

Comparism of Adsorption Behaviour of *Caryota Rumphiana* Flower and Goat Hooves to Lead and Manganese Ions in Aqueous Solution

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Abstract The adsorption of Pb²⁺ and Mn²⁺ ions by cellulosic (*Caryota rumphiana* flower) and keratinous (Goat hooves) materials was investigated in order to compare their adsorptive capability. The experiments were carried out by batch method at 30°C and the effect of initial metal ion concentrations and contact time were evaluated. Pb²⁺ and Mn²⁺ ions attained equilibrium within 60 and 120 minutes respectively for both cellulosic and keratinous material. The equilibrium data fitted the Freundlich adsorption isotherm. This study demonstrated that *Caryota rumphiana* flower and Goat hooves could be used as an alternative adsorbent to remove Pb²⁺ and Mn²⁺ ions from aqueous solution.

Keywords *Caryota Rumphiana*, Goat Hooves, Adsorption, Lead, Manganese, Contact Time

1. Introduction

The continuous increase in the level of heavy metal discharge into the environment posed serious threat not only to human health but the entire ecosystem[1]. Heavy metals are nonbiodegradable and thus persist in the environment. Therefore, the concentration of these metals must be reduced to acceptable levels before being discharged into environment.

Several conventional treatment technologies had been designed to remove or at least reduced the concentration of these toxic metals from aqueous solution, but most of them were not economical, in most cases are very expensive for developing country like Nigeria, as a result of high cost of treatment associated with wastewater. This necessitated the search for low cost adsorbents that have been reported to be environmental friendly. The use of agricultural and animal wastes for the removal of toxic and valuable heavy metals from waste water has continued to attract a lot of attention, principally because they are easily available and at no cost, and more importantly because they are capable of binding heavy metals by adsorption, chelation and ion exchange.

In addition, several agricultural and agricultural by products, animal wastes and industrial by-products have been reported as an alternative to high cost activated charcoal[2-5]. Cellulose materials such as saw dust[6], tobacco

Dust[7], water leaf[8] *Hevea brasiliensis* bark[9] and Keratinous material like Periwinkle shell[10] have been used to study heavy metals uptake from aqueous solutions. *Caryota rumphiana* flower beautify the environment, the beautiful flowers later turn into waste which constituted environmental nuisance as a result of lack of proper disposal, so also the goat hooves.

But there is no information on the comparative studies on *Caryota rumphiana* flower and goat hooves. Therefore, the objective of this work is to compare adsorption behaviour of *Caryota rumphiana* flower and goat hooves to lead and manganese ions in aqueous solution.

2. Materials and Methods

2.1. Sample Collection

The *Caryota rumphiana* flowers were collected from a garden in Ahmadu Bello University, Zaria and while the goat hooves were randomly collected within Jos Metropolis. They were washed with deionized water and later air-dried. The samples were individually ground to powdered form by mortar and pestle. The samples were then sieved through a 125 and 250 µm mesh size. The sample that was retained on 250 µm mesh size was used for sorption studies.

2.2. Aqueous Solution Preparation

Aqueous solution containing Pb²⁺ and Mn²⁺ ions were prepared from Pb(NO₃)₂ and MnSO₄.H₂O. 1000 mg/L stock solutions of each of the salts were prepared. Other concen-

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trations of 10, 20, 30, 40 and 50 mg L⁻¹ were obtained from this stock solution by serial dilution. Fresh dilutions were used for each experiment. The pH of the aqueous solution was adjusted to a pH 5 using either 0.5 M NaOH and 0.5 M HCl to prevent hydrolysis. The concentration of metal ions in aqueous solution was analyzed by Inductive Coupled Plasma- Optical Emission Spectrometer.

2.3. Adsorption Experiments

Batch studies carried out included time dependence and initial metal ion concentration dependence. The experiment was jointly carried out at the Chemistry Department of University of Jos, Plateau State, Nigeria as well as Chemistry Department of Federal University of Technology, Minna, Niger State, and Nigeria.

2.4. Effect of Sorption Time

0.5 g sample each of cellulosic and keratinous material was taken and shaken with 100 cm³ of a metal ion solution whose concentration was 5 mg dm⁻³. The bottles were shaken at various time intervals of 30 to 180 minutes at room temperature in a reciprocating shaker at 300 rpm. At the end of each contact period, the mixture was filtered using Whatman filter paper No. 42 and the filtrate was analyzed using the ICP-OES. The difference between the initial and final metal ion concentration was recorded as the amount of metal ion bound by the substrate.

2.5. Batch Adsorption Study

The equilibrium sorption was carried out at 30°C using a concentration range of 10- 50 mg dm⁻³. 0.5 g of the substrates was weighed into a 250 cm³ conical flask and 100cm³ of the metal ion solution was measured into each conical flask containing the substrates. The conical flask was shaken for 90 minutes at room temperature in a reciprocating shaker at 300 rpm. The substrates were removed from the mixture by filtration and the concentration of the residual ions in the solution was determined. The amount of metal ions adsorbed from solution was determined by difference.

2.6. Results

3. Discussion

The variation in the amount of metal ion bound to the substrates with contact time is shown in Figure 1 to 4. For *Cryota rumphiana* flower, Pb²⁺ and Mn²⁺ ions reached equilibrium at 60 and 120 minutes respectively, with amount adsorbed by the substrate at 58.15 mg/L for Pb²⁺ ion and 36.61 mg/L for Mn²⁺ ion. One interesting thing about this result was that the equilibrium time of adsorption by the Goat hooves material was the same as that of the cellulosic material, with the difference being in the amount adsorbed by the substrates. It was observed that after the equilibrium, the amount adsorbed by the substrates decreases steadily and

this could plausibly be due to the fact that the binding sites on the substrates were exhausted and further shaking only resulted in desorption[10].

In addition,[11] had earlier observed that in the multimetalsorption, the metal ions compete for the adsorption sites on the adsorbent. This competition affects the diffusion properties of the metal ions, hence decreases the amount of the metal ions removed. Thus, the metal ion that successfully reaches the adsorption site faster depends on the ionic radii and metal ion types. Competition among the metal ions for adsorption sites obviously affected the uptake level of metal ions. Based on these fundamental facts, the adsorption process was faster and more efficient for Pb²⁺ ion than for Mn²⁺ ion in both substrates. This was probably due to the size of the ions like Pb²⁺ ion which became smaller than Mn²⁺ ion when hydrated and as such is less susceptible to steric hindrance. This significantly enhances their chances of being adsorbed to the reactive sites because the heavily hydrated ions migrate slowly in aqueous solutions. This might be the reason why more of Pb²⁺ ion was able to adsorb than Mn²⁺ ion. This observation is in agreement with the works of[8] and[12].

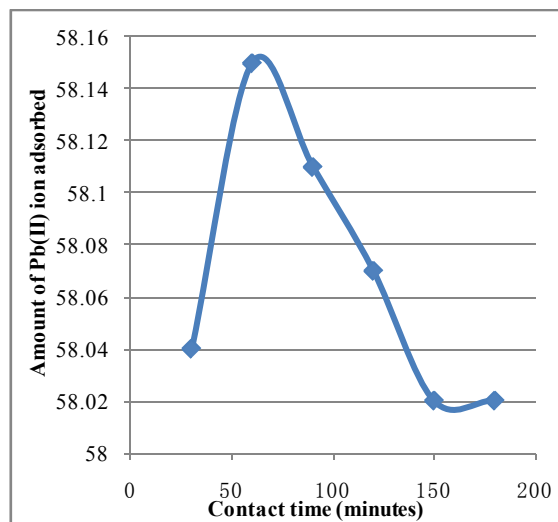


Figure 1. Effect of variation of contact time on the adsorption of Pb²⁺ ion on *Caryota rumphiana* flower at 30°C. The contact time was established within 60 minutes

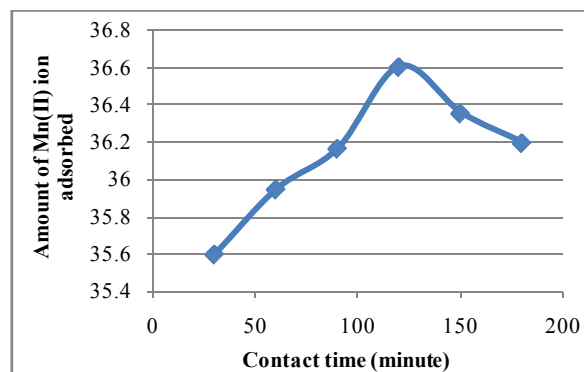


Figure 2. Effect of variation of contact time on the adsorption of Mn²⁺ ion *Caryota rumphiana* flower at 30°C. The contact time was established within 120 minutes

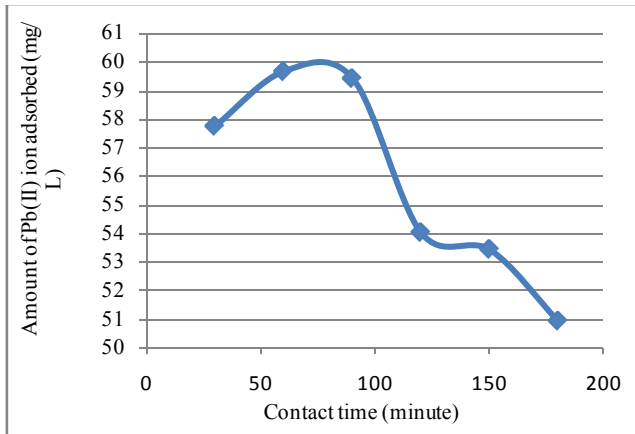


Figure 3. Effect of variation of contact time on the adsorption of Pb^{2+} ion Goat hooves at $30^{\circ}C$. The equilibrium time between the adsorbent and the adsorbate was 60 minutes

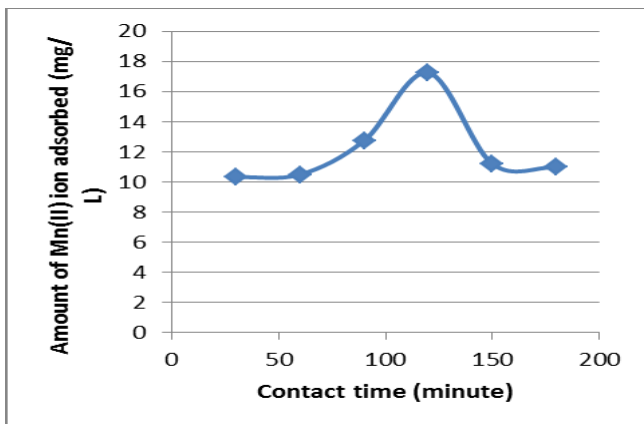


Figure 4. Effect of variation of contact time on the adsorption of Mn^{2+} ion Goat hooves at $30^{\circ}C$. The equilibrium time between the adsorbent and the adsorbate was 120 minutes

The variation in the amount of metal ion bound to the substrate with increasing concentration is illustrated in Figure 5 and 6. It was observed that as the concentration increased, a corresponding increase was recorded for the amount of Pb^{2+} ion adsorbed by the *Caryota rumphiana* flower than the amount of Mn^{2+} ion removed. This might be explained on the basis that at higher concentration levels, there was an increase in the number of metal ion competing for available binding sites on the substrate. This finding is in agreement with the work of [8, 13]. Whereas, in the case of Goat hooves, a different trend was observed for Mn^{2+} ions as increased concentration resulted to decreased amount adsorbed by the substrate. This observation is similar to what was reported by [14].

Further more, comparing the adsorption process of both substrates, it could be deduced that the adsorption of Pb^{2+} ion from the aqueous solution was more efficient than that of Mn^{2+} ion. This is probably due to the effect of the size of the hydrated ions like Pb^{2+} ion which became smaller than Mn^{2+} ion when hydrated and as such is less susceptible to steric hindrance. This is in agreement with the research conducted by [8].

Also, from the results obtained shown in Figure 5 and 6, it

was observed that the keratinous substrate (Goat hooves) adsorbed more of Pb^{2+} ions than the cellulosic substrate (*Caryota rumphiana* flower). This believes to be due to the presence of $-SH$ group on the keratinous substrate. On the other hand, the cellulosic material adsorbed more of Mn^{2+} ions than the keratinous substrate. This might probably be due to the presence of functional groups with high affinity for Mn^{2+} ion in the cellulosic substrate than it is present in the keratinous substrate.

Table 1 presents the Freundlich constant K_f obtained from the Freundlich isotherm represented in Figures 7 to 10 and the maximum uptake for both metal ions using the different substrates. The K_f which represents the adsorption capacity indicates a higher capacity for Pb^{2+} using the keratinous substrate with a value of 7.585 than with the cellulosic substrate with a adsorption capacity of 3.311 for Mn^{2+} ion was observed using the cellulosic substrate than with the keratinous substrate. Also, the K_f value of Pb^{2+} ion in both cases is greater than that of Mn^{2+} ion, confirming that Pb^{2+} ion has greater absorptivity than Mn^{2+} ion. Again, this is probably due to the effect of the size of the hydrated ions like Pb^{2+} ion which became smaller than Mn^{2+} ion when hydrated and as such is less susceptible to steric hindrance [14]. The values of correlation coefficient R^2 indicated that the adsorption process conforms to the Freundlich isotherms [15]. This as a result of the R^2 value which was greater than 0.900 in both substrates hence the adsorption was more of multi layered and physisorption type than uni-molecular layer [16]. The value of $1/n$ which was greater 0.700 but less than 1 indicates that Pb^{2+} and Mn^{2+} were favourably adsorbed by the substrates. A smaller value of $1/n$ indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent [17][18].

Table 1. Freundlich isotherm constants for the *Caryota rumphiana* flower and Goat hooves on $Pb(II)$ and $Mn(II)$ adsorption

Adsorbent /metal ion in solution	q_{max}	K_f	$1/n$	R^2
<i>Caryota rumphiana</i> flower/ $Pb(II)$	11.635	4.197	0.8735	0.9992
<i>Caryota rumphiana</i> flower/ $Mn(II)$	7.32	3.450	0.7447	0.9582
Goat hooves / $Pb(II)$	11.932	7.585	0.9772	0.9992
Goat hooves/ $Mn(II)$	3.450	1.654	0.8032	0.9090

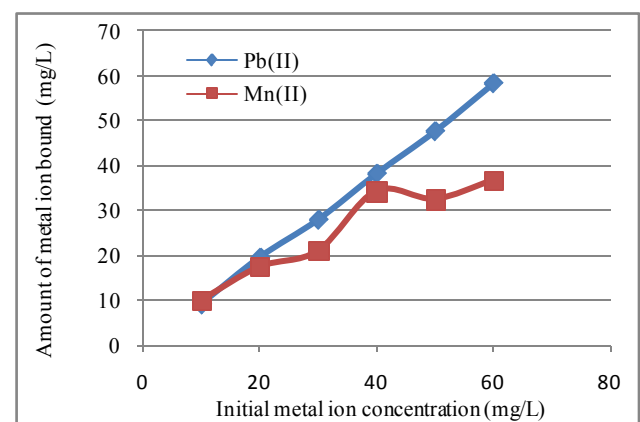


Figure 5. The effect of varying $Pb(II)$ and $Mn(II)$ ion concentration on the adsorption of *Caryota rumphiana* flower

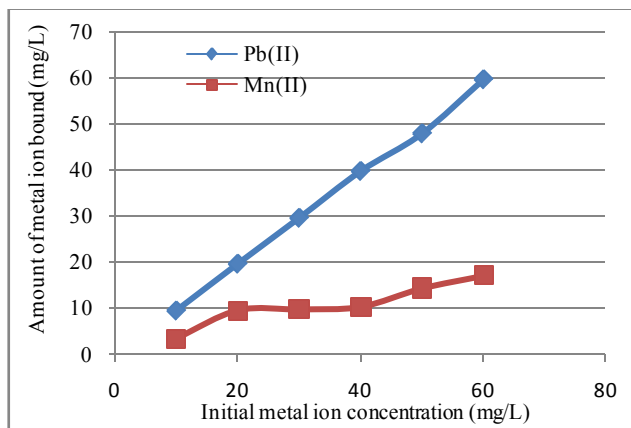


Figure 6. The effect of varying Pb(II) and Mn(II) ion concentration on the adsorption of Goat hooves

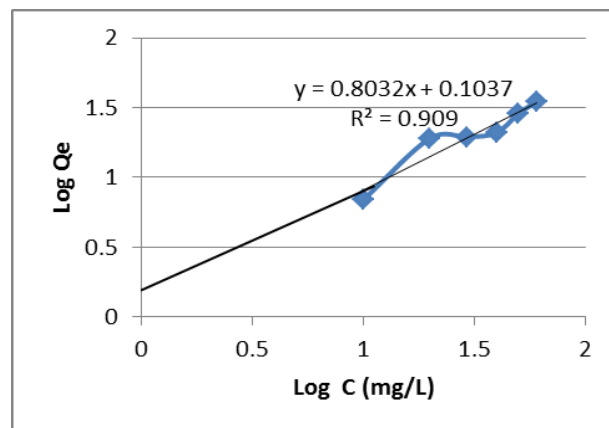


Figure 10. Freundlich isotherm for the adsorption of Mn (II) ion by Goat hooves

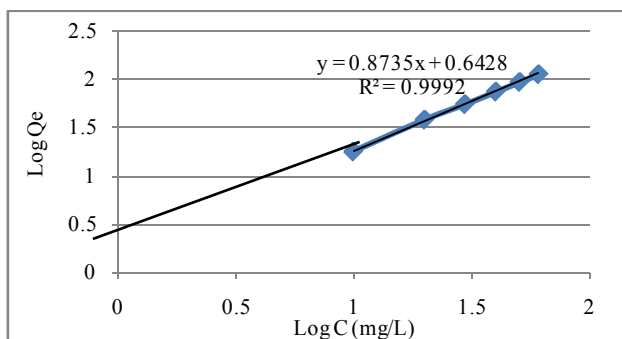


Figure 7. Freundlich isotherm for the adsorption of Pb (II) ion by *Caryota rumphiana* flower

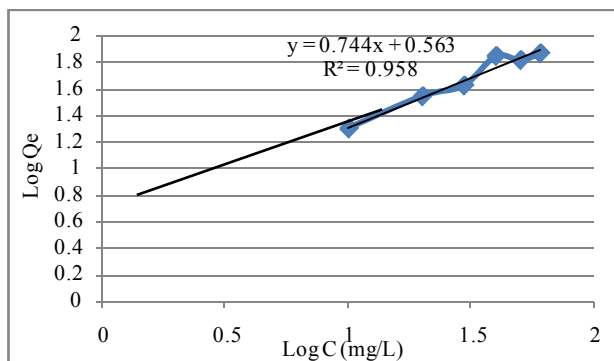


Figure 8. Freundlich isotherm for the adsorption of Mn (II) ion by *Caryota rumphiana* flower

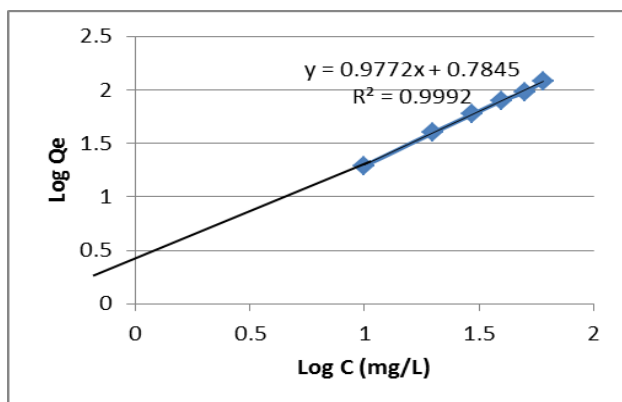


Figure 9. Freundlich isotherm for the adsorption of Pb (II) ion by Goat hooves

4. Conclusions

In this study, *Caryota rumphiana* flower powder and Goat hooves powder were used to adsorb lead and manganese ions from aqueous solution. Batch experiments showed that the adsorption process was dependent on both contact time and initial metal ion concentration. Using both substrates, equilibrium was established at 60 and 120 minutes for lead and manganese ions respectively. Adsorption of lead ion by the keratinous substrate was more efficient than with the cellulosic substrate while the cellulosic substrate was more effective for the sorption of manganese ion than with the keratinous substrate. The Freundlich isotherm fitted the equilibrium data for the both substrates. Finally, the preliminary study indicated a potential for the use of *Caryota rumphiana* flower powder and Goat hooves powder in the removal of heavy metals from aqueous solution.

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