Comparative Adsorption Studies of Hexavalent Chromium Ion On Acid-Modified and Raw Mangrove Sorbents

Cookey, A. Grace[1]; *Iboroma, S. Daopuye[2]; Maduelosi, N. Jane[1]

[1]Department of Chemistry, Rivers State University, Port Harcourt
[2]Rivers State Ministry of Environment & Natural Resources, Port Harcourt

Abstract- Adsorption capacities of acid-modified (MoMB and MoMR) and raw (RaMB and RaMR) mangrove bark and root sorbents on hexavalent chromium ion have been evaluated with respect to pH, adsorbent dosage, particle size, concentration of hexavalent chromium ion and contact time using batch adsorption technique. It was found that acid-modified mangrove sorbents exhibited higher adsorption capacities than raw mangrove sorbents. The adsorption of hexavalent chromium on both modified and unmodified mangrove biomass was found dependent on all variables considered. However, adsorption capacity decreased with increasing pH, adsorbent dosage and particle size but increased with contact time and concentration of hexavalent chromium ion. Adsorption data fitted best with Freundlich isotherm model. Kinetic study of the adsorption process favoured both first and second order models, suggesting physisorption and chemisorption, for MoMB and MoMR. The study revealed that acid-modified mangrove extracts are better adsorbents than raw mangrove extracts for the removal of hexavalent chromium ion from aqueous solution.

Index Terms- Hexavalent chromium ion, mangrove bark, mangrove root, adsorption capacity, particle size

I. INTRODUCTION

Chromium, a common heavy metal pollutant, exists in several oxidation states with the trivalent and hexavalent states as the most stable. Hexavalent chromium is more toxic than the trivalent form and primarily present in aqueous environment as chromate (CrO_4) and dichromate (Cr_2O_7) [1]. Salts of hexavalent chromium are very soluble and easily absorb and accumulate chromium metal in human body with subsequent detrimental impact on public health and the environment. In the past, conventional methods such as electrolytic, chemical precipitation, reverse osmosis, solvent extraction, reduction, ion exchange and adsorption on activated carbon were employed in the removal of hexavalent chromium from aqueous solutions. Due to environmental preservation and reduction of high operational cost associated with these conventional methods, researchers are continuously investigating the efficiency of various plant materials in adsorbing and thus removing hexavalent chromium ion from aqueous media [2 - 6]. The study of the adsorption of chromium (VI) by modified and unmodified mangrove leaf sorbents has been reported [7]. In this companion study, the efficiencies of modified mangrove bark and root (MoMB and MoMR) extracts and raw mangrove bark and root (RaMB and RaMR) extracts in removing hexavalent chromium ion from aqueous solution was investigated using batch adsorption process. The objective of this paper was to evaluate and report the adsorption capacities of acid-modified and raw mangrove bark and root sorbents on hexavalent chromium ion. The influence of process variables such as pH, adsorbent dosage, particle size, hexavalent chromium concentration and contact time were also stated.

II. MATERIALS AND METHOD

2.1 Collection of Mangrove Plant Parts (Adsorbent): Mangrove bark and root were collected from coastal forest near Bakana, a riverine community in Degema Local Government Area of Rivers State, Nigeria. Samples were washed thoroughly with tap water to remove dirt and soil particles and sun dried for 5 days to obtain completely dried biomass. The dried samples were milled to powder with a mechanical grinder, sieved into 5 different sizes using test sieves of different mesh sizes (150, 500, 1000, 1200 and 2000µm) and stored in tightly covered plastic containers for further analysis.

2.2 Modification of Adsorbents: 30g of powder was weighed into a beaker, 50ml of 0.5M Sulfuric acid (H_2SO_4) solution then added and left in an oven for 24hrs. The mixture was washed with de-ionized water and filtered. The samples were oven dried for 5hrs at 110°C, cooled and stored in a tight container for further analysis. The samples were labeled as Modified Mangrove Bark (MoMB) and Modified Mangrove Root (MoMR) sorbents. The untreated samples were labeled as Raw Mangrove Bark (RaMB) and Raw Mangrove Root (RaMR) sorbents.

2.3 Analysis of Adsorbent Surface Morphology: The morphology of the acid-modified and raw mangrove bark and root sorbents were analyzed using Phenonm world SEM-Pro (model X800-07334) Scanning Electron Microscope (SEM) at the Multi User Laboratory, Umaru Musa Yaradua University, Kastina, Kastina State, Nigeria.

2.4 Preparation of Hexavalent Chromium Ion Solution (Adsorbate): Stock solution (1000ppm) of hexavalent chromium

was prepared by dissolving 2.828g of Potassium dichromate ($K_2Cr_2O_7$) in 1 liter of deionized water. Working solutions (10ppm, 20ppm, 40ppm, 60ppm, 100ppm) were prepared from stock solution by dilutions from the stock.

2.5 Batch Adsorption Studies: Experimental procedures adopted were similar to that by Nduka *et al.* [7]. Hexavalent chromium solutions and mangrove samples were equilibrated in 75ml beakers using Stuart orbital shaker at a constant speed of 150rpm. Samples were withdrawn at predetermined time intervals and filtered using Whatman No. 1 filter paper. Adjustment of pH was actualized by adding drops of either HCl (0.1M) or NaOH (0.1M) solution to the mixture. Filtrates were analyzed for residual hexavalent chromium concentration using Agilent MP-AES 42100 atomic absorption spectrophotometer (AAS). All pH measurements were made using pocket-sized pH Meter (HANNA instrument: H196107 pH) and the amount of hexavalent chromium ion adsorbed (qe) was calculated using equation 1.

$$q_e = (\frac{C_o - C_f}{m}) \times V$$

$$(1)$$

where q_e is the amount of hexavalent chromium ion adsorbed (mg/g), C_o is the initial concentration of chromium (mg/l), C_f is the final hexavalent chromium ion concentration after treatment (mg/l), V is the volume of solution (l) and m is the mass of the adsorbent (g).

For pH effect, 0.5g of adsorbent of particle size 500μm was weighed separately and added to two different beakers containing 20ml of 40ppm hexavalent chromium ion solutions. The pH of the mixture was adjusted to 2. The mixture was covered and equilibrated using orbital shaker at the speed of 150rpm for 1hour. The mixture was filtered and the residual hexavalent chromium ion concentration determined using AAS. The procedure was repeated at various pH (4.0, 5.0, 8.0 and 9.0) for the modified (MoMB and MoMR) and raw (RaMB and RaMR) sorbents. For dosage effect, 0.25g mangrove sample (particle size = 500μm) was weighed into a beaker containing 20ml of 100ppm hexavalent chromium ion solution. The pH of the mixture was adjusted to 2. The solution was equilibrated at a constant speed of 150rpm for 60mins. The procedure was repeated for other dosages (0.5, 1.0, 1.5, and 2.0g) for both modified and raw mangrove bark and root. Similarly, 20ml solutions and 0.5g of various particle sizes (150, 500, 1000, 1200 and 2000μm) of both the modified and raw mangrove bark and root sorbents were used to study the effect of particle size. The mixture was filtered as in previous cases and the concentration of residual hexavalent chromium ion measured using AAS. The effect of hexavalent chromium ion concentration was investigated by equilibrating 0.2g of mangrove sample (particle size 500 μm) in 20ml of 10ppm hexavalent chromium solution at pH 2. The procedure was repeated using 20, 40, 60 and 100ppm hexavalent chromium solutions for both modified and raw mangrove bark and root sorbents at same pH. For contact time, 0.2g of adsorbent material of particle size 500μm was weighed and equilibrated with 20ml of 60ppm hexavalent chromium solution at

pH of 2 for 30 minutes. The procedure was repeated for 60, 90, 120, 150, 180, 210 and 240 minutes equilibration times.

2.6 Adsorption Isotherms: Adsorption isotherm data were generated using 0.2g of the 500μm particle size and by varying the concentration of hexavalent chromium ion between 10 and 100ppm at solution pH of 2. Other experimental procedures were followed and the isotherm properties evaluated using Langmuir and Freundlich adsorption isotherms; equations 2 and 3 respectively.

$$\frac{C_e}{q_e} = \frac{K_l}{q_{max}} + \frac{1}{q_{max}} C_e$$

$$(2)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

$$(3)$$

In equations 2 and 3, q_{max} represents the maximum adsorption (mg/g) at monolayer, C_e is the equilibrium concentration of the metal ion in solution, q_e is the amount of ion adsorbed per unit weight of the adsorbent, K_l is the Langmuir constant related to the affinity of binding sites for the metal ion, K_f and n are called Freundlich constants. K_f defines the relative adsorption capacity while n indicates the intensity of the adsorption.

2.7 Adsorption Kinetics: To investigate the kinetic properties of the adsorption process, 0.2g of the adsorbent (particle size = 500μm) was added to 20ml of 60ppm hexavalent chromium ion solution and agitated at intervals of 30, 60, 90, 120, 150, 180, 210 and 240mins. Other experimental procedures were followed and the kinetic properties computed using equations 4 and 5 of pseudo-first and second order reactions respectively.

$$\log(q_e - q_t) = \log q_e - (\frac{K_1}{2.303})t$$

$$(4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

$$(5)$$

where q_e and q_t represent the amount of chromium (vi) adsorbed at equilibrium and at a given time, t. K_1 and K_2 are the rate constants of the pseudo-first order and pseudo-second order adsorption processes, respectively.

All the experiments were carried out at ambient room temperatures which ranged between 29.5 and 30.5°C throughout the experimental period.

III. RESULTS AND DISCUSSION

3.1 Adsorbents Surface Morphology: SEM micrographs of 200 μm modified (MoMB and MoMR) and raw (RaMB and RaMR) mangrove sorbents are presented in figure 1. It appears that the surface morphologies of MoMB and MoMR have similar structures with tiny openings while those of RaMB and RaMR are more porous. These observations suggest that the acid-modified sorbents had more adsorptive sites than the raw sorbents.
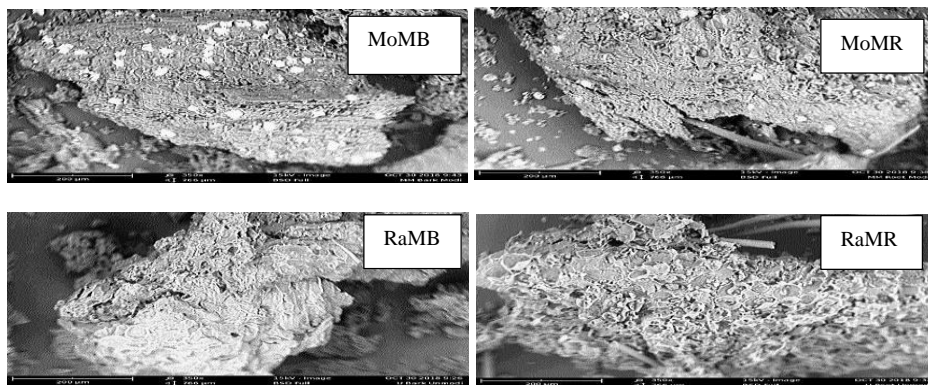
Figure 1: SEM Images of MoMB, MoMR, RaMB and RaMR

3.2 pH: The adsorption capacities of modified and raw mangrove sorbents on hexavalent chromium ion as function pH are illustrated in Figure 2. The plots show that the adsorption capacities of the modified mangrove bark and root were greater than those of unmodified and both decreased with increasing pH of the solution. Similar observations have been made on modified and unmodified mangrove leaf sorbents by Nduka *et al.* [7]. Ortiz *et al*. [9] also observed a decrease in chromium (VI) ion adsorption with increasing pH using acid-modified corn biomass as adsorbent. This suggest that at low pH the surface of the adsorbents became positively charged by protonation with hydrogen ions which probably promoted the binding of negatively charged hexavalent chromium ion on the surface of the adsorbent. At high pH, adsorption became low apparently due to repulsion as adsorbent surface became more negative.
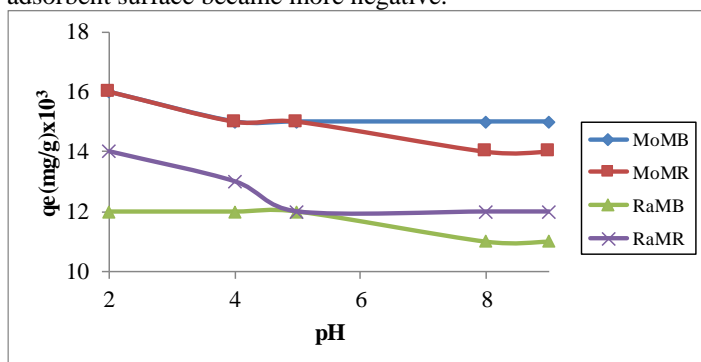

Figure 2: Plots of Equilibrium Adsorption Capacity (mg/g) as a Function of Solution pH.

3.3 Adsorbent Dosage: Plots of adsorption capacity against adsorbent dosage for MoMB, MoMR, RaMB and RaMR are illustrated in Figure 3. The results indicate an inverse relationship between adsorption capacities and the adsorbent doze. The results in Figure 3 describe a negative dependence of adsorption capacity on adsorbent dosage. However, modified sorbents exhibited higher adsorption capacity than the raw ones. The observed results suggest that increasing adsorbent dose increased adsorption binding sites without equivalent adsorbate to fill up the available

sites. Thus, the amount of adsorbate per unit adsorbent was reduced.
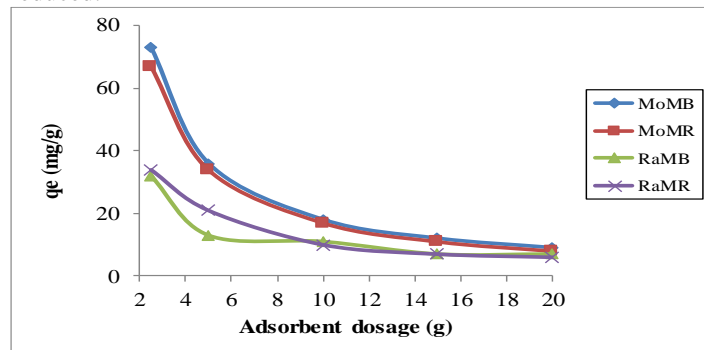

Figure 3: Plot of Equilibrium Capacity versus Adsorbent Dosage for the Adsorption of Hexavalent Chromium (VI) ion from Aqueous Solution using Modified and Raw Mangrove Sorbents.

3.4 Particle Size: The results of the effect of particle size on the adsorption of hexavalent chromium ion are displayed in Figure 4. The results describe an inverse relationship between adsorption capacity and adsorbent size. The observed decrease could be attributed to the fact that smaller particles have more surface area than the larger ones. Therefore, it can be inferred that the smaller the particle size, the larger the surface area and the more it tends to have higher adsorption capacity at a shorter equilibrium time.
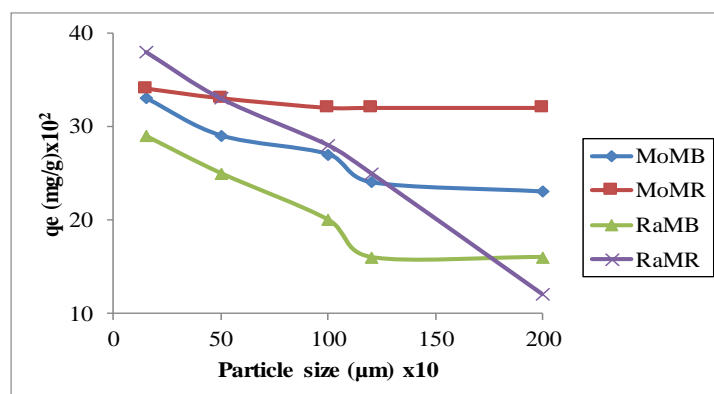
Figure 4: Plot of the amount of adsorbate (mg/g) against Particle Size (µm) for the Adsorption of Hexavalent Chromium (VI) ion from Aqueous Solution using Modified and Raw Mangrove Sorbents.

3.5 Hexavalent Chromium ion Concentration: Plots of adsorption capacity against hexavalent chromium ion concentration for MoMB, MoMR, RaMB and RaMR are presented in Figure 5. It describes positive dependence of adsorption capacity on concentration of hexavalent chromium ion. Similar observation was made by Olayinka *et al.* [10] on the adsorption of chromium (VI) from aqueous solution using adsorbents prepared from modified and unmodified coconut husk. The increase is possibly due to the fact that at higher concentration the active sites of the adsorbent would be surrounded with more hexavalent chromium ion, thereby enhancing the adsorption process. It is also observed in Figure 5 that modified sorbents exhibited higher adsorption capacity than the raw ones possibly due to their porous and wider surface feasibility.
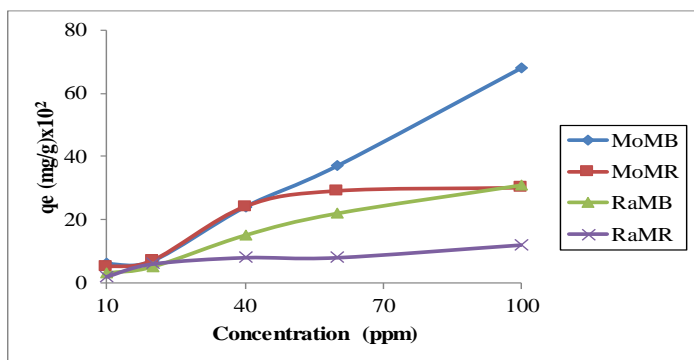

Figure 5: Plot of the amount of adsorbate (mg/g) versus Concentration of Adsorbate (ppm) Solution for the Adsorption of Hexavalent Chromium using Modified and Raw Mangrove Sorbents.

3.6 Contact Time: Adsorption capacities of MoMB, MoMR, RaMB and RaMR plotted as a function of contact time are displayed in Figure 6. The Figure shows that the capacity increased with increase in contact time but remained constant in all the adsorbents. Nduka *et al.* [7] made similar observation with mangrove leaf sorbent and attributed this behaviour to the availability of vacant binding sites on the adsorbents surface and long exposure time.
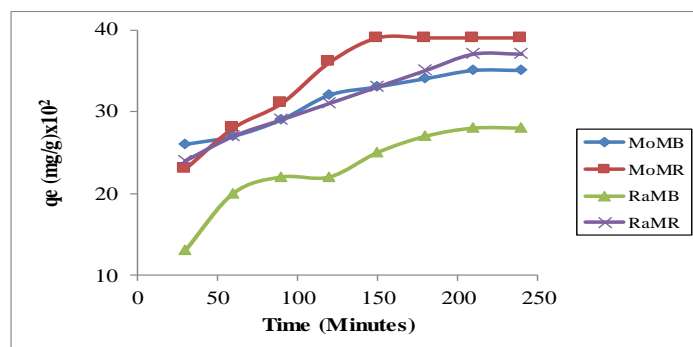

Figure 6: Plot of amount of Hexavalent Chromium Ion (mg/g) versus Contact Time (Minutes) for Modified and Raw Mangrove Sorbents.

Table 1: Isotherm Parameters for the Adsorption of Hexavalent Chromium Ion on Modified and raw Mangrove Sorbents

Adsorbent	Langmuir			Freundlich		
	Q_{max} (mg/g)	K_l (l/mg)	R^2	K_f (mg/g)	n	R^2
MoMB	-3.3333	-41.33	0.807	32.92	1.00	0.993
MoMR	1111.1	145.56	0.110	122.15	1.18	0.806
RaMB	-3.3333	-89.67	0.740	9.5017	0.76	0.978
RaMR	2500.0	76.50	0.307	18.4884	0.66	0.887

Table 2: Kinetic Parameters for the Adsorption of Hexavalent Chromium Ion on Modified and raw Mangrove Sorbents

Adsorbent	Pseudo-first Order			Pseudo-second Order		
	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg/min)	R^2
MoMB	1666.40	3.45×10^{-2}	0.898	3333	1.525×10^{-5}	0.996
MoMR	1500.34	3.89×10^{-2}	0.910	5000	5.333×10^{-6}	0.994
RaMB	1343.74	3.57×10^{-2}	0.782	3333	6.250×10^{-6}	0.994

| **RaMR** | 1511.80 | 3.55×10^{-2} | 0.733 | 5000 | 4.819×10^{-6} | 0.993 |

3.7 Isotherm and Kinetic Parameters: The validity of primary adsorption data as well as the significance of secondary data evaluated therefrom usually depends on best-fit correlation coefficient (R^2) values of regression plots. Langmuir and Freundlich adsorption parameters for the adsorption of hexavalent chromium ion from aqueous solution using MoMB, MoMR, RaMB and RaMR sorbents evaluated from isotherm plots (figures not given) are presented in Table 1. Correlation coefficient values $(R^2 \geq 0.81)$ obtained with Freundlich isotherm indicate good linearity. However, the low correlation coefficient values $(R^2 \leq 0.81)$ from Langmuir plots indicate non-conformity with the isotherm. It has been reported [7, 11] that favourable adsorption occurs when Freundlich parameter $n \leq 10$. The values of K_f and n indicate favourable and good adsorption capacity of the adsorbent for hexavalent chromium ion. However, higher values of these parameters for modified bark and root suggest that the adsorption of hexavalent chromium ion was more feasible on modified than raw adsorbent.

Table 2 shows the pseudo-first order and pseudo-second order kinetic parameters of MoMB, MoMR, RaMB and RaMR sorbents. Considering the perfect linearity $(R^2 > 0.91)$ and the pseudo-second order kinetic rate constants of 1.525×10^{-5}, 5.333×10^{-6}, 6.250×10^{-6} and 4.819×10^{-6} g/mg/min computed for MoMB, MoMR, RaMB and RaMR, the results (Table 2) suggest that chemisorption was the rate determining step in the adsorption of hexavalent chromium ion. Pseudo-first order rate constants $(3.45 \times 10^{-2}, 3.89 \times 10^{-2}, 3.57 \times 10^{-2}$ and 3.55×10^{-2} min^{-1}) computed for the adsorption process were relatively high. However, for MoMB and MoMR, both physisorption and chemisorption could be suggested considering the high R^2 values of 0.898 and 0.996 then 0.910 and 0.994 recorded in both pseudo-first order and -second order kinetics. Hence, modified MoMB and MoMR were better adsorbents than the raw RaMB and RaMR.

IV. CONCLUSION

The effectiveness of acid-modified and raw mangrove bark and root as adsorbents for hexavalent chromium ion in aqueous solution was studied as function of pH, adsorbent dose, particle size, hexavalent chromium ion concentration and contact time. It was found that modified mangrove adsorbents are more effective in adsorbing hexavalent chromium ion than the raw (unmodified) mangrove sorbents. It was also found that the effectiveness decreased with pH, particle size and adsorbent dose but increased with hexavalent chromium ion concentration and contact time. The isotherm data obtained fitted Freundlich model, implying heterogeneous surface coverage. Kinetic data suggests both physisorption and chemisorption for MoMB and MoMR. This study reveals that the acid-modified mangrove bark and root extracts are better adsorbents for the adsorption of hexavalent chromium ion than raw mangrove bark and root extracts. The investigations clearly indicate that acid-modified mangrove can be used as adsorbent for treatment of water containing hexavalent chromium ion.

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AUTHORS

First Author --- Cookey, A. Grace (PhD). Rivers State University, Port Harcourt, Nigeria. Email: cookey.grace@ust.edu.ng

Second Author --- Iboroma, S. Daopuye (PhD). Rivers State Ministry of Environment & Natural Resources, Port Harcourt, Nigeria.
Email: daopuye.iboroma1@ust.edu.ng

Third Author --- Maduelosi, N. Jane (PhD). Rivers State University, Port Harcourt, Nigeria. Email: janemaduelosi@yahoo.com

*Corresponding Author --- **Iboroma, S. Daopuye.** Email: daopuye.iboroma1@ust.edu.ng; Phone: +2347060837067