

Aqueous Phase Removal of Chromium and Cadmium Using *Moringa oleifera* pod Adsorbents: Equilibrium and Kinetic Modeling

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Abstract: Unmodified and Citric acid adsorbents were prepared from *Moringa oleifera* seed pod, characterized and evaluated for aqueous phase removal of chromium and cadmium ions. The effects of operational parameters such as initial chromium and cadmium solution pH and adsorbent dosage on equilibrium sorption were studied. Adsorption isotherms (effects of metal ion and kinetic experiments), was performed at (25 °C) furnished some equilibrium and kinetic parameters, respectively. Percentage removal RE% for chromium UMMP(85.09) and MMP (92.45) and cadmium UMMP (68.22) and MMP(76.480). Comparatively it seems that the capabilities of the adsorbents to remove chromium and Cadmium ions varied as UMMP < MMP, Portraying MMP as the more potent of the experimental adsorbents. Adsorption kinetics obeyed closely pseudo-second-order model. Adsorption of chromium and cadmium ions was well described by Freundlich isotherm as indicated by higher regression coefficient ($R^2 = 0.993$). Chromium and Cadmium uptake increases with increase in solution pH for the adsorbent. The optimal pH for adsorption was attained at pH 7, Maximum adsorption capacity Q_{max} (mg/g) for chromium UMMP(17.00) and MMP (18.42) and cadmium UMMP(13.64) and MMP(15.30) respectively. The adsorbents show a promising applicability in removal of chromium and cadmium ions from aqueous effluents.

Keywords: Adsorption, *Moringa Oleifera* Pod, Kinetics, Equilibrium, Chromium and cadmium ion, Waste water remediation.

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I. Introduction

The contamination of water by toxic heavy metals through the discharge of industrial, mining and agricultural waste is a serious environmental problem. (1). Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (2) thus, becoming concentrated throughout the food chain. Their presence in the wastewater of several industrial processes, such as electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing, mining and battery manufacturing, has brought about more environmental concerns due to their toxicity even at low Concentrations (3). Metals which are significantly toxic to human beings and ecological environment, include arsenic (As), Chromium (Cr), Copper (Cu), Cadmium (Cd), Nickel (Ni) Lead (Pb), Manganese (Mn), Mercury (Hg), Zinc (Zn), Iron (Fe), etc. Excessive human intake of Cadmium (Cd) leads to damage of kidney and renal system, Skeletal deformation (Itai-Itai), Cardiovascular diseases and hypertension. Severe gastro intestinal irritation,. Muscular pain, anemia, teeth discoloration, loss of smell, necrotic changes in the liver and kidney also occurs. cadmium is a known carcinogen (4) Chromium exists primarily in trivalent and hexavalent state in aquatic environment. The trivalent Chromium is relatively non-toxic and is an essential trace nutrients in human diet, but the hexavalent Chromium is very toxic, being a mutagen and a potential Carcinogen (5). It also causes skin irritation resulting in ulcer formation. Over exposure to Cr (vi) leads to liver damage, pulmonary congestion and Oedema.

Removal of toxic heavy metals from waste water has conventionally been accomplished by various methods such as chemical precipitation, electrochemical reduction, solvent extraction, ion exchange, reverse osmosis, electrodialysis [6, 7, 8]. All these methods are very expensive. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent (9). Despite its extensive use in the water and waste water treatment industries, activated carbon still remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the introduction of low cost alternatives to commercially affordable activated carbon (10)

The low cost agricultural waste products are much widely being studied for their adsorption efficiency. These products are readily available at low cost. Research has been done on many materials like Sugar cane bagasse (11), rice hull [12], oil palm shell [13], neem bark (14), Coconut husk (15), Corn Cobs (16), banana and orange peel (17), Maize leaf (18), and different agricultural by products. Chemical modification improves the adsorption capacity and stability of adsorbents. The aim of this study is to study the feasibility of using Unmodified and Modified *Moringa Oleifera* seed pod as adsorbent for the removal of metal ions Cr(VI) and Cd (II) from waste water.

II. Materials And Method

Adsorption Experiment

All chemicals are of certified analytical grade. Cadmium Nitrate $Cd(NO_3)_2$, Potassium dichromate $K_2Cr_2O_7$, were used as the source of Cd(II) and Cr(vi) in the synthetic waste water. Instruments include Fourier Transform Infrared spectrophotometer (FTIR-8400S Shimadzu Japan), UV-visible Atomic absorption spectrophotometer (Jenway-6405spectra, Japan), analytical weighing balance (Adam Equipment Co, Ltd US), and Muffle furnace (Carbolite, UK), mechanical shaker (Heldolp Unimax 2010, Germany).

Preparation and characterization of adsorbent

Moringa oleifera pods were sourced from Idah Native town in Kogi State, Nigeria. The seeds were deshelled and the pods washed thoroughly with tapwater and rinsed with distilled water to remove debris and other impurities. The were sundried for 3 days and ground into powder with mortar and pestle and finally sieved with 2mm mesh filter paper. The sieved sample was then carbonized at a temperature of $300^{\circ}C$. for one hour, pulverized and sieved with 2 mm mesh to give Unmodified *M. oleifera* seed pod adsorbent (UMMP). Part of the carbonized *M. oleifera* seed pod was steeped in a 0.6 M Citric acid for 2 hours at $25^{\circ}C$ for chemical activation. The slurry was filtered and residue washed repeatedly with distilled water followed by oven drying, over night at $105^{\circ}C$ to give the Modified *M. oleifera* seed pod adsorbent (MMP) as adopted by 19)

Batch Adsorption Experiments

Standard Cadmium and chromium stock solution (1000mg/L) were prepared from there salts by dissolving 2.1032g of Cadmium Nitrate and Chromium by dissolving 2.827g of Potassium Dichromate in 1L of deionized water. The effect of solution pH on chromium and cadmium recovery was studied by treatment of 50-mL aliquots chromium and cadmium solution adjusted to different pH (3, 5, 7, 9 and 11) with 0.5-g of the adsorbents for 4 hour at laboratory temperature ($25^{\circ}C$). The effect of adsorbent dosage was investigated by contacting different masses (0.05, 0.1, 0.15, 0. 2 and 0.25g) of the adsorbents with 50 mL of the metal ion solution at a given pH 7. Effect of metal ion concentration developed at temperatures ($25^{\circ}C$) by dispersing separate 0.25-g portions of the adsorbents in 50-mL aliquots of each standard (100, 120, 140, 160, 180 200 mg/L) metal ion solution with the aid of a mechanical shaker for 4 hour. Adsorption kinetic experiments were performed by contacting 0.5-g portions of the adsorbents dispersed with 50-mL aliquots of 100 mg/L cadmium and chromium solutions at 30, 60, 90, 120, 150 and 180 min on a shaker at ($25^{\circ}C$). Residual metal ion concentrations in the solutions before and after adsorption were measured using Atomic absorption spectrophotometer following the manufacturer's specification. In all cases, the amount of metal ions recovery per gram of adsorbents, Q_e (mg/g) and removal efficiency, RE (%) were calculated using Equation (1) and (2), respectively (20, 21, 19)

$$Q(mg / g) = [(C_o - C) / m_a] V \quad (1)$$

$$RE(\%) = [(C_o - C) / C_o] \times 100 \quad (20)$$

Where C_o and C are the initial and residual metal ion concentrations (mg/L), respectively, V is the aliquot of metal ion solution used (L); and m_a is the mass of adsorbent (g) used for a particular batch treatment.

III. Results And Discussion

Effect of pH Solution

From figure (1) and (2) it clearly showed that percentage adsorption for *MMP* and *UMMP* increases with solution pH until equilibrium at pH7 was reached. The percentage removal and adsorption capacity of Cr(VI) on *MMP* and *UMMP* was found to be 92.45% and 18.49mg/g, and 85.06% and 17.0mg/g respectively. While for Cd(II) it was found to be 76.48% and 15.30mg/g for *MMP* and 68.22% and 13.64mg/g for *UMMP* respectively. The pH of the solution was found to have a great affinity on the adsorption of Cr(VI) and Cd(II)

ions. The adsorption increased sharply in the pH range 3 to 7 attaining equilibrium at pH 7. The lower adsorption capacity observed at low pH may be explained on the basis of electrostatic repulsive forces between positively charge H_3O^+ and the metal ions. At low pH values, the concentration of H_3O^+ is higher than that of the metal ions, and hence, these ions are adsorbed on the active sites of the adsorbent leaving the H_3O^+ ions. Competing effect of H_3O^+ decreased with increase of the pH until equilibrium is attained.

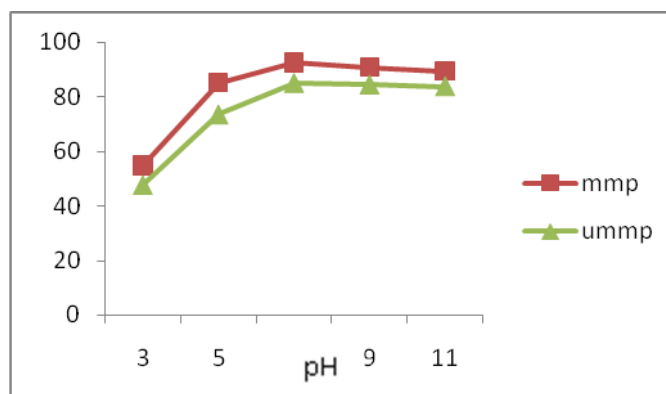


Figure 1 Effect of initial pH on Cr(VI) removal Onto MMP and UMMP.

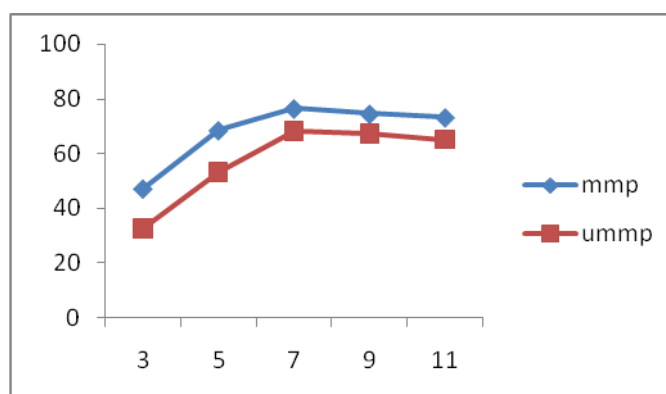


Figure (2) Effect of initial solution pH on Cd(II) on MMP and UMMP

Effect of Adsorbent Dosage

The adsorbent dosage was varied from 0.05-0.25g to study the effect of UMMP and MMP on the adsorption of Cr (vi) and Cd (II) respectively. The concentration of the metal ions was taken as 100mg/dm³ and other parameter were kept constant. The result is presented in figure (3) for Cr(VI) and figure (4) for Cd(II). Figure (3) shows the removal of Cr (vi) for UMMP and MMP The percentage adsorption increased from 38.80 to 85.06% for UMMP and 54.32 to 92.45% for MMP. Figure (4) shows the removal for UMMP and MMP for Cd(II) respectively. The percentage adsorption increased from 23.39-68.22% for UMMP and 37.47-76.48% for MMP. The data clearly shows that (MMP) is more effective than (UMMP) for the removal of metal ions.

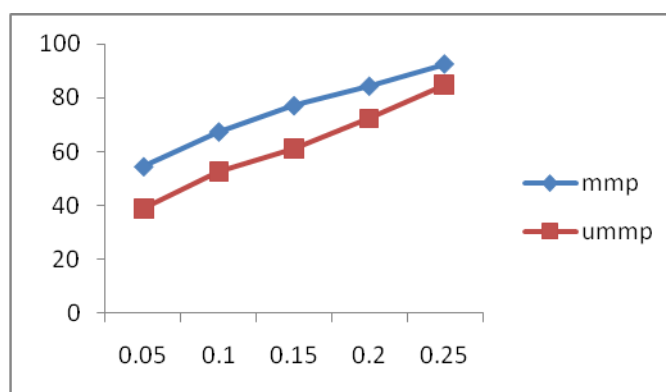


Figure: 3 Effect of adsorbent dose on Cr(VI) removal onto MMP and UMMP

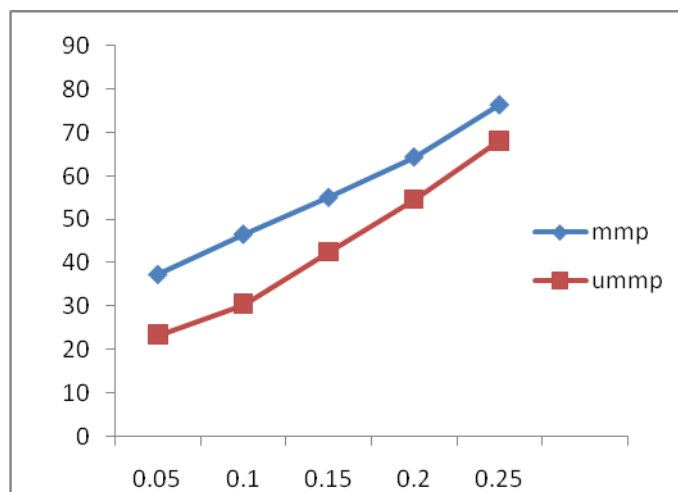


Figure 4: Effect of adsorbent dose on Cd(II) removal onto MMP and UMMP

3.2 Effect of initial metal ion concentration.

The effect of initial cadmium Concentration in the range of 100 to 200mg/dm³ on adsorption was investigated. From figure 5 and 6 it was evident that as the concentration of metal ions Cr(VI) and Cd(II) increased, the amount adsorbed was also increased but there was decrease in the percentage removal. This is because the initial metal ions concentration provides the necessary driving force to overcome the resistance to the mass transfer of metal ions between the aqueous phase and the solid phase (21) in the working initial concentration range (100mg/l < C_o< 200mg/l studied, amount adsorbed for Cr(VI) ranged from 18.49mg to 31.59mg/g for MMP and 17.01mg/g to 26.45mg/g for UMMP and 92.45% and 85.06% respectively. For Cd(II) the amount adsorbed ranged from 15.30mg/g to 20.11mg/g for MMP and 13.64mg/g to 17.98mg/g at 76.48% and 68.22% respectively. From the result it was observed that higher adsorptive capacities were recorded for Cr(VI) than Cd(II) ion for both adsorbents. Comparatively, the efficiency of metal ion removal was higher for MMP than UMMP. Higher adsorptive capacities recorded for MMP relative to UMMP explicable by the enhanced surface functionality achieved via citric acid modification.

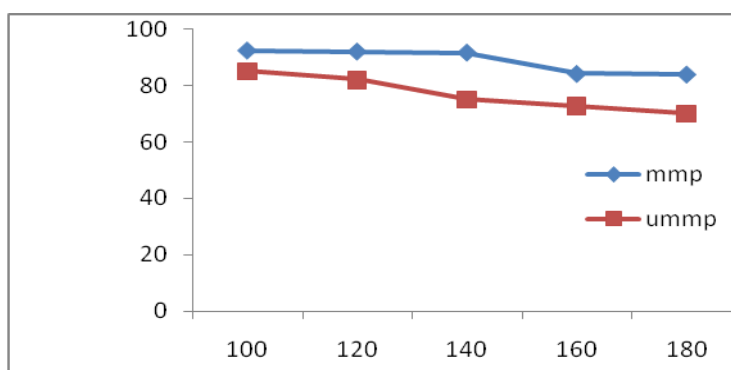


Figure 5: Effect of metal ion concentration on Cr(VI) removal onto MMP and UMMP

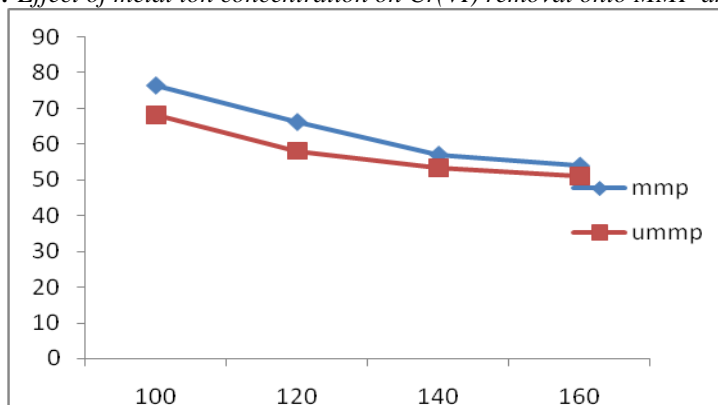


Figure 6: Effect of initial metal ion concentration of Cd(II) onto MMP and UMMP.

3.3 Effect of contact time:

The adsorption of Cr(VI) and Cd(II) increased with increasing contact time as shown in figure 7 and 8. The results revealed that the percentage removal for Cr(VI) onto MMP and UMMP increase with contact time until an equilibrium time of 120 minutes and the corresponding highest removal efficiency were 92.45% and 84.06% respectively. The percentage removal of Cd(II) onto MMP and UMMP also increased with contact time until equilibrium time of 150 minutes and the corresponding highest removal efficiency were 76.48% and 68.22% respectively. The time required to attain this state of equilibrium reflects the maximum Metal ion adsorption capacity of the adsorbent.

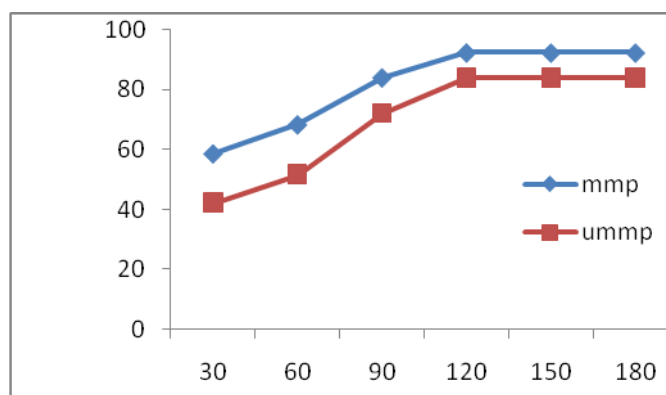


Figure 7: Effect of Contact time on Cr(VI) removal onto MMP and UMMP.

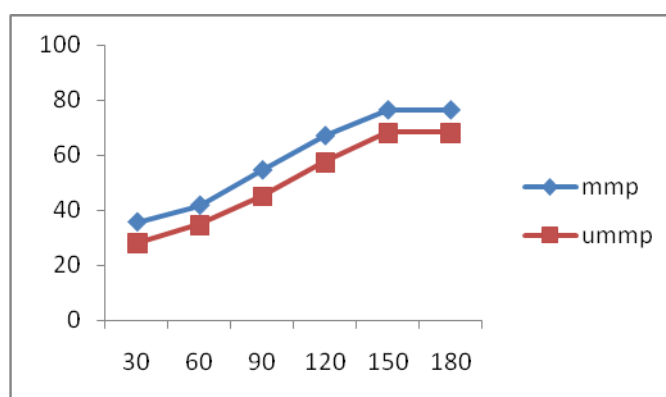


Figure 8: Effect of Contact time on Cd(II) removal onto MMP and UMMP.

Adsorption Isotherms

Adsorption equilibrium isotherms are basic requirements for designing any adsorption system. The adsorption isotherm indicates how the adsorbate distributes between the liquid phase and the solid phase when the adsorption process reaches equilibrium. Adsorption isotherm expresses the mathematical relationship between the quantity of adsorbate and equilibrium concentration of adsorbate remaining in the solution at constant temperature. In this study, adsorption data were analyzed with Langmuir and Freundlich isotherm models.

Langmuir Isotherm Model.

The linearized form of the Langmuir isotherm equation is;

$$\frac{C}{Q} = \frac{C}{Q_{\max}} + \frac{1}{K_L Q_{\max}}$$

Where, Q_e (mg.g^{-1}) represents the amount of adsorbate adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration (mg/L), Q_0 is the maximum equilibrium uptake (mg.g^{-1}) and ' K_L ' refer to the

Langmuir constant (L/mg), When C_e/Q_e was plotted against C_e , straight line with slope $1/Q_0$ was obtained (figure 9 and 10) indicating that the adsorption of metal ions on UMMP and MMP follows the Langmuir Isotherm. The Langmuir constants " K_L " and " Q_0 " were calculated from this Isotherm and their values are given in Table 1.

The Langmuir Isotherm can also be expressed by a separation factor (R_L) which is given by the equation

$$R_L = \frac{1}{1 + K_L C_0}$$

Where, K_L is the Langmuir constant and C_0 the highest metal ion concentration (mg/g). The value of R_L indicates the type of the Isotherm to be either unfavorable ($R_L < 1$) Linear ($R_L = 1$), favourable ($0 < R_L < 1$) or Irreversible ($R_L = 0$). In this work, the value of R_L was found to be less than 1 and greater than 0 indicating the favorable adsorption of Cr(vi) and Cd (II) ions for MMP and UMMP respectively.

3.4.2 Freundlich Isotherm

The well known logarithmic form of Freundlich model is given by the following equation

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration of the metal ions and K_f and n are Freundlich constants. The Plot of $\log q_e$ versus C_e (figure 9 and 10) gives a linear graph with a slope of $\frac{1}{n}$ and intercept of $\log K_f$. Freundlich constants (K_f and n) were calculated and recorded in Table (2).

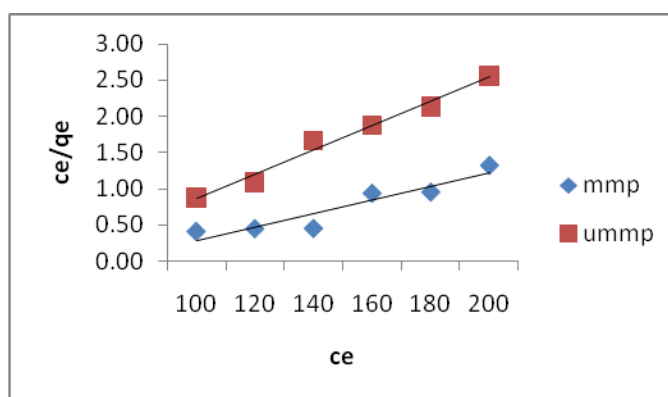


Figure 9: Linearized Langmuir isotherm adsorption of Cr(VI) onto MMP and UMMP

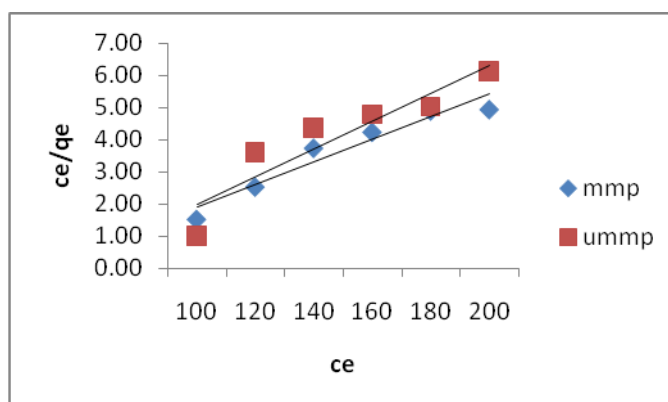


Figure 10: Linearized Langmuir Isotherm Adsorption of Cd(II) onto MMP and UMMP

Table 1: Langmuir Isotherm parameter for the adsorption of Cr(VI) and Cd(II) onto MMP and UMMP

Metal ions	Adsorbent	Qe mg/g	K_L (L/mg)	RL	R^2
Cr(VI)	MMP	2.985	0.634	0.016	0.982
Cr(VI)	UMMP	5.291	2.054	0.048	0.879
Cd(II)	MMP	1.422	0.591	0.017	0.931
Cd(II)	UMMP	1.156	0.779	0.013	0.857

Table 2: Freundlich Isotherm parameter for the adsorption of Cr(VI) and Cd(II) onto MMP and UMMP adsorbent.

Metal ions	Adsorbent	K_F (mg/l)	1/n	R^2
Cr (VI)	MMP	$7.5 \times 10^2 \cdot 0.104$	0.952	
Cr (VI)	UMMP	$6.0 \times 10^2 \cdot 0.086$	0.977	
Cd (II)	MMP	$4.49 \times 10^2 \cdot 0.052$	0.933	
Cd (II)	UMMP	$3.4 \times 10^2 \cdot 0.061$	0.956	

The higher regression values (table 1 & 2) showed that the equilibrium data for Cr(VI) and Cd(II) fitted well into both Langmuir and Freundlich isotherms. Based on the correlation coefficients (R^2), the equilibrium was slightly better fitted in the Freundlich adsorption isotherm than the Langmuir equation.

Adsorption Kinetics

The adsorption study was tested for two models, pseudo first order and pseudo second order model. The pseudo first order model; was studied with Lagergren equation; $\log(q_e - q_t) = \log q_e - K_1 t$ Where q_e is the amount of metal ion adsorbed (mg/g), q_t refer to the amount of metal ion adsorbed at any time, t (min), K_1 is the equilibrium rate constant of Pseudo-first-order adsorption in min. A linear graph of $\log(q_e - q_t)$ versus t was plotted and the constant value of K_1 and q_e were obtained from the slope and intercept as shown in table 3.

Pseudo second order kinetics; was studied with Blanchard equation; and the linearized equation is; $t/q_t = 1/K_2 q_e^2 + 1/q_e t$ a linear graph of t/q_t versus t was plotted and K_2 and q_e were calculated from the intercept and slope of the graph. The result is shown table (4). Based on the value of linear regression coefficient, R^2 , the value for Pseudo second order Kinetic model were higher than the First order Kinetic. The R^2 value for MMP and UMMP for Cr(VI) ion are 0.993 and 0.966 respectively while that of MMP and UMMP Cd(II) ions are 0.938 and 0.906. Samples with regression coefficient, (R^2) close or equal to one is accepted for a given model and relatively high R^2 value indicates that the model successfully describe the adsorption kinetics, Hence, Pseudo second order was found to be a better fit for adsorption of Cr(VI) and Cd(II) ions. This is in agreement with (15, 21, 20)

Table 3: Pseudo first order parameter Cr(VI) and Cd (II)

Metal ion	MMP			UMMP		
	K_1	q_e (mg/g-1)	R^2	K_1	q_e (mg/g-1)	R^2
Cr(VI)	-1.476	4.299	0.8600	-1.824	9.464	0.8490
Cd(II)	-0.490	2.745	0.9450-0.482	2.732	0.9450	

Table 4: Pseudo second order parameter Cr(VI) and Cd (II)

Metal ion	MMP		R^2	UMMP		R^2
	K_2	q_e exp(mg/g-1)		K_2	q_e (mg/g-1)	
Cr(VI)	1.384	1.250	0.993	1.312	2.475	0.966
Cd(II)	1.3200	3.743	0.9381.342	5.056		0.906

IV. Conclusion

Unmodified and citric acid *M. oleifera* seed pod carbon adsorbents prepared in this study showed a favorable adsorptive behavior toward metal ion. Equilibrium metal ion removal was well modeled by Freundlich isotherm. Adsorption kinetic obeyed closely the Blanchard pseudo-second-order kinetic model. The adsorbents may find potential use in the removal of metal ions Cr (VI) and Cd (II) from aqueous effluents and wastewaters.

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