ADSORPTION OF Cr^{6+} ONTO UNMODIFIED AND HYDROCHLORIC ACID MODIFIED AFRICAN NUTMEG POD (MONODORA MYRISTICA) FROM AQUEOUS SOLUTION.

ABSTRACT

The removal of Cr^{6+} from aqueous solution using unmodified and hydrochloric modified African nutmeg pod was studied. The effects of particle size, pH and initial metal ions concentration adsorbed were investigated. The amount of metal ion adsorbed increased as the initial metal ion concentration increased and also decreased at low pH of 2 for both modified and unmodified African nutmeg pod. 400 µm and 250 µm were the optimum particle sizes for both modified and unmodified African nutmeg pod respectively, values given as 75.8 mg/g for the modified and 93.39 mg/g for the unmodified. Generally, it was observed that the unmodified African nutmeg pod showed greater adsorption capacity than the modified African nutmeg pod. The equilibrium experimental data were examined via Langmuir and Freundlich isotherm models. Freundlich isotherm model gave the best fit for the data in both unmodified and modified African nutmeg pod based on the correlation coefficients (R^2 values) gotten. The results of the study showed that the African nutmeg pod is efficient for the removal of Cr^{6+} from aqueous solutions especially when unmodified.

Keyword: Adsorption, pH; particle size; metal ion concentration; African nutmeg pod

INTRODUCTION

The continuous quest to rid various aspects of the environment of hazardous pollutants entails the persistent search for cost-saving technologies based on unconventional materials and methods through research and development. Recently, a great deal of interest in research for the removal of heavy metals from aqueous solutions have focused on the use of agricultural by-products in bioremediation of heavy metal ions, which is known as biosorption. Environmental pollution by toxic heavy metals occurs through industrial, military and agricultural processes [1]; smelting, petroleum refining, glass and ceramic manufacturing industries [2]. Other sources of heavy metals also exist and these have increased as a result of the increase in urbanization and industrialization. Heavy metals released by a number of industrial processes are major pollutants in a marine, ground and even treated wastewaters [3]. Heavy metals cannot degrade into harmless products [2] in the environment hence have become a major threat to plants, animal and human life due to their bioaccumulation tendency and toxicity and therefore must be removed from municipal and industrial effluents before discharge. Chromium metal and Cr(III) ions are stable and non-toxic. However, there are some of its water-soluble compounds which are extremely irritants and are highly toxic. Chromium as a trace element is essential for fat and sugar metabolism still chromium aerosols can affect health in a concentration above 2.5mm/cm^3 [4]. This element also exists as chromate and chronic acid in wastewater from certain industries such as chromium plating and leather treatment processes. The harmful effect of chromium is mainly caused by hexavalent chromium. The Environmental Protection Agency (EPA) has found chromium potentially to cause skin irritation or ulceration due to acute exposure at levels above maximum contaminates level. Chromium also causes cancer and damage to the liver, kidney circulatory, nerve tissue and dermatitis due to long term exposure [5]. Due to toxicity and bioaccumulation of these metals, It is, therefore, necessary to develop different technologies for controlling the concentration of these metals in effluents [6], different treatment techniques have been developed to remove both dissolved and suspended heavy metal ions from industrial and municipal effluents. Conventionally, the following physicochemical methods are employed for the removal of heavy metals from effluents: Oxidation and reduction, precipitation, filtration, reverse osmosis, electrochemical treatment and evaporation [7], but due to their several disadvantages such as unpredictable metal ion removal, high reagent requirement, formation of sludge and its disposal in addition to high installation and operation costs [8], considerable attention has been devoted to develop unconventional materials like agricultural by-products for the removal of heavy metals from wastewater since these animals and plant-based by-products represent unusual resources; they are widely available and environmentally friendly [9-10]. Adsorption has now been recognized as an effect and economic method for the removal of pollutants from wastewaters. Search for newer treatment technologies for removal of toxic metals from wastewater has directed attention to biosorption [11] which has been considered as an alternative technology for industrial wastewater treatment [12]. In this work, African nutmeg pod was used to detoxify Cr^{6+} from simulated industrial wastewater due to its lignocellulosic nature. According to Smith et al [13], the range for lignocellulosic material is 40% - 50%, lignin is from 15% - 20% while hemicellulose is from 25% - 35% and African nutmeg pod was found to have a greater percentage of compositions; hemicellulose is 42%, lignin is 35% while lignocellulose is 55% hence the interest in finding out its feasibility of adsorbing heavy metals from solutions as a lingo-cellulosic material with the following objectives: To examine the effectiveness of using modified and unmodified African nutmeg pod for the removal of Cr^{6+} from aqueous solution; to compare the adsorptive capacities of the unmodified and modified African nutmeg pod; to investigate the effect of variation in the initial metal ion concentration, particle size and pH of the solution and to describe the adsorption process of Cr^{6+} by the unmodified and modified African nutmeg pod through adsorption isotherms.

2 MATERIALS AND METHODS

African nutmeg (*Monodora myristica*) was gotten from Umuafia Ibeku in Umuahia North and Ntalakwu Oboro in Ikwuano L.G.A., both in Abia State and processed to get the pod which was thoroughly washed with deionized water in order to remove debris and other impurities from the surface of the biomass. It was cut into small pieces, air dried and grounded into tiny particle size using a manually operated grinder. The meal gotten from the sample (adsorbent) was further dried in an oven at about 50 ^oC. It was removed after twelve hours from the oven and sieved through a test-sieve with a rotating shaker where different sizes of the sample particle were obtained. There was an abundance of four particle sizes (250 µm, 354 µm, 400 µm, 3360 µm) of the sample from the sieving process for the study.

These particle sizes obtained were activated by soaking 200 g of each of the size in dilute nitric acid solution (HNO_3) of 2% v/v overnight (24 hrs) at room temperature. This process is termed adsorbent activation. After 24 hrs, each soaked particle size of the sample was filtered with a Whatman filter paper and washed thoroughly with de-ionized water and air-dried. Each sample was finally dried in an oven at 105 ^oC for about 6hrs. It was then removed from the oven after 6 hrs and stored in different containers according to their various sizes, thus ready for adsorption of metal ions from their solution. The activated African nutmeg pod represented the unmodified biosorbent used for the experiments and was then stored in different air-tight glass containers. The treatment of the adsorbent with 2 % (v/v) nitric acid (HNO_3) solution, mainly aids the removal of debris or soluble bio-molecules that might interact with metal ions during sorption and as well help in the opening of the micropores of the adsorbent. This will definitely change the surface characteristics of the biomass.

100 g portion of the activated sample was modified through hydrochlorination as method reported by [14]. Specifically, a 100g portion of the activated sample was modified by soaking into 1000 cm^3 of 0.3 M hydrogen chloride (hydrochloric acid) for 24 hours at 29 ^oC. After 24 hours, the hydrochlorinated sample was filtered with filter paper, washed with deionized water and then with methanol, it was finally washed with deionized water and dried at 50 ^oC for 12 hours and was then stored in a different air-tight glass container.

1000 mg/l stock solution of chromium was prepared from its salt K_2CrO4. This was done by dissolving 1 g of the salt in 1000 cm^3 of deionized water and made up to the mark of the volumetric flask. The solution represented the metal ion solution (wastewater) of 1000 mg/l concentration. From the stock solution of 1000 mg/l, various aliquots (5 cm^3, 4 cm^3, 3 cm^3, 2 cm^3, 1 cm^3 and 0.5 cm^3) were pipetted into beakers and made up to the mark of 50 ml volume with deionized water to give a range of concentration between 100mg/l and 10 mg/l i.e. (100 mg/l, 80 mg/l 60 mg/l, 40 mg/l, 20 mg/l and 10mg/l). The initial concentration of metal ion solution used for the adsorption study on investigating the effects of particle size and pH was 100 mg/l (prepared as aliquot from the stock of 1000 mg/l of the metal ion). On the other hand, the concentration of 80 mg/l, 60 mg/l, 40 mg/l, 20 mg/l and 10 mg/l (prepared from stock by serial dilution) as initial concentration were used to investigate the effect of variation in the initial concentration of metal on adsorption. Equilibrium sorption of Cr^{6+} ion onto African nutmeg pod was studied with respect to particle size, pH and initial metal ion concentration. To determine the effect of particle size on Cr^{6+} ion adsorption from aqueous solution; I g each of the four different particle sizes for both unmodified and modified samples was transferred into several 250 cm^3 beakers containing 50 cm^3 of 100 mg/l. The beakers were corked and the solution shaken intermittently with rotating shaker for one hour. It was done at 30 °C and a pH of 7.5. After one hour duration, the mixtures were filtered with Whatman filter paper and the filtrate collected into labelled sample bottles for the determination of the final metal ion concentration by FAAS (Buck model 200A). The pH of the metal ion solution was varied at a various range of 2,4,6,8 and 10 at a constant temperature of 30 °C and an initial concentration of 100 mg/l. 50 cm^3 portion of the metal ion solution of 100 mg/l concentration was introduced into various flask containing 1 g of each of unmodified and modified samples (354 μm) after adjusting the pH of the metal ion solutions with 0.1 M HCl for low pH and 0.1 M NaOH for higher pH and pH values of 2,4,6,8 and 10 were obtained. Each mixture was shaken intermittently with a rotating shaker for 1 hour and then filtered rapidly. The final pH of each filtrate after adsorption was also determined and the final metal ion concentration of each filtrate was determined using FAAS (Buck model 200A). The Equilibrium adsorption of Cr^{6+} ion onto unmodified and modified samples was carried out using 50 cm^3 of various concentration (100 mg/l, 80mg/l, 60mg/l, 40 mg/l, 20mg/l and 10 mg/l) at constant metal ion-substrate contact period of 1hour, at 30 °C and pH of 7.5. The mixtures were agitated with a rotating shaker for 1 hour and the final metal-ion concentrations in the filtrate were determined by FAAS (Buck model 200A).

3. RESULTS AND DISCUSSION

The concentrations of Cr^{6+} adsorbed by unmodified and modified African nutmeg pod at various particle sizes are shown in Table 1 while Figure 1 shows the plot on the variation of the amount of Cr^{6+} adsorbed by different particle sizes of unmodified and modified African nutmeg pod. From the table, it can be seen that the particle size of 250 μm showed greater adsorption capacity on the metal ions from solution in the unmodified sample while the particle size of 400 μm showed greater adsorption capacity in the modified sample. This is as a result of the larger surface area accompanied with smaller size particle which means abundant availability of active sites on the biomass. The unmodified particle sizes have higher adsorption capacity than the modified. A similar trend had been observed on the removal of Cr (VI) using *Pitchellobium dulce benth* [15].

Table 1: Initial concentrations of Cr^{6+} adsorbed by unmodified and modified African nutmeg pod at various particle sizes and at 298K.

Particle size (μm)	Cr^{6+}(mg/g) adsorbed by UANP	Cr^{6+}(mg/g) adsorbed by MANP
3360	86.7	63
400	89.9	75.8
354	82.1	68.9
250	93.39	67.4

UANP = Unmodified African Nutmeg Pod MANP = Modified African Nutmeg Pod

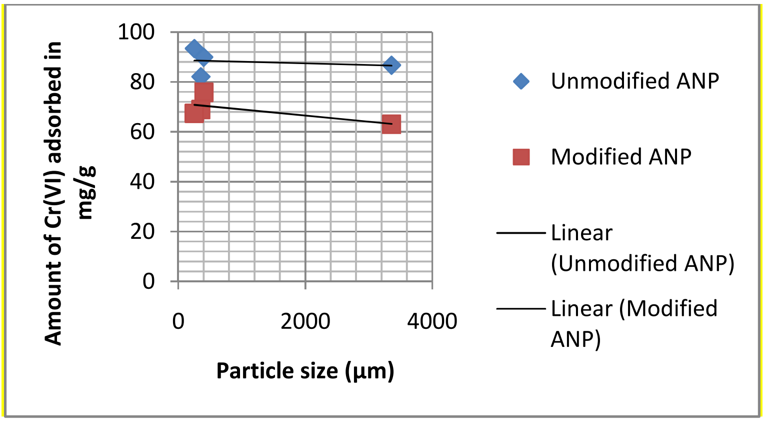

Figure 1: Plot on the effect of various particle sizes on the adsorption of initial concentrations of Cr^{6+} onto UANP and MANP.

Effect of pH on initial concentrations of Cr^{6+} adsorption by unmodified and modified African nutmeg pod is presented in Table 2.

Table 2: Initial concentrations of Cr^{6+} adsorbed by UANP and MANP from aqueous solutions at various pH and at 298K.

pH	Cr^{6+}(mg/g) adsorbed by UANP	Cr^{6+}(mg/g) adsorbed by MANP
2	98.84	98.79
4	96.37	95.57
6	96.24	94.19
8	95.09	94.95
10	92.92	94.70

It can be seen from Table 2 that the maximum adsorption of Cr^{6+} by both unmodified and modified African nutmeg pod occurred at low pH. For the unmodified African nutmeg pod, optimum removal of Cr^{6+} occurred at pH 2 with a removal efficiency of 98.84 % while for the modified African nutmeg pod, maximum removal for Cr^{6+} was at the same pH of 2 with percentage removal of 98.79 %. The maximum removal of Cr^{6+} at low pH for both unmodified and modified African nutmeg pod may be due to increased protonation (H^+) by the neutralization of the negative charges at the surface of the biosorbent which facilitates diffusion process and provides more active sites for the biosorbent [16]. Results also showed that the unmodified African nutmeg pod showed a better affinity for the metal ions than the modified African nutmeg pod. Figure 2 shows the variations on the plot of the effect of pH on the adsorption of Cr^{6+} by unmodified and modified African nutmeg pod (UANP and MANP) respectively.

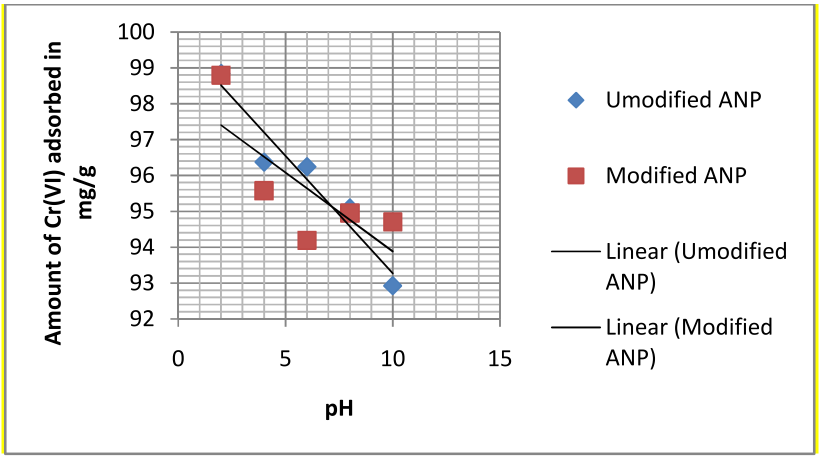

Figure 2: The plot showing the effect of pH on the adsorption of the initial concentration of Cr^{6+} by UANP and MANP.

Table 3: Amount of Cr^{6+} adsorbed by UANP and MANP from an aqueous solution containing various initial metal ion concentrations at 298 K.

Initial metal ion concentrations.	Cr^{6+}(mg/g) adsorbed by UANP	Cr^{6+}(mg/g) adsorbed by MANP
10	9.24	7.78
20	17.46	13.26
40	33.96	29.9
60	51.72	36.5
80	71.21	49.3
100	88.50	56.5

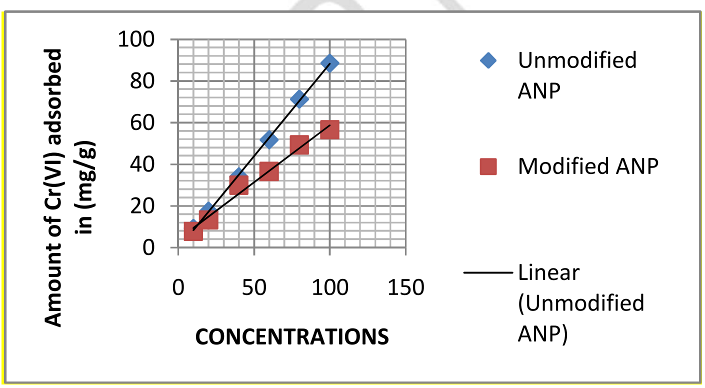

Figure 3: The plot showing the effect of initial metal ion concentrations on the adsorption of Cr^{6+} by UANP and MANP.

Table 3 revealed that maximum concentrations of Cr^{6+} (88.50 mg/g) adsorbed by unmodified African nutmeg pod were higher than those adsorbed by modified African nutmeg pod (56.5 mg/g) indicating that modification reduces its adsorption capacity. From the results presented in Table 3, it is evident that the extent of adsorption of Cr^{6+} by unmodified and modified samples of African nutmeg pod increases with increase in concentration. The relationship between the degree of surface coverage and concentration of adsorbent at constant temperature is often treated in terms of adsorption isotherms. In this study, data obtained from the study were fitted into different adsorption isotherms and from the results obtained, the best isotherm that described the adsorption characteristics of Cr^{6+} onto African nutmeg pod was Freundlich adsorption isotherm.

The expression establishing the Freundlich adsorption isotherm in a linearized form can be written as follows [17];

$$ln q_e = ln K_F + \frac{1}{n} ln C_e \quad (1)$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), K_F is the Freundlich adsorption constant (L/g), $(dm^3/g)^n$ related to the adsorption capacity and C_e is the equilibrium concentration of the adsorbate (mg/l). From equation 1, the Freundlich isotherm plot is fitted by plotting values of ln q_e against ln C_e and the slope of the plot should be equal to the reciprocal of n while the intercept should be equal to K_F(L/g). Figs. 4 and 5 showed Freundlich adsorption isotherms for the adsorption of Cr^{6+} by before and after modification respectively. Values of Freundlich adsorption parameters deduced from the plots are presented in Table 4. From the results obtained, it can be seen that values of R^2 approached unity (0.869 – 0.974) in all cases indicating the application of Freundlich adsorption model for the adsorption of Cr^{6+} by unmodified and modified samples of African nutmeg pod. The suitability of the Freundlich isotherm to the adsorption of the studied ion also implies that there is multilayer adsorption with non-uniform distribution over the heterogeneous surface [18].

According to [19], 'n' values between 1 and 10 show favourable adsorption conditions and the range of values of n in this study was within 1.323 to 1.531 for the adsorption process, indicating beneficial adsorption for the present study. The fit of the experimental adsorption data to the Freundlich isotherm model indicates that the forces of adsorption by the African nutmeg pod are likely to be governed by physisorption.

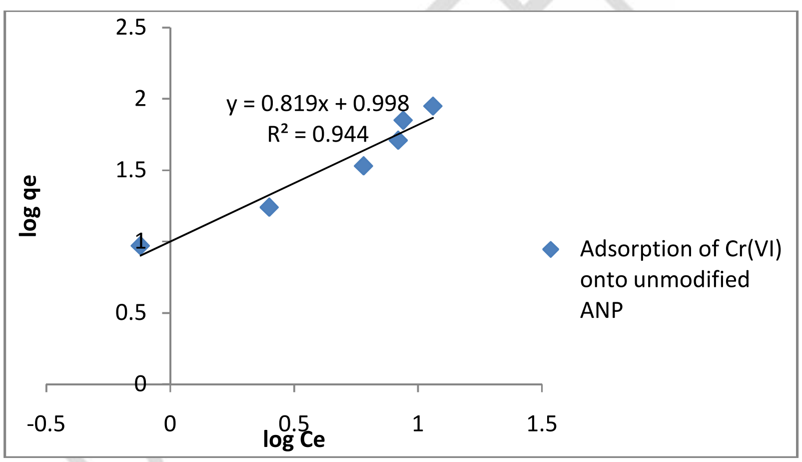

Fig 4: Freundlich isotherm plot of log q_e vs log C_e for adsorption of Cr^{6+}onto UANP

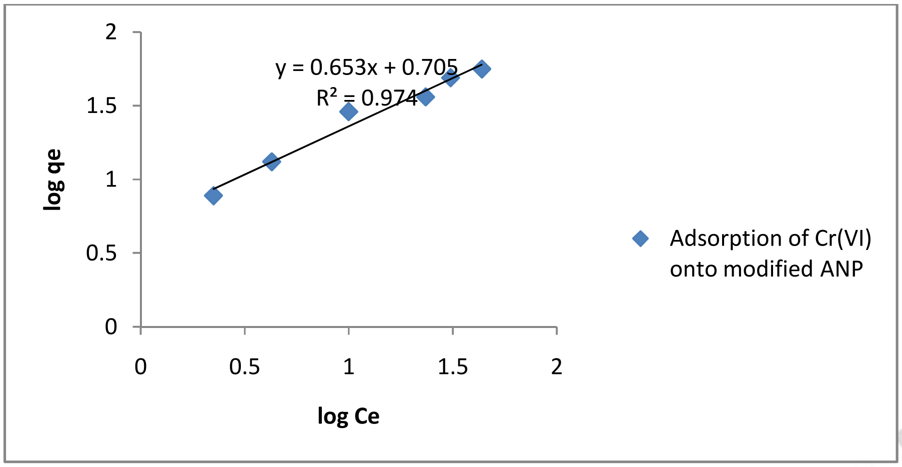

Fig 5: Freundlich isotherm plot of log q_e vs log C_e for adsorption of Cr^{6+} onto MANP.

Table 4: The Freundlich isotherm constants for the adsorption process.

Constant (units)	Cr^{6+}(mg/g) adsorbed by UANP	Cr^{6+}(mg/g) adsorbed by MANP
n	1.323	1.531
k_{F} (L/g)	10.328	5.070
R^2	0.869	0.974

CONCLUSION

Conventional methods of heavy metals removal are expensive, hence the use of low cost and environmentally friendly biosorbent should be implemented. In this study, both unmodified and hydrochloric acid modified African nutmeg pod were investigated in the removal of Cr^{6+} from aqueous solution considering pH, particle size and initial metal ion concentration as an important parameters. From the data, the following conclusions were made; that African nutmeg pod was able to adsorb Cr^{6+} from its solution, that the smallest particle size (250 μm) showed greater adsorption than others in unmodified while particle size of 400 μm showed greater adsorption than others for modified, that the amount of metal ions adsorbed increased with increase in the initial metal ion concentrations and that at pH of 2, both unmodified and modified African nutmeg pod gave better adsorption. . Finally that the suitability of the Freundlich isotherm to the adsorption of the studied ion also implies that there is multilayer adsorption with non-uniform distribution over the heterogeneous surface.

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