

ZINC UPTAKE FROM AQUEOUS SOLUTIONS USING *MORINGA OLEIFERA* SEEDS AND COMMERCIAL ACTIVATED CARBON

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Abstract

Batch experimental studies were conducted to investigate the adsorption of zinc ions on Moringa oleifera seed (MOS) adsorbent in comparison with commercial activated carbon (CAC). The effects of adsorbent dose (0.2-1.2g) and contact time (20-120min) were evaluated. Metal removal efficiencies increased with increase in adsorbent dose to 38 and 54% for MOS and CAC respectively. CAC provided better metal removal, however the MOS was not pretreated before use. The Langmuir isotherm best described the adsorption process, with MOS and CAC having maximum monolayer adsorption capacities of 0.735 and 1.249 mg/g respectively. The adsorption kinetics followed the pseudo-second order model. Overall, MOS can be applied in the removal of zinc ions from aqueous solutions. However the relatively low adsorption capacities and removal efficiencies achieved highlight the need for chemical pre-treatment and system optimization to improve the performance.

Keywords: Zinc, Moringa seeds, Adsorption, Isotherms, Activated carbon, Kinetics

1. Introduction

Heavy metals pollution from industrial effluents is a major environmental problem [1]. These metals are persistent, non-biodegradable and harmful to humans and animals [2]. Hence, heavy metal removal is a critical aspect of industrial wastewater treatment before discharge. Conventional metal removal methods include chemical precipitation, flotation, coagulation-flocculation, ion-exchange and adsorption [1-2]. Chemical coagulation and precipitation are commonly associated with excessive sludge generation. Adsorption is an effective method of heavy metal removal, with activated carbon being the most widely used. However due to the relatively high cost of activated carbon, several studies have focused on the use of low-cost adsorbents, with promising results [3].

Moringa oleifera is a tropical tree which is widely cultivated for diverse nutritional and medicinal applications. The seed consists of 34.1% protein, 15% carbohydrate and 15.5% lipids [4]. The active agents present in the seeds have been identified as proteins with cationic peptides consisting of positively charged amino acids and glutamine residues with molecular weights ranging from 6-16kDa [5-6]. Moringa leaves, seeds, husks, pods, bark and biomass have been applied in the removal of some metal ions from aqueous solutions due to its low-cost and abundance, with varying adsorption capacities and removal efficiencies reported [3, 7-12]. Some researchers investigated the use of chemically activated moringa seed powder for the removal of lead and chromium from aqueous solutions [9]. The adsorption of iron and manganese using moringa seed husk was evaluated with removal efficiencies >80% reported [12].

The aim of this study was to investigate the removal of zinc ions from aqueous solutions using raw moringa seed powder in comparison with commercial activated carbon. The effects of adsorbent dose and contact time were studied and the adsorption process was evaluated using Langmuir and Freundlich isotherms and pseudo –first order and pseudo-second order kinetic models.

2. Materials and Methods

2.1. Preparation of Adsorbents and Aqueous Solutions

Moringa oleifera seeds (MOS) were collected from a tree in a household yard. The husks were removed and the seeds were rinsed thoroughly with distilled water to remove dirt. They were sun-dried and ground to obtain fine moringa seed powder. The commercial activated carbon (CAC) used was purchased from a chemical and reagent shop.

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Zinc(II)chloride salt was dissolved in distilled water to prepare stock solution. Working solutions were prepared by appropriate dilutions to achieve the required metal concentrations. Hydrochloric acid was used for pH adjustment. All reagents used were of analytical grade.

2.2. Batch Adsorption Experiments

Batch adsorption experiments were conducted to investigate the performance of the adsorbent. All adsorption experiments were conducted at room temperature (28-30°C). The pH of metal solutions was adjusted to 5 to prevent precipitation of metal ions at higher pH values or competition for binding sites between metal ions and hydrogen ions at lower pH values [13]. The pH was adjusted using 1M HCL or NaOH solution.

The effect of adsorbent dosage was evaluated by adding varying weights of adsorbent (0.2-1.2g) to 50mL solutions with initial metal ion concentration of 35.5mg/L. The solutions were agitated for 120 minutes using magnetic stirrers. The effect of contact time was investigated by adding 1.2 g of adsorbent to 50mL solutions with initial metal ion concentration of 35.5mg/L. The samples were stirred for 20, 40, 60, 80 and 120 minutes. Samples were withdrawn from the solutions at the end of each experimental run. They were filtered using a Whatman No1 filter paper, acidified to pH<2 and refrigerated prior to metal analysis. The initial and residual metal concentrations were analyzed using an atomic absorption spectrophotometer (AAS).

The percentage metal adsorption was calculated using the formula:

$$\% \text{ Removal} = \frac{C_o - C_e}{C_e} \times 100 \quad (1)$$

The amount of metal ions adsorbed per unit mass of adsorbent (mg/g) was calculated using the formula:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where C_o and C_e are the initial and final metal concentrations of metal ions in aqueous solution (mg/L), V is the volume of solution (L) and m is the mass of adsorbent (g).

2.3. Adsorption isotherms

The Langmuir and Freundlich isotherms were used to evaluate the adsorption process. The Langmuir equation is based on the assumption of monolayer adsorption and is represented in the linearized form as [14]:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{C_e}{q_{max}} \quad (3)$$

The Linearized form of the Freundlich isotherm described multilayer adsorption over a heterogeneous surface and can be represented linearly as [14]:

$$\text{Log} q_e = \text{Log} k_F + (1/n) \text{Log} C_e \quad (4)$$

Where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_{max} is the maximum monolayer coverage capacity (mg/g), k_L is the Langmuir isotherm constant (L/mg), k_F is the Freundlich isotherm constant (L/mg) and n is a measure of adsorption intensity.

2.4. Adsorption kinetics

The pseudo-first and pseudo-second order kinetic models were used to fit the experimental data and to evaluate the adsorption kinetics. The pseudo-first order model which is based on the assumption of reversible interactions between the adsorbate and adsorbent is expressed as [15]:

$$\text{Log} (q_e - q_t) = \text{Log} q_e - (k_1 t / 2.303) \quad (5)$$

The pseudo-second order model which is based on the assumption of chemisorption as the rate limiting step is expressed in the linearized form as [15]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

Where q_e and q_t are the amount of metal ions adsorbed per unit mass of adsorbent at equilibrium and time t respectively (mg/g), k_1 is the pseudo-first order adsorption rate constant (L/min), k_2 is the pseudo-second order adsorption rate constant (g/mg min) and t is time(min).

3. Results and Discussion

3.1. Effect of Adsorbent Dose

The effect of adsorbent dose on the percent uptake of zinc ions was examined at pH 5 by varying the dose from 0.2 to 1.2g as illustrated in Figure 1. The removal efficiencies increased with increase in adsorbent dose from 8% (at 0.2g) to 38% (at 1.2g) for MOS and 12% (at 0.2g) to 54% (at 1.2g) for CAC across the range of doses studied.

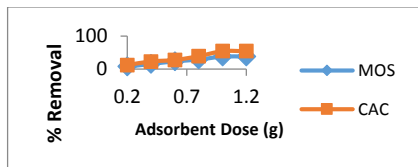


Figure 1: Effect of varying adsorbent dose on the percent removal of zinc ions by MOS and CAC.

The removal efficiency of CAC was greater than MOS at all adsorbent doses applied. Maximum uptake was observed at 1.2g for both adsorbents. Similar observations have been reported in the literature, with increased metal uptake attributed to the increased availability of active sorption sites [12, 16].

3.2. Effect of Contact Time

The contact time is an important factor that influences metal adsorption. Figure 2 shows the percent removal of zinc ions from aqueous solutions by MOS and CAC as a function of contact time (20-120 min). It was observed that metal removal increased with increase in contact time. Metal uptake occurred rapidly within the first 60-80 minutes followed by slower adsorption from 80 to 120 minutes.

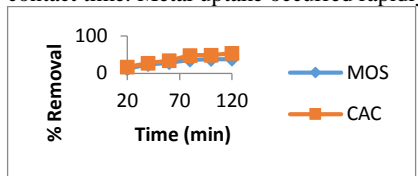


Figure 2: Effect of contact time on the percent removal of zinc ions by MOS and CAC.

The removal efficiencies of MOS and CAC were 38% and 54% respectively after 120 minutes of treatment. The initial rapid metal uptake was due to the availability of active sites for adsorption. However as more accessible sorption sites were filled, the rate of adsorption decreased [17].

3.3. Adsorption Isotherms

The experimental data were fitted using the Langmuir and Freundlich isotherms as shown in Figures 3 and 4. The isotherm parameters are presented in Table 1. The Langmuir isotherm clearly provide a better fit for the MOS ($R^2=0.9513$) and CAC ($R^2=0.7597$) adsorption data based on the correlation coefficients. The Langmuir isotherm is based on the assumption that adsorption is homogeneous with monolayer adsorption occurring on a fixed number of sites with no interaction between adjacent molecules [14]. The maximum monolayer capacities were 0.735 and 1.249mg/g for MOS and CAC respectively. Furthermore $n>1$ indicates that a physical process was favorable [18].

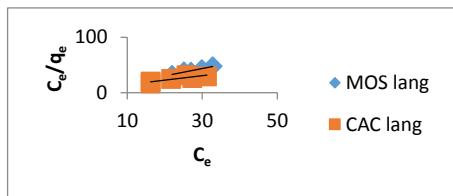


Figure 3: Langmuir isotherm plots for the adsorption of zinc ions on MOS and CAC.

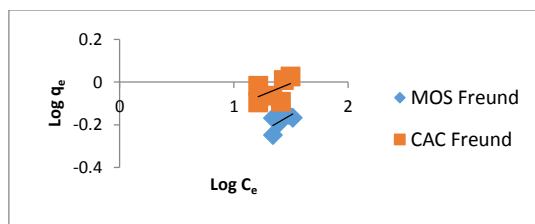


Figure 4: Freundlich isotherm plots for the adsorption of zinc ions on MOS and CAC

Table 1: Langmuir and Freundlich isotherm parameters

Adsorbent	Langmuir			Freundlich		
	$q_{max}(mg/g)$	k_L	R^2	k_F	$1/n$	R^2
MOS	0.735	0.485	0.9513	0.2423	0.3075	0.3546
CAC	1.249	0.122	0.7597	0.4645	0.2177	0.2475

3.4. Adsorption Kinetics

The efficiency of metal uptake is dependent on the rate of transfer of the ions from the solution to the adsorbent surface. The pseudo-first order and pseudo-second order models were used to analyze the adsorption data as shown in Figures 5 and 6. The kinetic parameters are shown in Table 2. The pseudo-second order model provided a better fit as shown by the higher R^2 values of 0.9603 and 0.9483 for MOS and CAC respectively. These results suggest that chemisorption may be the rate limiting step, thus implying that chemical interactions between the metal ions and the adsorbents led to the formation of strong covalent bonds [15]. Some metal removal studies using a wide range of adsorbents have also reported higher correlations for the pseudo-second order model [11, 14, 18].

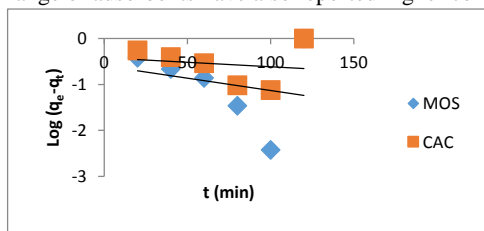


Figure 5: Pseudo-first order kinetic plots for the adsorption of zinc ions on MOS and CAC.

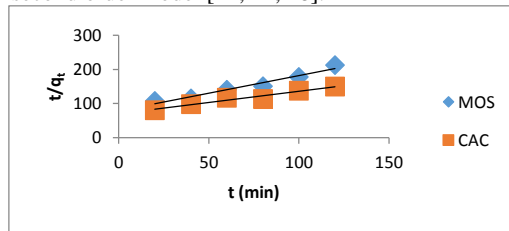


Figure 6: Pseudo-second order kinetic plots for the adsorption of zinc ions on MOS and CAC.

Table 2: Pseudo-first and pseudo-second order kinetic constants

Adsorbent	Pseudo-first order			Pseudo-second order		
	k_1 (L/min)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
MOS	-0.012	0.255	0.0552	0.014	0.966	0.9603
CAC	-0.004	0.379	0.0273	0.006	1.525	0.9483

4. Conclusion

This study focused on the removal of zinc ions from aqueous solutions using *Moringa oleifera* seed powder (MOS) and commercial activated carbon (CAC). The effects of adsorbent dose and contact time on metal removal were investigated. The removal efficiencies increased with adsorbent dose and contact time for both adsorbents studied, with the CAC providing higher levels of efficiency. The maximum uptake was 38 and 54% for MOS and CAC respectively at an initial zinc concentration of 35.5mg/L and adsorbent dose of 1.2g. The Langmuir isotherm provided a better fit for the experimental data, with maximum monolayer adsorption capacities of 0.735 and 1.249 mg/g for MOS and CAC respectively. The adsorption kinetics followed the pseudo-second order model, thus indicating that chemisorption was the most probable rate limiting step. The relatively low adsorption capacities and removal efficiencies achieved highlight the need for chemical pretreatment to increase the adsorption capacity of MOS by ‘opening up’ the sorption sites and system optimization to improve treatment outcomes.

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