

REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION USING MORINGA OLEIFERA PODS AS BIOSORBENT

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ABSTRACT

Moringa oleifera pod was prepared as abiosorbent to remove Chromium (VI) metal in an aqueous solution. The *Moringa oleifera* pod powder was characterized with FT-IR (Fourier transform Infrared) which shows the presence of nitro, carbonyl, and hydroxyl groups. The effects of varying operational parameters like pH, contact time, initial ion concentration, temperature, and adsorbent dosage were studied. The maximum bio-sorption capacity of the biosorbent was observed at pH 2 with 98.72%. The adsorption isotherm was studied at 30°C and at a constant initial concentration of the Chromium (VI) metal. The Langmuir and Freundlich isotherms were adopted to analyse the equilibrium data obtained. The adsorption of Chromium(VI) metal unto *Moringa oleifera* pod biosorbent conforms to both the Langmuir and Freundlich isotherms with the R² value of 0.9873 and 0.9731 respectively. This study suggests that *Moringa oleifera* pod has a potential as a good biosorbent for the removal of Cr (VI) from wastewater.

KEYWORDS: *Moringa Oleifera* Pod, Chromium (VI) Ion, Adsorption Isotherm, Biosorption.

INTRODUCTION

The environmental pollution and degradation resulting from the excessive discharge of hazardous heavy metals is at an alarming rate. They are mostly released as effluents from the industries like mining, metallurgical work, electroplating, tanning, metal finishing, battery manufacturing, and chemical manufacturing [1]. These heavy metals are not like organic pollutants that can be easily degraded [2], they tend to pose a long-term hazard to the environment due to their bioaccumulative nature. Some of these heavy metals that are toxic

to humans and the environment are Nickel (Ni), Lead (Pb), Iron (Fe), Mercury (Hg), Copper (Cu), Zinc (Zn), Manganese (Mn), Chromium (Cr), etc. These metals have a high level of toxicity even at low concentration and they are always present in the wastewater of most industrial processes, so these have brought about more environmental concerns due to their toxicity even at low concentrations [3]. Chromium is found primarily as hexavalent and trivalent in the aquatic environment [4].

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Chromium is relatively non-toxic in the trivalent state and is an essential trace nutrient in the diet of human, but can become extremely dangerous when it is in higher concentrations. The hexavalent Chromium is highly toxic and its effect includes nose bleeding, skin rashes, infection of the respiratory tract, hepatic diseases, cancer of the lung and immune system suppression [5]. Chromium gets into the human body through different means such as breathing, skin contact, eating or drinking chromium-contaminated substances. The methods that have been adopted for the removal of these metals include membrane separation, ion exchange, and chemical precipitation are expensive with very low selectivity and ineffectiveness in removing the metals completely [6]. This has instigated researches on treatment technologies that are economically viable and environmentally sustainable. From recent studies heavy metals have been shown to be effectively removed with low-cost agricultural waste products like Sugarcane bagasse [7], palm pressed fibers and coconut husk [8], rice hull [9], water fern *Azolla filiculoidis* [10], oil palm shell [11], peat moss [12], Maize leaf [13], Corn Cobs [14], duckweed *Wolffia globosa* [15], Coconut husk [16], banana and orange peel [17], modified banana peels [18] neem bark [19], *Rhizopus nigricans* [20]. With chemical modification and stability, adsorption capacity of adsorbents can be improved. The aim of this study was to assess the effectiveness of using *Moringa oleifera* pods as a biosorbent to remove Chromium (VI) metal from aqueous solution by varying conditions of a solution such as pH, contact time, adsorbent dosage, initial ion concentration, and temperature of the system.

MATERIALS AND METHODS

ADSORBENT COLLECTION AND PREPARATION

The Adsorbent (*Moringa oleifera* pods) were collected from farm yards in Akure, Ondo state,

Nigeria. The pods were separated from debris and sand particles and then dried for about 1 week. The dried pods were pulverized to powdery form with a mechanical grinder. A method used in a previous research [21] was modified and employed to treat the biosorbent. 100g of the biosorbent was then treated with 2000ml of 0.1M of HNO_3 with a continuous stirring for 2 hours in order to remove any hard metals as well as improving the surface area of the biosorbent. The resulting solution was washed with 500ml of distilled water for three times and then sun-dried for 6 hours. 70g of the bio-sorbent left after the acid treatment was extracted with 400ml of methanol for the removal of organic and inorganic matter present at the surface of the sorbent. This process was carried out for about 150 minutes. The pH of the biosorbent was adjusted to 7 with 0.1M NaOH, rinsed with distilled water and then dried in the oven for 1 hour. The prepared samples were placed in an air-tight container and placed in a refrigerator at 4°C

PREPARATION OF CR (VI) SOLUTION

The 1000ppm stock solution of **Cr(VI)** was prepared by weighing 5.657839g of (K_2CrO_7) on a weighing balance and diluting with distilled water in a 2litre conical flask to the mark. Working solutions of several concentrations were prepared from the stock solution by diluting factor formula.

$$C_1V_1 = C_2 \quad \text{eq. 1}$$

Where V_1 , C_1 , V_2 , and C_2 , represents the initial volume, initial concentration, final volume and final concentration respectively.

BIOSORPTION INVESTIGATION

2.5ml of the stock solution was placed into a conical flask of 50ml and diluted with distilled water up to the mark to prepare the working solution of 50 ppm. Furthermore, 1g of *Moringa oleifera* pods was added at a temperature of

30°C and then agitated for 10 minutes. The pH of the medium was investigated by adjusting the pH using 0.1 M HCl and 0.1 M of NaOH through a pH range of 1.5-6.0.

2ml of the aliquots were taken from the resulting solution, diluted with 25ml of distilled water and the solutions were decanted to remove adsorbed particles and filtered. The filtrates were then analysed with Atomic absorption spectroscopy for the determination of the concentration of chromium ion in the solution. The effect of various parameters such as contact time, adsorbent dosage, initial metal ion concentration and temperature were carried out following the same procedures and experimental conditions.

The percentage adsorption was determined by using the equation below:

$$\frac{C_0 - C_e}{C_0} \times 100 \quad \text{eq.2}$$

Where C_0 and C_e represent the initial concentration and final the concentration of Chromium (VI) ion in the solution respectively.

RESULT AND DISCUSSION

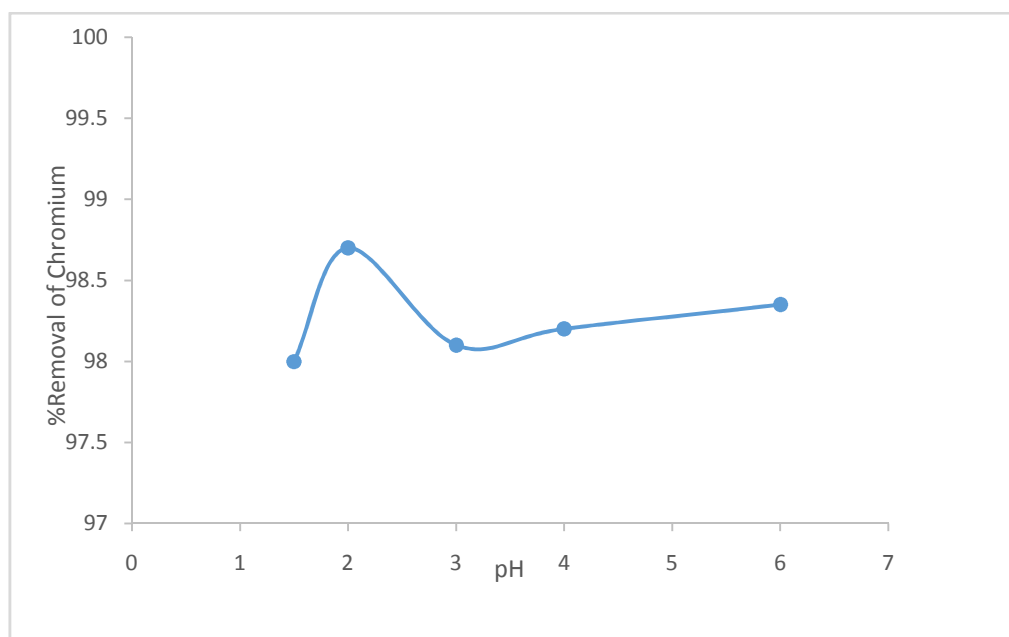


Figure 1. Effect of pH on Cr (VI) ion Adsorption with *Moringa oleifera* pods. Experimental conditions: Initial Chromium solution concentration-50 ppm, *Moringa oleifera* seed powder dosage- 1 g, Time- 10 min, Temperature- 30°C, pH 1.5-6

EFFECT OF PH

The effect of pH on the adsorption of Cr(VI) by *Moringaoleifera* pods is shown in Figure 1. The curve can be divided into three stages. The first stage represents a sharp increase in the percentage adsorption of the metal ion between pH 1.5 and 2, with maximum adsorption at pH of 2. At an acidic pH of 2, the adsorption of Cr (VI) was observed to be highest because the adsorption surface is highly protonated and this results in the rapid removal of HCrO_4^- from the solution because of an electrostatic interaction based adsorption [23]. The pH 2 was also observed as the pH of maximum adsorption from similar research done by [21] using *Moringa oleifera* as biosorbent for the removal of Cr(VI) and [23] using Green Moringa Tea Leaves as biosorbent for the removal of Cr(VI) from aqueous solution. The second stage showed a sharp decrease in the percentage of adsorption from pH 2 to 3. Moreover, when pH is increased, surface protonation decreases and this is associated with the decrease in the adsorption at pH above 2.

Finally, in the third stage of the curve, the percentage of adsorption increases gradually from the pH of 3. The adsorption of Cr(VI) is pH dependent and the pH of the solution will determine which of the species HCrO_4^- , H_2CrO_4 , CrO_4^{2-} , or $\text{Cr}_2\text{O}_7^{2-}$ will be dominant. At the pH of 2, Cr(VI) has a dominant form of HCrO_4^- , but at $\text{pH} > 7$ its dominant form is CrO_4^{2-} based on the values of pK_a [24] [25]. There is as well strong competition for the available site on the adsorbent between OH^- and CrO_4^{2-} at higher pH and this will result in decrease of available site for adsorption of Cr(VI), showing the decrease in the effective removal of Cr(VI). It can be deduced that adsorption of the metal ion is greatly achieved in a more acidic medium using the adsorbent.

EFFECT OF CONTACT TIME

The percentage removal of Cr(VI) from the aqueous solution with time is shown in Figure 2. By varying the contact time, percentage efficiency of the adsorbent with time was

investigated. The result revealed a rapid uptake of Cr(VI) by the adsorbent from 0-15 minutes followed by a steady uptake from 15-60 minutes. This behaviour showed that great amount of adsorption was achieved between 0-15 minutes. Also, increase in contact time results in the increase in the amount metal adsorbed onto the adsorbent until a point where the available adsorption sites present on the adsorbent is getting saturated with the biosorbent. This aforementioned point is assumed to be the point where the amount of metal adsorbed onto the biosorbent from the solution were in a dynamic equilibrium state with the amount being adsorbed from the biosorbent into the solution. A similar observation was obtained by [21] where they used *Moringa oleifera* as biosorbent for the removal of Cr(VI), and [26] using biomass obtained from *Moringa oleifera* for the removal of Pb(II) and Cr(III). This is an important result because equilibrium time is an imperative parameter for the economical treatment of wastewater system [27].

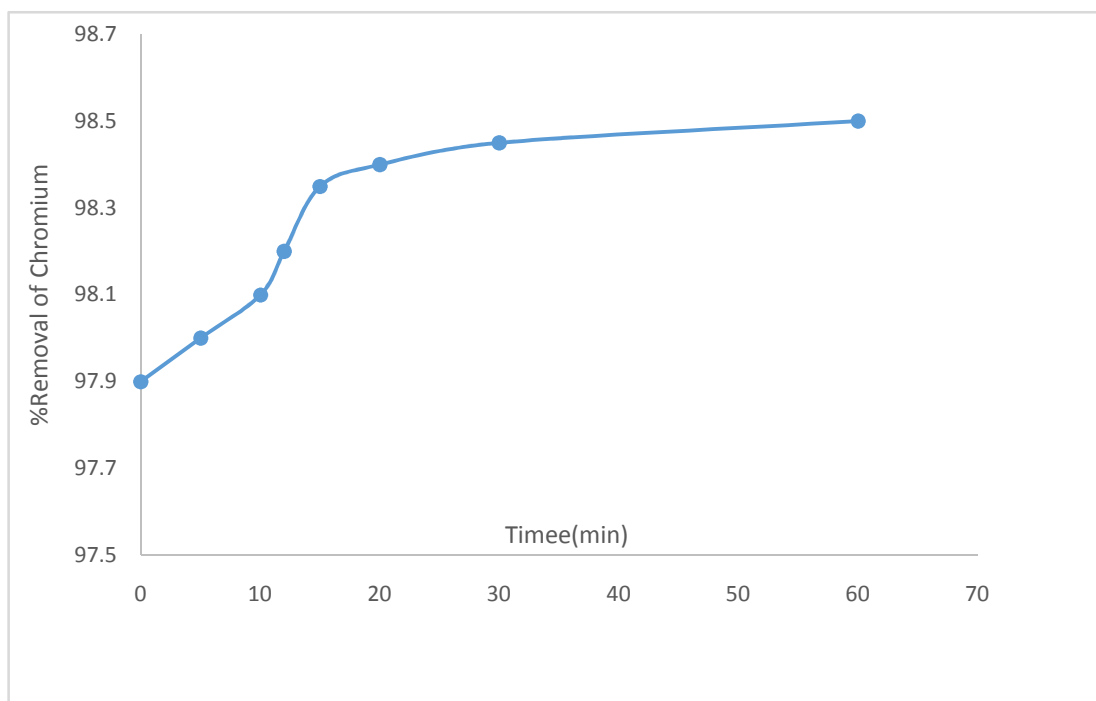


Figure 2. Effect of Contact time on Cr(VI) ion Adsorption with *Moringa oleifera* pods. Experimental conditions: Initial Chromium solution concentration - 50 ppm, *Moringa oleifera* seed powder dosage- 1 g, pH 2, Temperature- 30°C, Time- 0-60 min

EFFECT OF ADSORBENT DOSAGE

The relationship between the percentage removal of Cr (VI) and adsorbent dosage was revealed by Figure 3. From the curve, it can be deduced that the rate of adsorption of the metal ion increased progressively with increase in adsorbent dosage. The Increase in the adsorption of the metal ion with increasing adsorbent concentration might be attributed to the higher

biomass/metal ratio which will result to a higher metal uptake capacity of the adsorbent causing more available sites for metal increases as the amount of adsorbent increased. Furthermore, this phenomenon agrees with similar researches done by [28] on Cadmium sorption by *Moringastenopetala* and *Moringa oleifera* seed powders, and [18] on the removal of Cr (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent.

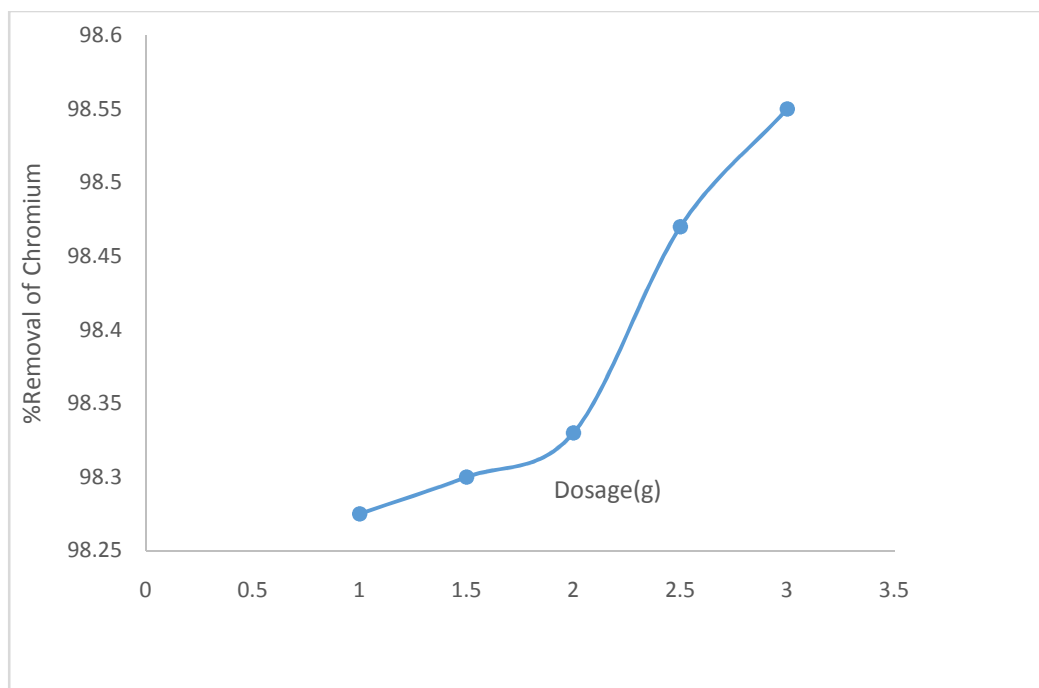


Figure 3. Effect of Adsorbent Dosage on Cr (VI) ion Adsorption with *Moringa oleifera* pods. Experimental conditions: Initial Chromium solution concentration- 50 ppm, *Moringa oleifera* seed powder dosage- 1 g, pH 2, Temperature-30°C, Time- 0-60 min

EFFECT OF INITIAL METAL ION CONCENTRATION

The effect of initial metal ion concentration on the rate of adsorption was displayed by Figure 4. It was observed that increase in the concentration of the adsorbate gave a corresponding increase in the percent adsorption. This observation could mean that as the concentration of the adsorbate increases, the number of available molecules per binding site of the adsorbent increases. The attendant

effect of this is a possibility of higher binding of the molecules to the adsorbent (i.e. the probability of chemical interaction between the adsorbent and the adsorbate is enhanced due to the high availability of molecules of adsorbate in solution). The overall trend is consistent with the observed phenomenon. This observation is supported by similar works done by [29], [30], [31], and [32]. They also observed a progressive increase in the adsorption of metal ions from aqueous solution as the adsorbate concentration was increased.

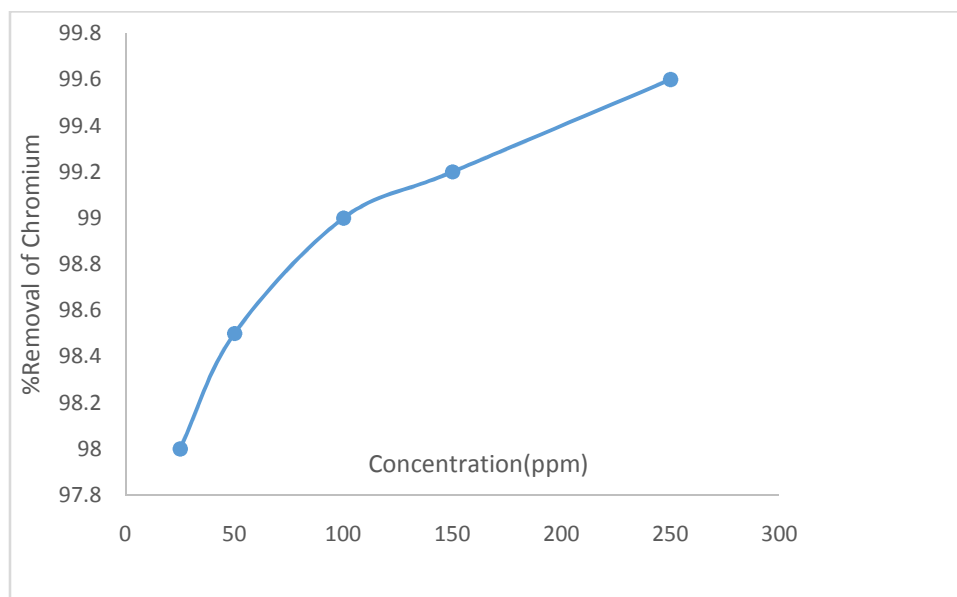


Figure 4. Effect of Cr (VI) ion concentration on Adsorption with *Moringa oleifera* pods. Experimental conditions: - *Moringa oleifera* seed powder dosage- 1 g, pH 2, Time- 0-60 min, Temperature-30°C, Cr (VI) concentration-25-250 ppm

EFFECT OF TEMPERATURE

The effect of temperature on the adsorption of Cr (VI) onto *Moringa oleifera* pod was reported by Figure 5. It was observed that the percentage adsorption of Cr(VI) increases with increase in temperature from 30°C to 70°C. Hence, the higher the temperature, the greater the rate and degree of adsorption. There is a linear

relationship between temperature and rate of reaction. This observation showed that the adsorption of Cr(VI) onto *Moringa oleifera* pods is an endothermic process. This observation corresponds to other similar research by [21] where it was observed that increase in temperature facilitated an increase in the rate of adsorption of the metal ion from the aqueous solution.

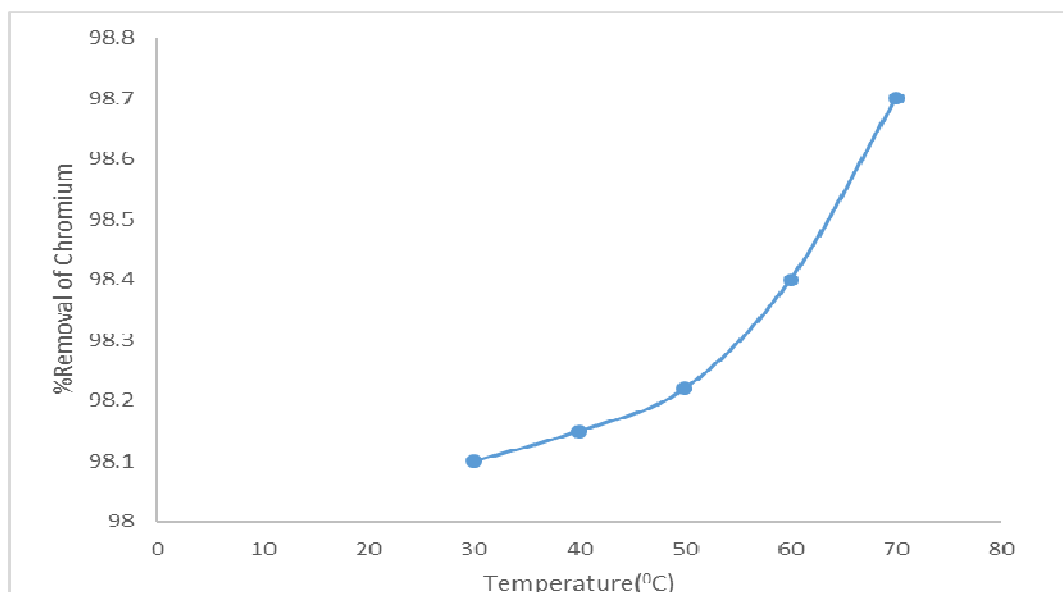


Figure 5. Effect of Temperature on Cr (VI) ion Adsorption with *Moringa oleifera* pods. Experimental conditions: Initial Chromium solution concentration- 50 ppm, *Moringa oleifera* seed powder dosage- 1 g, pH 2, Time- 0-60 min, Temperature-30-7

ADSORPTION ISOTHERM

The adsorption studies were carried out at a constant initial concentration of the Chromium metal. The Langmuir and Freundlich isotherms

were adopted to analyse the equilibrium data obtained. The amount of metal ion adsorbed onto carbon adsorbent (mg/g) was represented against the equilibrium concentration of metal ion in aqueous solution.

Table 1. Adsorption isotherm constants and coefficients

Langmuir Isotherm		Freundlich Isotherm	
Q _{max} (mg/g)	1.9346	N	-58.4795
K _L (Lmg ⁻¹)	5.8407	K _F	2.4502
R ²	0.9873	R ²	0.9731

THE LANGMUIR ISOTHERM

The model of Langmuir isotherm is defined by the assumption that the maximum adsorption is correspondent to a saturated monolayer of the molecules of adsorbate present on the surface of the adsorbent and that the adsorption energy is constant and that transmigration of adsorbate does not take place at the surface. This isotherm depicts the distribution of metal ions at equilibrium between the liquid and the solid

phases. The Langmuir adsorption isotherm can be represented by the following equation:

$$\frac{C_e}{Q_e} + \frac{1}{Q_m K_L} + \frac{C_e}{Q_e} \quad \text{eq. 3}$$

Where Q_e(mgg⁻¹) represents the amount of metal ion adsorbed at equilibrium, C_e (mgL⁻¹) represent the equilibrium concentration, K_L(Lmg⁻¹) and Q_m (mgg⁻¹) are the Langmuir constants which is related to the energy and capacity of adsorption respectively.

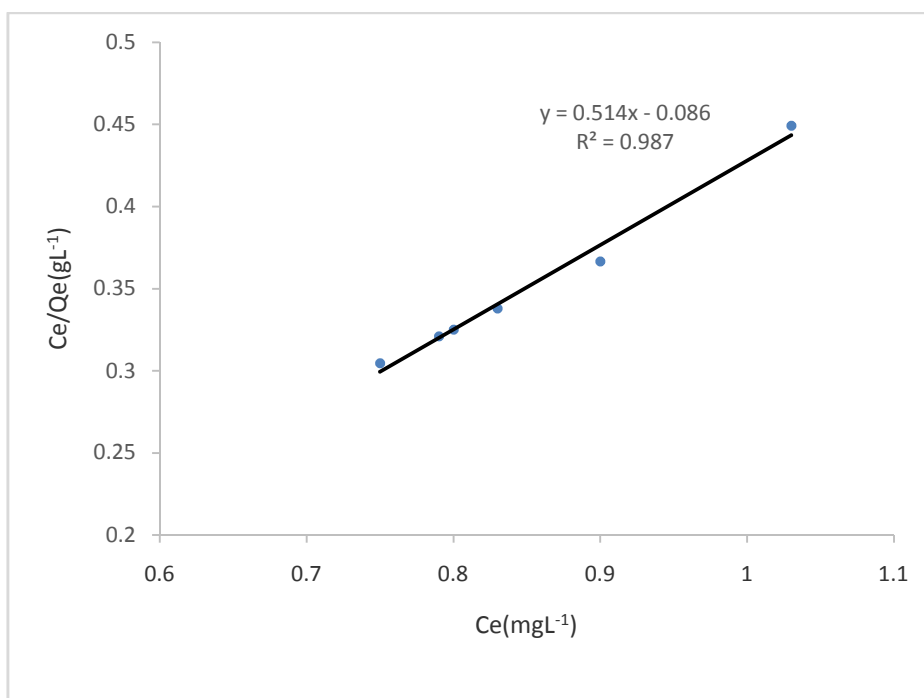


Figure 6. Langmuir isotherm for the adsorption of Cr(VI) on *Moringa oleifera* adsorbent

A plot of C_e/Q_e against C_e corresponds with the linearized Langmuir equation. The value of the correlation coefficient R² (0.9873) according to Figure 6 and Table 1 was close to 1. This confirms

that the data for the metal correlates with the Langmuir isotherm. The capacity of adsorption, Q_m defined as the maximum capacity of adsorption corresponds to the complete

monolayer coverage and this showed that the mass capacity of *Moringaoleiferapods* for Cr^{6+} is 1.9346 (Table 1). The chemistry of the metal (which includes parameters like charge, Pauling electro negativity an ionic radius), type of metal binding(covalent or electrostatic), and affinity for the binding sites determine the binding strength of the metal to a biomass [33].

THE FREUNDLICH ISOTHERM

The Freundlich model was used to estimate the adsorption intensity of the metal ions on the carbon adsorbent surface.

The Freundlich equation is given as:

$$Q_e = K_f C_e^{1/n} \quad \text{eq. 4}$$

This equation is given in a linearized form as follows:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{eq. 5}$$

Where K_f (mg/g) and n represents the Freundlich constants integrating every factor influencing the process of adsorption which includes intensity

and capacity of adsorption. The constants were calculated from the slope and the intercept of the graph derived from a plot of $\log Q_e$ against $\log C_e$ as shown in Figure 7.

From the plot of $\log Q_e$ against $\log C_e$, the slope of the graph is given as $1/n$ and the intercept given as $\log K_f$. The value K_f was calculated from the slope and n from the intercept of the graph, where the value of K_f was the antilog of the intercept and the value of n the inverse of the slope.

The Freundlich isotherm shows whether or not the adsorption process occurred with ease. The adsorption of $Cr(VI)$ onto *Moringa oleifera* pods follows the model of the Freundlich isotherm under the conditions of study with an R^2 value of 0.9731 (Figures 7 and Table 1).The n value of less than 1 showed that the biosorption of $Cr(VI)$ onto the biosorbent is a chemical process [26]. According to a previous research, n value for $Cr(VI)$ was gotten as -2.597, and it was then inferred from their research that the biosorption $Cr(VI)$ was favourable on *Moringa oleifera* [26].

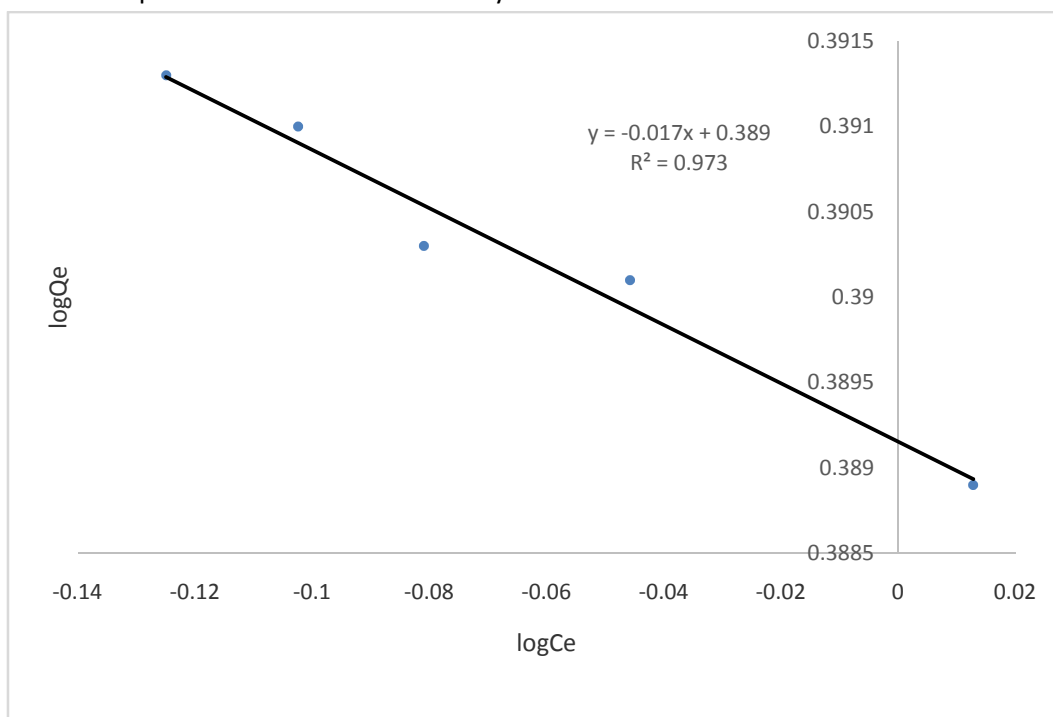


Figure 7. Freundlich isotherm for the adsorption of $Cr(VI)$ on *Moringa oleifera* adsorbent

CONCLUSION

Moringa Oleifera podsbiosorbent has a great potential for the removal of Cr(VI) from contaminated wastewater. The maximum biosorption capacity of the biosorbent was observed at pH 2 with 98.72%. The adsorption of chromium metal onto *Moringa oleifera* pod adsorbent conforms to both the Langmuir and Freundlich isotherms with the R^2 values < 1 and are dependent on parameters such as pH of the solution, contact time, metal ion concentration, and adsorbent dosage.

The values of R^2 for Langmuir is gotten as 0.9873 and 0.9731 for Freundlich indicating that the Langmuir isotherm model fitted better than the Freundlich. This study suggests that *Moringa oleifera* pod has a potential as a good biosorbent for the removal of Cr^{6+} from wastewater and Langmuir model can better be used to illustrate the biosorption of Chromium (VI) on this biomass.

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