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Biosorption of Cr³⁺, Pb²⁺, and Cd²⁺ ions from aqueous solution using modified and unmodified millet chaff

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ABSTRACT

The potential of both the modified and unmodified millet chaff- an agricultural solid waste as adsorbent were investigated in this work. The adsorbent was used to remove Pb²⁺, Cr³⁺ and Cd²⁺ ions from aqueous solution. The effects of contact time, pH, temperature, concentration and adsorbent dose in addition to adsorption isotherm were investigated. The result showed that both the modified and unmodified millet chaff sorbed more than eight-five percent of the metal ions investigated. For the time dependent study, metal ion adsorption onto the chaff biomass was very rapid within 30 to 120 minutes. The optimum pH for the metal binding to the biomass was found at 4.5 while at the room temperature of 30⁰C, the metal binding was effective. As the adsorbent dose increased from 0.5g to 2.0g, the higher the metal ions adsorption unto the millet biomass. The sorption process was examined by means of Langmuir isotherm. The result showed that Langmuir model provides an appropriate description of metal ion sorption process unto millet biomass. This result showed that millet chaff biomass is good adsorbent for the removal of metal ions from aqueous solution.

INTRODUCTION

The problem associated with heavy metal ions in the environment have appeared to be consistent in recent times especially in developing countries like Nigeria. These heavy metals are introduced into the environment mainly through anthropogenic sources which include mining, agro-based industries, pharmaceutical industries, oil and steel-based industries. Unlike the toxic organic pollutants that in many cases can be biodegradable, the metals that are released into the environment tend to persist indefinitely accumulating in living tissues through the food chain,

[1]. Metals of particularly toxic significance in human health include As, Zn, Au, Ag, Cu, Hg, Pb, Cr, Co and Mn, [2]. Essential elements include Fe, Zn, Cu, Mo, Cr, Co and Mn, and these essential metals can also be toxic in high concentrations or dosage. A metal may be regarded as toxic if it impairs the growth or metabolism of cells when it is given above a certain concentration i.e. if the exposure level is sufficiently high to exceed the tolerance level [3]. Most of the heavy metals are carcinogenic, a problem assumed to be related to their electronic structure. Even the metals considered to be essential for all forms of life may become problematic when in excess. Excess Cu for instance accumulates in the liver. Its toxicity is highly pH dependent and it is reported to be toxic to fish at lower pH values [4]. Instance of stomach cancer in human has been found in regions where Zn:Cu ratio of the soil exceed certain limits. Nickel is toxic and is relatively wide spread in the environment [5]. It is used in industries such as metal plating, cadmium-nickel battery and alloys (coinage). Lead is used as lead-acid battery, gunpowder, soldering lead applications among others. Chromium has both beneficial and detrimental properties. Two oxidation states persists in the environment; Cr^{3+} and Cr^{4+} which have contrasting toxicities, mobilities and bioavailabilities. Whereas Cr^{3+} is essential in human nutrition (especially in glucose metabolism); most of the hexavalent compounds are toxic, several can cause lung cancer. While Cr^{3+} is relatively innocuous and immobile, Cr^{4+} moves readily through soils and aquatic environment and is a strong oxidizing agent capable of being absorbed through the skin [6].

Chromium and its compounds are widely used in electroplating, leather tanning, wood preservations, paint and pigment, textile, steel fabrication and in canning industries. These metals find their ways into the aquatic environment through wastewater discharge [7]. These metals tend to accumulate in the aquatic organisms since they are non-biodegradable, feeding on such aquatic organisms such as fish, crabs, or using such contaminated water can lead to metal poisoning in man.

Giving the problems associated with metal pollution of the environment, attempts have been made by researchers in the past and at present geared towards the removal of these metals from the environment. A wide range of physical and chemical processes are available for the removal of these toxic metals from the environment. The methods includes; the use of activated carbon, activated sludge, powdered carbon, chemical coagulation, sedimentation and filtration, ion-exchange etc [8]. The above conventional methods, though effective, are not economically feasible for small and medium scale industries because of their relatively high costs [9], and [10]. Hence the need to explore cost effective alternative methods of adsorption for the treatment of metal contaminated wastewater in the environment.

There are some readily available naturally occurring agricultural wastes that possesses potentials as cheap adsorbents. In this regard, modified and unmodified cassava and yam peels [11], maize cobs [12], modified pumpkin seeds [13], modified groundnut shells [14], orange peels [15], palm kernel shells [16] have all been used and found to be effective in the removal of metal ions from their aqueous solution. In this research work, waste from millet-the chaff is used to carry out adsorption studies of metal ions from aqueous solutions. Millet or sorghum is a cereal crop cultivated and consumed extensively in the northern part of the country Nigeria. Millet can be eating as a whole, but is most often processed by fermentation into other food products such as pap (*akamu*)-a popular weaning food used by most families in Nigeria, as well as *kunu*- a

popular drink of high nutritive value. The processing technology is known to generate enormous wastes which is the residue (chaff) got after filtration of the ground fermented millet to produce the above mentioned food products. It is this waste which is thrown away indiscriminately to litter the environment since they are of no value to the user that is used to carry out adsorption studies of metal ions from aqueous solution in this research work. This type of waste which represents yet another form of solid agricultural waste and which comes in greater quantities because of the rate of generation is yet to be exploited in the area of adsorption studies for the removal metal ions from aqueous solution. Success in this research will create a value to the millet chaff hitherto regarded as something of no value to man and at same time as a way of getting rid of their presence in the environment.

EXPERIMENTALS SECTION

Sample Collection and Preparations

The millet used in this work was purchased from Keffi central market. It was washed clean of dust with water, soaked in clean water for about 4 hours. The soaked millet was then blended with an electric blender to form a paste. This was then filtered using a mesh while washing the residue formed each time with distilled water. The cleaned residue now the chaff is taken and sun-dried for 2 days. The residue now in powdered form was further passed through 354mm mesh to retain finer particles which were then kept in air-tight plastic containers ready for analyses. All reagents used were of analytical grades, purchased and used without further purifications. One half of the powdered millet chaff was modified by the method of Marshal [17]. For the purpose of modification, a portion of the millet chaff was soaked in 0.3M HNO₃ overnight, filtered and washed thoroughly with distilled water severally and sun-dried for 3 hours. This treatment is good for the removal of debris or soluble biomolecules that might interact with metals during sorption. The above treated chaff was then blended with 0.6M Citric acid for 4 hours in a proportion of 1.0 gram of chaff to 7.0 cm³ of the acid. This acid treated chaff (modified chaff) was washed with distilled water severally to remove excess acid. Finally the modified chaff was dried at 50°C in the oven for 1 hour and sieved to particle size of 450 um and was used for the adsorption studies.

Adsorption Studies

Adsorption was carried out on the modified and unmodified millet chaff according to the previous work of Marshal [17]. The procedure basically involves adding a giving amount of the prepared chaff into already prepared dilute solutions of the heavy metals i.e lead, chromium and cadmium. The set ups were prepared in batches and were subjected to different conditions such as temperature, pH, contact time, metal ion concentrations and adsorbent dose, after which filtration of the chaff biomass from the solution is carried out. The concentrations of the heavy metals left in the various solutions (filtrate) was then determined using an atomic absorption spectrometer (AAS). In all the different experimental conditions, 20cm³ of the metal solution containing 2000Mg/l each of lead, chromium and cadmium ions were prepared in three different beakers. 1.0g of chaff biomass was added to each of the beakers labeled 1 to 3. Beaker 1 was placed in a thermostat set to 30°C while beakers 2 and 3 were subjected to temperatures 60°C and 90°C respectively for temperature effect. The effect of pH was studied by adjusting the pH in the 3 beakers with 0.5M HCl and 0.1M NaOH such that the pH in the 3 beakers were adjusted to 4.5, 8.0 and 10.0 respectively. A Jenway pH meter 3020 was used to measure the pH of the

solution. For the contact time effect, the pH in the 3 beakers were adjusted to 4.5, with temperature at 30°C and biomass weight of 2g with constant agitation and analyses done at intervals for a total period of 3 hours. The effect of adsorbent dose was obtained by adding 0.5g, 1.0g and 2.0g of the chaff biomass to each of the 3 beakers. All the set-ups were agitated under various conditions for 3 hours, after which filtration followed and the filtrate analysed for metal ion concentration by AAS. The effect of metal ion concentration was done by taken 20cm³ of metal ion solution in three different beakers 2500ppm, 1000ppm and 2000ppm of each of the metals. These solutions were treated in the same way as pH, contact time and adsorbent dose were determined. The solutions were filtered at specified times and the filtrate analysed with AAS.

RESULTS AND DISCUSSION

The result for the metal ion adsorption of the modified and unmodified millet chaff for contact time, pH, temperature, concentration and adsorbent dose are presented in Tables 1-5 while Table 6 is the linear Langmuir isotherm parameters and the sorption of Pb²⁺, Cr³⁺ and Cd²⁺ ions for the same samples. The result of the analyses showed that the millet chaff is a good adsorbent for the metal ions under study. This is regardless of whether the chaff is in the modified or unmodified form, however the modified chaff showed an enhanced level of metal ion adsorption as compared with the modified type.

Effect of Contact Time

The effect of contact time on the adsorption of the three metal ions by the modified and unmodified millet chaff biomass is presented in Table 1. The result of the analysis show that the more the time (30-120 minutes) the higher the metal ion adsorption. This is similar to the result obtained by [18] in the removal of Cu²⁺ and Pb²⁺ ions from aqueous solution using non living *spirogyra neglecta*. However, under the same experimental conditions, it is observed that the unmodified millet chaff gave a better adsorption than the modified type, though the difference here is not significant enough. Using different biomasses similar adsorption trends have been observed by other workers; [19] in the use of cassava waste for the removal of Cd²⁺, Cu²⁺ and Zn²⁺ ions from aqueous solution.

Table 1: Effect of contact time on modified and unmodified millet chaff for uptake of Cr³⁺, Pb²⁺ and Cd²⁺ ions.

Equilibrium concentration (mg/l)			Amount adsorbed (mg/g)			
Conc.(ppm)	Unmodified			Pb	Cr	Cd
	Pb	Cr	Cd			
30	2.3217	74.8918	0.1372	0.9988	0.9619	0.9999
60	1.7617	75.5562	0.0627	0.9991	0.9622	0.9996
120	1.1817	76.2312	0.1213	0.9994	0.9625	0.9999
Modified						
30	6.0213	78.3175	27.7723	0.9969	0.9608	0.9861
60	4.1328	76.6805	23.2302	0.9979	0.9616	0.9883
120	3.3711	72.1351	20.1517	0.9983	0.9639	0.9899

The uptake and unadsorbed Pb^{2+} , Cr^{3+} and Cd^{2+} ions concentrations at the end of 30, 60 and 120 min. are given as equilibrium values. [20], observed in their work on acid pretreated *Mucor rouxi* that adsorption of metal ions is not influenced by the presence of acid on the adsorbent which is also in agreement with the observation of some researchers [21] in their work on *A.niger* this is attributed to the binding of H^+ ion to the biomass after acid treatment which is responsible for the reduction of adsorption of heavy metals.

Effect of pH

The result of the effect of pH on the adsorption of Pb^{2+} , Cr^{3+} and Cd^{2+} ions from aqueous solution is shown in Table 2. The pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of the adsorbate reactions.

Table 2; Effect of pH on unmodified and modified millet chaff for the uptake of Cr^{3+} , Pb^{2+} and Cd^{2+} ions.

pH	Equilibrium concentration (mg/l)			Amount adsorbed (mg/g)		
	Pb	Cr	Cd	Pb	Cr	Cd
	Unmodified					
4.5	2.1816	75.6418	0.0544	0.9989	0.9621	0.9999
8.0	3.1471	76.3351	0.1251	0.9984	0.9618	0.9999
10.0	3.7611	77.2511	1.5225	0.9981	0.9613	0.9992
	Modified					
4.5	0.0356	59.8457	0.1555	0.9999	0.9700	0.9999
8.0	1.2710	62.4746	0.1834	0.9993	0.9687	0.9999
10.0	2.6615	63.2751	1.3742	0.9986	0.9683	0.9993

The result showed that Pb^{2+} , Cr^{3+} and Cd^{2+} ions sorption for the biomass under study was high at a pH of 4.5 for both the modified and unmodified millet chaff. The modified millet chaff however, showed a higher adsorption capacity than the unmodified type and there was a decrease in sorption between the pH of 8.0 and 10.0 i.e as the pH increases. This binding behaviour of metal ions unto the chaff biomass is similar to the findings of some researchers [22] in adsorption of Calcium and Zinc ions by cassava waste biomass in aqueous solution. And according to a group of researchers [23], most plants are made up of lignin and cellulose that contain several types of functional groups. These groups can be responsible for the typical cation exchange characteristics of most biomaterials. This is with the case of millet chaff used in this work.

Temperature effect

Temperature is one of the most important factors which affect the process of adsorption. From Table 3 it was clear that adsorption capacity of the biomass was maximum at the room temperature of 30°C showing physio-sorption processes. The amount of Pb^{2+} , Cr^{3+} and Cd^{2+} ions adsorbed was higher at 30°C for both the modified and unmodified millet chaff biomass, but adsorption was more effective on the modified biomass than the unmodified type. Increasing the temperature to 90°C did not favour adsorption much thereby decreasing adsorption capacity.

Some researchers [23] found out that the magnitude of the metal adsorbed as the temperature is increased continues to decrease as the temperature is increased.

Table 3: effect of temperature on modified and unmodified millet chaff for uptake of Cr³⁺, Pb²⁺ and Cd²⁺ ions.

Equilibrium concentration (mg/l)			Amount adsorbed (mg/g)			
Temp. (°C)	Unmodified			Pb	Cr	Cd
	Pb	Cr	Cd			
30°	0.7105	70.2077	0.0710	0.9996	0.9648	0.9999
60°	38.1320	96.1916	20.8529	0.9809	0.9619	0.9895
90°	38.6781	77.1240	22.3617	0.9806	0.9614	0.9888
Modified			Pb	Cr	Cd	
Temp. (°C)	Pb	Cr				
30°	0.3280	61.4410	0.2135	0.9998	0.9692	0.9998
60°	1.2361	65.8111	0.1250	0.9993	0.9670	0.9999
90°	1.8769	78.3420	0.9617	0.9990	0.9633	0.9995

This finding also revealed that most metal ions were removed between temperatures of 30 to 60°C. This is because adsorption being exothermic process, increasing the temperature will lead to the attractive forces between biomass and metal ions becoming weaker thereby leading to sorption decreases. Also at high temperature, the thickness of boundary layer decreases due to the tendency of the metal ion to escape from the biomass surface to the solution phase which result in a decrease in adsorption as temperature is increased [24].

Table 4: Effect of metal ion concentration on modified and unmodified millet chaff for uptake of Cr³⁺, Pb²⁺ and Cd²⁺ ions.

Equilibrium concentration (mg/l)			Amount adsorbed (mg/g)			
Conc. (ppm)	Unmodified			Pb	Cr	Cd
	Pb	Cr	Cd			
250	3.1563	76.9393	25.5612	0.9873	0.6922	0.8977
1000	1.9811	75.3692	23.2890	0.9980	0.9246	0.9769
2000	0.1821	70.2681	20.1168	0.9999	0.9648	0.9899
Modified			Pb	Cr	Cd	
Conc. (ppm)	Pb	Cr				
250	1.2480	74.1168	1.0672	0.9950	0.7035	0.9957
1000	1.2553	72.9629	0.1029	0.9987	0.9270	0.9998
2000	0.1186	70.8131	0.0673	0.9999	0.9645	0.9999

Effect of initial metal ion concentration

The result of the analyses have shown that the uptake of Pb²⁺, Cr³⁺ and Cd²⁺ ions increases with increase in metal ion concentration from 250 - 2000ppm for the different metal ions with other parameters such as adsorbent dose of 1.0g at a pH of 4.5 and a room temperature of 30°C while agitation is kept optimum. The modified millet chaff however, showed a better adsorption capacity as the ion concentration is increased than the unmodified type. For the biomass, about 98% of the metal ions were removed within 30 minutes, thereafter the percent of metal ion removal remained mainly nearly constant as further increase in the metal ion concentration leads to the saturation of the biomass surface.

This same adsorption trend have been reported by some researchers; [23] in wide cocoyam (*caladium bicolos*), that the higher the metal ion concentration the higher the adsorption capacity,[19] in the use of chemically modified and unmodified cassava waste had reported the same pattern. Table 4 show the effect of concentration on the removal of metal ions from their aqueous solution.

Effect of Adsorbent Dose

Table 5 shoe the effect of adsorbent dose on the amount of Pb^{2+} , Cr^{3+} and Cd^{2+} ions adsorbed by the millet chaff biomass. The result showed that the metal ions adsorbed increased with an increase in adsorbent dosage from 0.5 to 2.0g while keeping other parameters (pH, agitation speed, temperature and contact time) constant. The increase in adsorption of the amount of adsorbent is obvious due to increasing biomass surface area. It is interesting to note that the saturated values of Pb^{2+} , Cr^{3+} and Cd^{2+} ions removal efficiency of millet chaff adsorbent are different from one another due to the extent of surface modification. This also implies that adsorbent type and quality is an important factor in the effectiveness of adsorption .The variation in adsorption capacities between the different adsorbents may be ascribed to the adsorbent type and surface groups responsible for interaction with the metal ion.

Table 5: Effect of adsorbent dose on modified and unmodified millet chaff for uptake of Cr^{3+} , Pb^{2+} and Cd^{2+} ions.

Equilibrium concentration (mg/l)			amount adsorbed (mg/g)			
Unmodified						
Adsorbent Dose (g)	Pb	Cr	Cd	Pb	Cr	Cd
0.5	3.0137	75.2585	2.4671	0.9984	0.9623	0.9987
1.0	0.3923	71.5489	1.3423	0.9998	0.9642	0.9993
2.0	0.2172	69.2214	0.9211	0.9999	0.9653	0.9995
			Modified			
0.5	1.2134	71.4163	0.2756	0.9993	0.9642	0.9998
1.0	0.1132	65.8111	0.1250	0.9999	0.9670	0.9999
2.0	0.0127	60.7421	0.0527	0.9999	0.9696	0.9999

However the presence of functional groups does not necessarily guarantee its accessibility as a sorption site due to the possible co-existence of other type of barrier [25]. The result agrees with the findings of some researchers [26], who reported that Pb^{2+} and Cd^{2+} ions uptake was increased with increase in the weight of non- living biomass of *Aspergillus flarus*. Similarly other workers have reported increased adsorption with increasing biomass weight [27], which was due to the unsaturation of the active sites per surface area on biomass involved in Pb^{2+} binding within the range of biomass weight.

Adsorption isotherm

Adsorption information for a wide range of adsorbate concentrations are most frequently described by adsorption models such as Langmuir or Freundlich isotherm which relates

adsorption density (q_e) (metal uptake per unit weight of adsorbent to equilibrium concentration (C_e) in the bulk fluid, [28]. Adsorption data of Cr^{3+} , Pb^{2+} and Cd^{2+} ions into modified and unmodified millet chaff have been analysed with the help of Langmuir model to evaluate the mechanistic details associated with the adsorption process. The Langmuir isotherm is chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorption surface, that the energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface, [28].

Which is represented by

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}$$

And the linear form of the equation can be written as

$$C_e/q_e = 1/bQ^0 + C_e/Q^0$$

Where q_e is the amount of heavy metal ion adsorbed per unit mass of adsorbent (mg/g) at equilibrium phase of metal ion (C_e) in mg/l. Q^0 and b are Langmuir constants indicating sorption capacity and energy of adsorption respectively. The plot of C_e/q_e verses C_e at different temperatures were found to be linear indicating the applicability of the Langmuir model as presented in Figures 1 and 2.

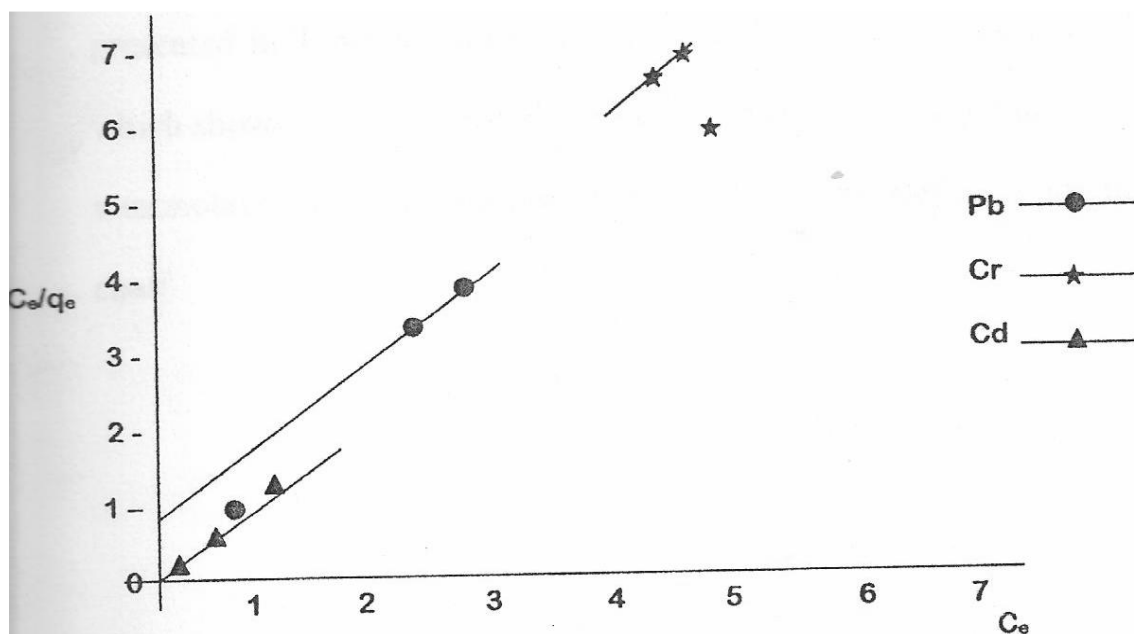


Figure 1: Langmuir equilibrium isotherm model for sorption of Pb^{2+} , Cr^{3+} and Cd^{2+} ions unmodified millet chaff biomass.

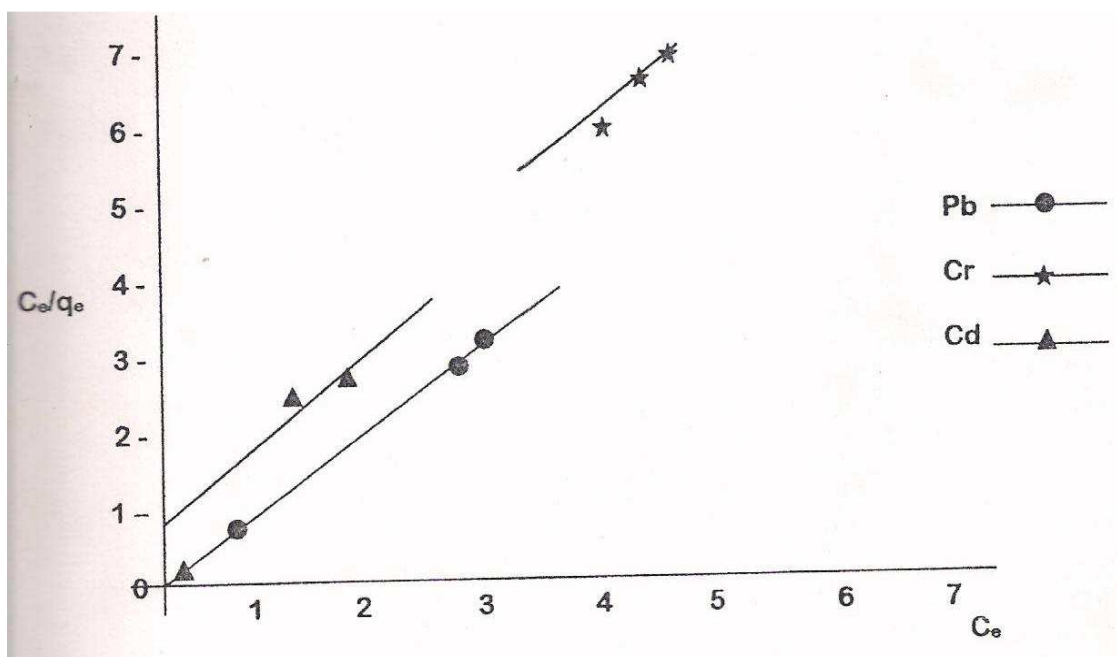


Figure 2: Langmuir equilibrium isotherm for sorption of Pb^{2+} , Cr^{3+} and Cd^{2+} ions unto modified millet chaff biomass.

The parameters Q^0 and b have been calculated and the result presented in Table 6. From the result q_e has a smaller value than Q^0 which shows that the adsorption of heavy metal ions unto millet chaff is a monolayer type one that does not fully cover the surface of the millet chaff.

Table 6: linear Langmuir isotherm parameters for modified and unmodified millet chaff biomass

Metal ion	q_e	b	Q^0
Unmodified			
Pb^{2+}	0.9994	0.96	3.2
Cr^{3+}	0.9922	0.93	9.3
Cd^{2+}	0.9998	0.99	14.14
Modified			
Pb^{2+}	0.9977	1.0	10.0
Cr^{3+}	0.9621	0.92	2.30
Cd^{2+}	0.9881	1.0	5.0

CONCLUSION

Millet chaff biomass- a solid agricultural waste of low value and an emerging environmental pollutant of concern have been found to be a good adsorbent for the removal of Pb^{2+} , Cr^{3+} and Cd^{2+} ions from aqueous solution using both the modified and unmodified forms of it. The modification of the millet chaff biomass with Citric acid however, was observed to enhance the adsorption capacity of the biomass under the same experimental conditions.

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