e = \ln Q_D - 2B_D RT \ln(1 + \frac{1}{C_e}) \quad (8)$$

Where Q_e and C_e are the metal ion sorbed at equilibrium (mg/g) and equilibrium concentration (mg/L) respectively, Q_D is the Dubinin-Radushkevich constant related to the degree of sorbate sorption by the sorbent surface and B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface from infinite distance in the solution [15]. A linear plot of $\ln Q_e$ against $RT \ln(1 + 1/C_e)$ gives the gradient as $-2B_D$ and the intercept as $\ln Q_D$ from which the adsorption isotherm parameters can be calculated [31]. The apparent energy of adsorption (E_D) is calculated using the relationship in equation 9:

$$E_D = 1 / (2B_D)^{1/2} \quad (9)$$

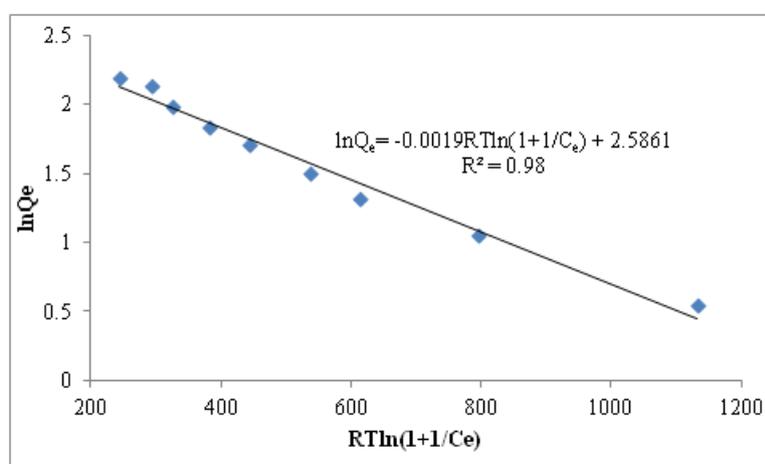


Fig 8. Dubinini-Radushkevich plot for zinc sorption onto ATZM leaf powder.

The very high and good correlation of determination on Fig 8 depicts good fit for the Dubinin-Radushkevich isotherm for the data. The D-R parameters are shown in Table 1. The maximum sorption capacity of the sorbent revealed a high degree of sorbate sorption by the sorbent compared to that obtained by El-Said during the sorption of Pb(II) ions onto rice husk and its ash [26]. The Q_D values obtained during the sorption of Al(III), Co(II) and Ag(I) onto fluted pumpkin waste biomass were all less than 8 mg/g [32]. The biosorption of Zn^{2+} ions onto ATZM leaf powder followed a physisorption process since physisorption processes have adsorption energies less than 40 kJ/mol [31]. The positive E_D implied that the sorption process was endothermic and that the sorption process would increase with increase in solution temperature. Similar results were obtained by Oladoja et al [33] during the sorption of Congo red onto palm kernel coat and by [30] during the sorption of atrazine onto sheanut shells.

Table 2. Langmuir constant, Q_o , for different adsorbents.

Biosorbent	Sorbate	q_m (mg/g)	Reference
<i>E. crassipes</i> root powder	Zn(II)	12.50	[9]
Bone ash	Zn(II)	21.20	[34]
Wood ash	Zn(II)	7.50	[35]
Green microalga	Zn(II)	4.31	[36]
Red mud	Zn(II)	12.56	[37]

Green coconut shell	Zn(II)	17.08	[38]
Maize stalks	Zn(II)	30.30	[7]
Sunflower stalks	Zn(II)	30.70	[7]
Carrot residues	Zn(II)	29.60	[7]
Oil palm ash	Zn(II)	10.66	[39]
Maize leaf powder	Zn(II)	2.80	[8]
<i>Myriophyllum spicatum</i>	Zn(II)	15.59	[40]
<i>Saccharomyces cerevisiae</i>	Zn(II)	1.73	[41]
<i>Pseudomonas putida</i> CZ1	Zn(II)	17.70	[42]
ATZM leaf powder.	Zn(II)	74.04	Current study

Table 2 shows the comparison of the Langmuir maximum sorption capacity, Q_0 , of different biosorbents to that of ATZM obtained in this study. The Q_0 of ATZM is 26.4 times greater than that of untreated maize leaf powder [8] and is 3 to 30 times greater than that of other biosorbents presented. Acid treated *Zea mays* finds a better place in the biosorption field and it needs further investigations using real effluent.

V. CONCLUSIONS

The acid treated *Zea Mays* leaf powder proved to be an excellent biosorbent for Zn^{2+} ions from aqueous solution at optimum conditions of pH 5, contact time of 120 minutes and a biomass dosage of 5 g/L. An easy separation beneficial sorption, physical and endothermic in nature was involved in the sorption process. It has high maximum adsorption capacity, sorption favorability and adsorption intensity and hence implementable.

VI. FUTURE WORK

Further research on column sorption studies employing industrial effluent rich in Zn^{2+} ion concentration need to be done. Real effluent is rich in Fe(III), Ca(II) and Mg(II) ions. The effect of these ions on the sorption of zinc onto ATZM leaf powder needs to be investigated.

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