

Equilibrium Studies for Adsorption of Zn^{2+} on to Acid Treated Kikuyu Grass *Pennisetum Clandestinum* Biomass

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Abstract: *The feasibility of using *Pennisetum clandestinum* biomass as low-cost adsorbent for the removal of Zn^{2+} was investigated in batch studies. The Freundlich, Langmuir, Dubinin Raduskevich and Temkin adsorption isotherms were used to analyze the experimental data. The kinetic analyses of the adsorption processes were performed using pseudo-first order and pseudo-second order kinetic models. The Langmuir isotherm adequately described the adsorption of Zn^{2+} onto the material. The maximum adsorption capacity q_{max} was found to be 25.34 Mg/g. The Langmuir dimensionless constant, separation factor (RL) was between $0 < RL < 1$, indicating favorable adsorption. The heat of adsorption (kJmol⁻¹) obtained were generally somewhat low, indicating physisorption of Zn^{2+} to the adsorbates. For the kinetic studies, the pseudo -second order model suitably described the removal of Zn^{2+} by *Pennisetum clandestinum* biomass.*

Keywords: Adsorption; Isotherms, Kinetics, *Pennisetum clandestinum* biomass, Zinc (II) ions

1. Introduction

Over the years, the discharge of heavy metals into the water bodies and ecosystem remain as one of the most elusive and pervasive environmental threat to health. Heavy metal ions are stable and persistent to environment changes. This is because; they cannot be either degraded or destroyed [1]. In Kenya, the rapid increase in industrialization has compounded the situation due to the discharge of highly concentrated effluent into the aquatic systems. Various treatment methods have been employed metals from industrial effluents. These methods include biosorption, complexation, chemical oxidation or reduction, chemical precipitation, reverse osmosis, ion exchange, solvent extraction, membrane filtration, coagulation, phyto extraction and evaporation [2]. Biosorption is one of the most cost-effective methods due to its ease to operate, high efficiency and low maintenance cost. Moreover it utilizes low cost biodegradable agricultural wastes. The other treatment alternatives may have some disadvantages such as high consumption of reagent and energy, incomplete metal ion removal, low selectivity, high operational cost and problem in disposing the secondary waste generated during the treatment process [2]. The release of zinc into groundwater resources occurs largely via anthropogenic activities such as mining or through industrial production. The main sources of zinc in the environment are manufacturing of brass and bronze alloys and galvanization [3]. Further, it is also utilized in paints, rubber, plastics, cosmetics and pharmaceuticals [3]. Zinc is an essential element for life and acts as micronutrient when present in trace amounts. Zinc gives rise to serious poisoning cases. The main symptoms of zinc poisoning are dehydration, electrolyte imbalance, stomachache, nausea, dizziness and

neuropathy [4]. Currently, kikuyu grass *Pennisetum clandestinum* biomass mowed from institution fields does any commercial application. There is need for investigation on its suitability as a biosorbent. This is not only dependent on its adsorption capacity, but also on the energy and kinetics of adsorption. In the present study, the feasibility of using *Pennisetum clandestinum* biomass for the removal of Zn^{2+} was investigated through isotherm and kinetic studies.

2. Biosorption Isotherms

The equilibrium relationships between adsorbent and adsorbate are best explained by sorption isotherms [5]. They describe the relationship between the mass of the adsorbed component per biosorbent mass and the concentration of its component in solution. Determination of equilibrium parameters provides important information that used in designing of adsorption systems [6]. The performance and the biosorbent ability for adsorbing Zn^{2+} from aqueous solution were evaluated by Langmuir and Freundlich models. Temkin and Dubinin-Raduskevich were used in providing information on the heat of adsorption and verifying results from Langmuir and Freundlich isotherms [7]. Langmuir model assumes that the sorption of metal ions occurs in monolayer coverage of biosorbent surface. All the active sites are same and symmetrical (homogenous). The adsorbate binding is independent the adjacent site occupancy. The single site is occupied by a single adsorbate particle adsorption is equal to the rate of desorption [8]. The linearised isotherm is given by equation 1.

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{bQ_{max}} + \frac{C_{eq}}{Q_{max}} \quad (1)$$

A plot of $\frac{C_{eq}}{q_{eq}}$ against C_{eq} gives a straight line from which Q_{max} and b can be obtained. Where q_{eq} corresponds to the amount of solute ions, C_{eq} is the solute concentration in aqueous solution after equilibrium is reached. Q_{max} represents practical limitation adsorption capacity due to saturation of identical sites. b is an affinity constant for binding sites. A high value of b indicates a high affinity of the biosorbent for the sorbate. The increase or decrease in the value of b with increase in temperature explains the thermodynamic feasibility of the biosorption as endothermic or exothermic [9]. The isotherm shape can be used to predict whether an adsorption system is "favorable" or "unfavorable." The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L . It is a dimensionless constant given by equation 2 [10].

$$R_L = \frac{1}{1 + Q_{max} C_o} \quad (2)$$

Freundlich is an empirical isotherm model that considers heterogeneous adsorption on the adsorbent surface and multilayer adsorption surface coverage is done by the adsorbate. This model works from very low range of concentration gradient of adsorbate ion to intermediate concentration. The linearised isotherm is given by equation 3.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

Temkin isotherm assumes the temperature-dependent linear decrease in the heat of adsorption [11]. This isotherm is used to explain the sorption of metal ion on heterogeneous surface. The linearised isotherm is given by equation 4.

$$q_e = B \ln A_T + B \ln C_e \quad (4)$$

corresponding to the maximum binding energy Where A_T is Temkin isotherm equilibrium binding constant, b_T is Temkin isotherm constant, R is universal gas constant, T is the absolute temperature and B is Constant related to heat of sorption. The magnitude of A_T provides guidance on selection of the adsorbent. Dubinin-Radushkevich isotherm assumes the heterogeneous surface characteristic of the adsorbent. The model has often successfully fitted high and the intermediate range of concentrations data well. The model assumes the sorption of metal ions on energetically non-uniform surface. [12]. The isotherm is represented by equation 5.

$$q_e = (q_s) \exp(-K_{ad} \epsilon^2) \quad (5)$$

Where, q_e is amount of adsorbate in the adsorbent at equilibrium, q_s is theoretical isotherm saturation capacity, K_{ad} is the Dubinin-Radushkevich isotherm constant and ϵ is the Polanyi potential.

2.1 Kinetics of Biosorption

The adsorption kinetic studies describe the solute uptake rate which in turn controls the residence time of adsorbate uptake at the solid-liquid interface. Biosorption kinetics is described traditionally by the pseudo first order model of Lagergren or by pseudo second order kinetics. The pseudo first order model assumes that the presence of physical forces of attraction between adsorbate and adsorbent particles. The binding of adsorbate with the adsorbent is reversible and non-dissociative. It also considers that the rate of binding of adsorbate species with adsorbate particle is directly proportional to the number of vacant active species on the surface of the adsorbent. [13]. The linearised model is given by equation 6.

$$\log(q_e - q_t) = \log q_e - \frac{K_L t}{2.303} \quad (6)$$

Where K_L , is the Lagergren constant, q_e is the metal adsorbed at equilibrium, q_t is the metal adsorbed at a given time and t is the time taken for the adsorption to take place. The pseudo-second order equation is based on the assumption that the rate-limiting may be chemical adsorption [14]. Linearised pseudo – second order model is given by equation 7.

$$\frac{t}{q_t} = \frac{1}{K' q_e^2} + \frac{t}{q_e} \quad (7)$$

Where K' is the pseudo – second order rate constant of adsorption, q_e is the metal adsorbed at equilibrium, t is the time taken for the adsorption to take place and q_t is the metal adsorbed at a given time [12].

3. Experimental

3.1 Preparation of stock of metal

All the chemicals procured and applied in this study were analytical grade. Stock solution of Zn^{2+} was prepared using $Zn(NO_3)_2 \cdot 6H_2O$ in deionised water. Desired concentrations of Zn^{2+} were prepared by diluting 1000 mgL^{-1} of the stock solution.

3.2 Preparation of the adsorbent

In the laboratory the kikuyu grass *Pennisetum clandestinum* biomass was sorted to remove unwanted materials then washed thoroughly with tap water to remove soil particles. A sample of the *Pennisetum clandestinum* biomass was digested and analyzed for metal ions. The remaining sample was soaked in 0.01M nitric acid for 1 hour and then rinsed with distilled water until a pH near neutral was obtained. The biomass was sun dried for 2 weeks. The resultant dry *Pennisetum clandestinum* biomass was ground to 0.5 mm mesh. The ground *Pennisetum clandestinum* biomass was stored in plastic bottles. The resultant *Pennisetum clandestinum* biomass was subjected to FTIR, ash and moisture content analysis.

3.3 Batch Adsorption studies

Sorption capacity of *Pennisetum clandestinum* biomass was determined by contacting 1.000 g of *Pennisetum clandestinum* biomass with 100 mL Zn²⁺ solutions of known concentration (20-100 mgL⁻¹) in 250 mL Erlenmeyer flasks. Then shaken on a temperature-controlled shaker maintained at 25 ± 0.5 °C. The suspensions were agitated at 125 rpm, filtered out at the end of predetermined time intervals of 5, 10, 15, 20, 25, 30, 60, 120, 240, 480 and 720 minutes. The residual metal ions were analyzed using Atomic Absorption Spectrophotometric analysis (Analyst200 AA, Perkin Elmer, USA). The temperature used was 20, 25, 30, 35, 40, 45, 50 and 55 ± 0.5 °C. Temperature was regulated using water bath model SB3D. The effect of sorbate to sorbent ratio for the percentage and unit metal sorbate sorption capacity of the *Pennisetum clandestinum* biomass sorbent was determined by varying the solid mass phase between 1 and 6 g L⁻¹ of *Pennisetum clandestinum* biomass. The effect of pH on the metal sorption by *Pennisetum clandestinum* biomass was evaluated in the range of 2.0- 8.0. The initial pH of the metal solution was adjusted to the desired pH value using 0.1 M HNO₃ and 0.1 M NaOH. Effect of initial metal concentrations (10, 25, 50, 75, 100, 200 and 300 mgL⁻¹) were also been determined throughout the study. *Pennisetum clandestinum* biomass and metal-free blanks were used as the experimental control. In order to avoid discrepancy experimental results, the experiments were performed in triplicate and the average values were used in data analysis. The metal ion uptake was calculated using equation 8.

$$q_e = \frac{V(C_o - C_e)}{M} \quad (8)$$

The percentage of metal adsorption by the adsorbents was calculated using equation 9.

$$\text{Percentage adsorption (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (9)$$

Where, C_o and C_e represented the initial and equilibrium concentrations (mg/L), V is the volume of solution and the M weight of adsorbent (g).

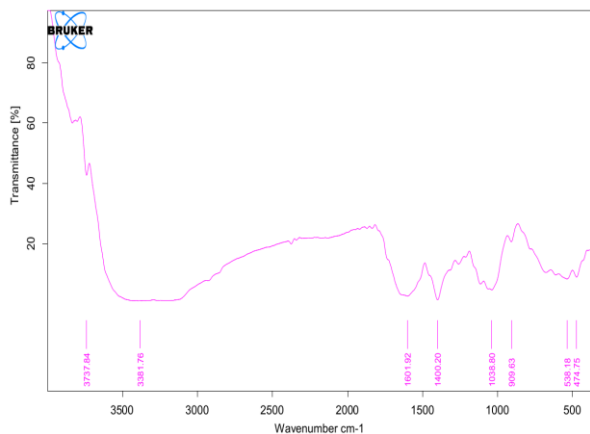


Figure 1: FTIR analysis for kikuyu grass *Pennisetum clandestinum* biomass before Zn²⁺ adsorption

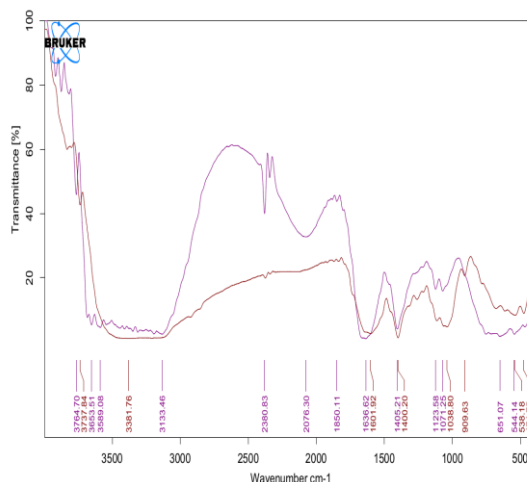


Figure 2: FTIR analysis for *Pennisetum clandestinum* biomass after adsorption of Zn²⁺.

The FTIR spectrum for the surface functional groups for *Pennisetum clandestinum* biomass is presented in figures 1 and 2. The spectrum shows distinct peaks at 1000-1300 CM⁻¹ (C-O stretch), 1670-1820 CM⁻¹ (C=O stretch), 2500- 3300 CM⁻¹, (O-H stretch) and 3300-3500CM⁻¹ (N-H stretch).

Table 4.3: Results for moisture and ash content of *Pennisetum clandestinum* biomass.

Biosorbent	Moisture content	Ash content
<i>Pennisetum clandestinum</i> biomass	88.12	33.54

The results show that *Pennisetum clandestinum* biomass has the high percentage of water content and low ash content. These results show that large quantities of raw kikuyu grass *Pennisetum clandestinum* biomass may be required to prepare the biosorbent.

3.4 Effect of contact time

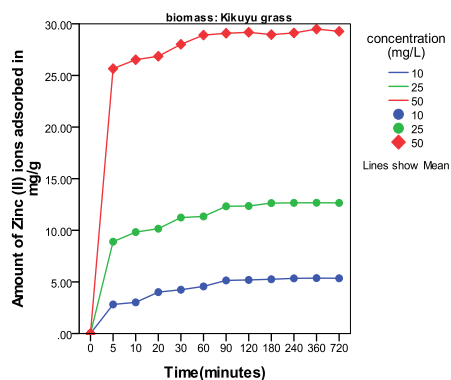


Figure 3: Effect of contact time for adsorption of zinc (II) ions at, 10 mg/L pH 6.0 and temperature 25±0.5°C.

The effect of contact time was studied on adsorption of Zn²⁺ onto *Pennisetum clandestinum* biomass was studied using initial concentrations of 10 25 and 50 ml/L. The results are shown in figure 3. The results show that the rate of adsorption is rapid within the first 30 minutes for the three initial concentrations. Thereafter it slows down and the equilibrium was attained after 90 minutes. According to [14], a constant adsorption is indicative of equilibration due to saturation of

adsorption sites. Rapid adsorption of metal ions during the initial stages was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant sites on the adsorbent.

3.5 Effect of sorbent dosage

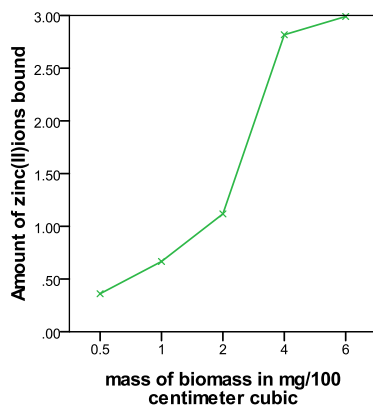


Figure 4: Effect of sorbent dosage on adsorption of Zn^{2+} at initial concentration of 10 mg/L, pH 6.0 and temperature $25 \pm 0.5^\circ C$.

The effect of sorbent dosage on the adsorption of Zn^{2+} is shown in figure 4. The results show increase in adsorption with the adsorbent dosage. The increase in adsorption may be due to more surfaces and functional groups being available on the adsorbent [17]. After a sometime the adsorption decreases and eventually equilibrium is attained. This may be attributed to due to the overlapping of the adsorption sites as a result of overcrowding adsorbent particles [18]. Some adsorption sites become more difficult to reach due to their position in deeper pores. Another consequence may be the reduction of activated sites at the surface of the adsorbents and also the matter rate transfer of *Pennisetum clandestinum* biomass at the surface of the adsorbents, this means that the quantity of *Pennisetum clandestinum* biomass adsorbed per unit mass of adsorbent has it limit with the adsorbent dosage. Similar result has been obtained by [18] during the removal of malachite green using *Hydrilla Verticillate* biomass.

3.6 Effect of pH

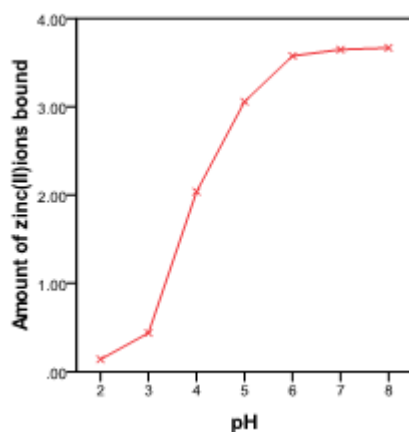


Figure 5: Effect of pH on adsorption of Zn^{2+} at 10 mg/L, temperature $25 \pm 0.5^\circ C$

The effect of pH on adsorption of Zn^{2+} onto *Pennisetum clandestinum* biomass is shown in figure 5. The results show that there was increase in adsorption of Zn^{2+} with the increase in pH. The maximum adsorption took place at pH of 6. [16] investigating adsorption of Zn^{2+} on kaolinite and metakaolinite, found out that at pH greater than 6.0, the solubility of zinc decreased resulting in their precipitation as hydroxide with no significant increase in percentage adsorption. The results show that adsorption of Zn^{2+} onto the adsorbent considered is pH dependent. The increase in metal adsorption with increase in pH is due to a decrease in competition between hydrogen ions and metal ions for the surface sites and also due to decrease in positive surface charge [16]. At a lower pH value, the removal Zn^{2+} of seems to be inhibited. This may be due to adsorption competition between hydrogen ions and Zn^{2+} on the available adsorption sites, because at low pH the medium contains a high concentration of hydrogen ions rather than Zn^{2+} .

3.7 Effect of temperature

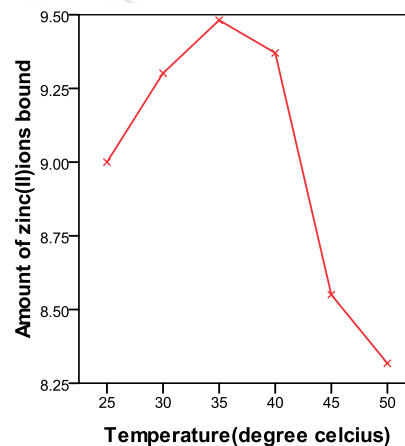


Figure 6: Effect of temperature on adsorption of Zn^{2+} at initial concentration of 10mg/L, pH 6.0

The effect of temperature on the adsorption of Zn^{2+} onto *Pennisetum clandestinum* biomass is shown in figure 6. The results show that there was an increase in the amount of the Zn^{2+} adsorbed when the temperature was increased up to $35^\circ C$ thereafter there was a decline. [19] in their study on adsorption of Zn (II) ions on *Carica papaya* root powder obtained similar results. They suggested that the enhancement of the adsorption capacity when temperature is increased could be due to increased mobility and diffusion of ionic species. The decline in adsorption capacity may be as a result of deterioration of the material at high temperatures [7].

3.8 Effect of initial concentration

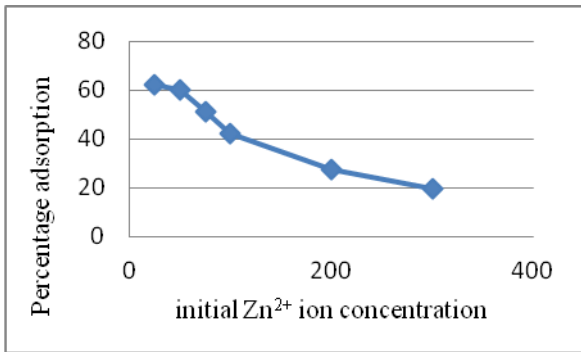


Figure 6: Effect of initial concentration at pH 6, temperature 25±0.5°C

The effect of initial concentration on adsorption of Zn²⁺ is shown in figure 6. The results show that percentage adsorption decreased with increase in initial concentration. The adsorbent has a limit number of active sites, and fewer of them are available at equilibrium sorption at higher Zn²⁺ loading levels. Furthermore metal ions are left unabsorbed in solution due to the saturation of binding sites. For a given adsorbent dosage, the amount of metal ion adsorbed per unit area of the adsorbent removal of the metal ions decreased with an increase in the initial concentration. On the other hand increase in adsorption capacity was realized as the initial concentration was increased. This is because a higher metal concentration means a greater driving force for mass transfer from the aqueous solution to the solid adsorbent.

3.9 Adsorption isotherms

Figures, 7, 8, 9 and 10 show the fits of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms for adsorption of Zn²⁺. Table 2 gives a summary of the parameters for the isotherms.

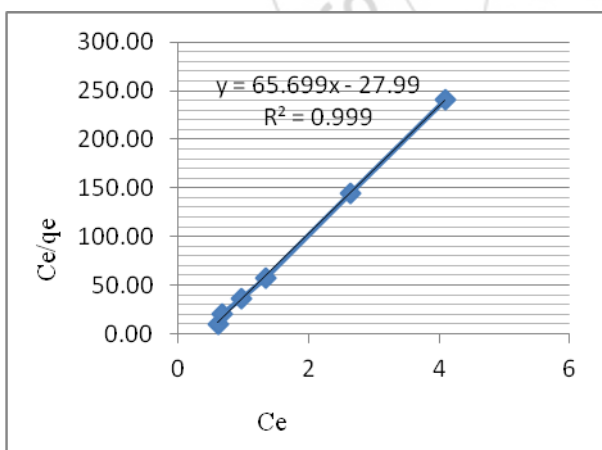


Figure 7: Linear plot of Langmuir biosorption isotherms for adsorption of Zn²⁺ at initial concentration of 10 mg/L, pH 6.0, temperature, 25±0.5°C and adsorbent dose of 2 g/L.

Table 3: Parameters for Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms

Isotherm	Parameters	Zn ²⁺
Langmuir	K _L S/mg	0.03
	q _{max} Mg/g	25.34
	R _L	3.98
	R ²	0.99
Freundlich	K _F (L/g)	1.90
	$\frac{1}{n}$	0.91
	R ²	0.96
Temkin	K _T (L/g)	0.16
	B _T (S/mol)	89.44
	R ²	0.98
Dubinin-Radushkevich	K _{ad} (Mol ² /Kj ²)	-2E-05
	q _s (Mol/j)	147.20
	E	2.24
	R ²	0.89

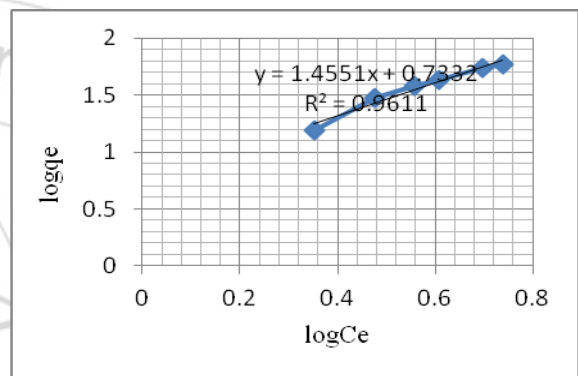


Figure 8: Linear plot of Freundlich adsorption isotherms for adsorption of Zn²⁺ initial concentration of 10 mg/L, pH 6.0, temperature, 25±0.5°C and adsorbent dose of 2 g/L.

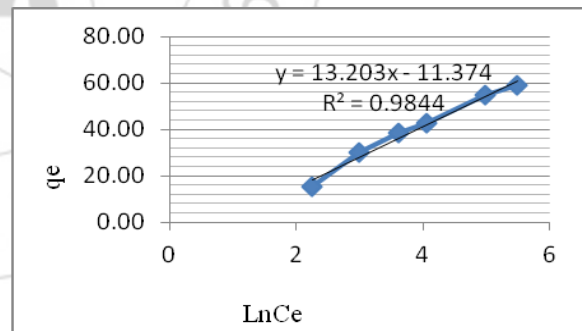


Figure 9: Temkin isotherms for adsorption of Zn²⁺ at initial concentration of 10 mg/L, pH 6.0, temperature, 25±0.5°C and adsorbent dose of 2 g/L.

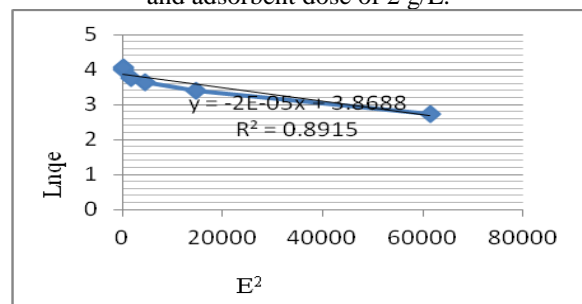


Figure 10: Dubinin Radushkevich isotherm for adsorption of Zn²⁺ at initial concentration of 10 mg/L, pH 6.0, temperature, 25±0.5°C and adsorbent dose of 2 g/L.

The results indicate that the R^2 values for Langmuir and Freundlich fitting for Zn^{2+} adsorption were 0.99 and 0.96 respectively. While the R^2 values for Temkin and Dubinin Radushkevich were 0.98 and 0.86 respectively. The results suggest that Langmuir fits better followed by Temkin, Freundlich, and lastly Dubinin Radushkevich isotherms. The high R^2 for Langmuir adsorption indicates surface homogeneity of the adsorbent and monolayer adsorption [20]. The separation factor R_L was found to be 3.98. This suggests that the adsorption is favorable and that the material under investigation may be suitable for adsorption. This also implies that we have Van der Waals attractions bonding the adsorbent and adsorbate particles. The energy of adsorption for the *Pennisetum clandestinum* was found to be 2.24 kJ/mol. This suggests that, physical adsorption dominates the process of adsorption over a uniform surface.

3.10 Kinetics of Zn^{2+} adsorption

Table 4: Parameters of first order Lagergren and Pseudo second order kinetic models.

First order Lagergren		Pseudo second order	
K_L	R^2	K'	R^2
0.036	0.96	0.18	0.99

The linear regression R^2 the result show that pseudo second order gave a better fit than first order Lagergren. The adsorption of the metal ions increases sharply at the beginning of the process followed by a slower uptake as the equilibrium is approached. This is probably due to a larger surface area of the adsorbent available. According to [21] the metal-biosorbent reactions may be the rate limiting step.. [22], made a similar observation when they assessed metal sorption by the marine algae.

3.11 Desorption studies

Biosorbent	Cycle 1	Cycle 2	Cycle 3	Cycle 4
<i>Pennisetum clandestinum</i> biomass	68.0	52.40	48.60	33.20

After 4 desorption cycles the percentage desorption dropped from 68 to 33 %. This could be attributed to the deterioration of the material with time [23].

4. Conclusions

The results of this work indicate that *Pennisetum clandestinum* biomass is a promising material for sequestering heavy metal from industrial effluents. adsorption data fitted the Langmuir model and the maximum adsorption capacity q_{max} was found to be 25.34 Mg/g. Kinetic analyses showed that the adsorption followed a pseudo second order.

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