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Adsorption of Pb, Cd, Zn, Cu and Hg ions on Formaldehyde and Pyridine Modified Bean Husks

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ABSTRACT: Adsorption of Pb(II), Cd(II), Zn(II), Cu(II) and Hg(II) ions on formaldehyde and Pyridine modified bean husks were determined. The adsorption capacity of formaldehyde modified bean husks (mg/g) was: Pb^{2+}, 5.01; Cd^{2+}, 3.63; Zn^{2+}, 2.18; Hg^{2+}, 1.82; Cu^{2+}, 1.58 and that of pyridine modified bean husk was: Hg^{2+}, 6.92; Cd^{2+}, 3.63; Pb^{2+}, 2.64; Zn^{2+}, 2.48; Cu^{2+}, 1.91. The Freundlich equation parameter 1/n for the metal ions were found to be less than unity which indicates that adsorption of metals on bean husks have increased as a result of modification. The calculated value from Freundlich adsorption parameter (K_F) and Langmuir adsorption parameter (q_{max}) showed that the adsorption capacities of the metal ions are in order of $Pb^{2+} > Cd^{2+} > Zn^{2+} > Hg^{2+} > Cu^{2+}$ for formaldehyde modified bean husks and $Hg^{2+} > Cd^{2+} > Pb^{2+} > Zn^{2+} > Cu^{2+}$ for pyridine modified bean husks. The binding capacity study showed that the formaldehyde modified bean husks could be employed in the removal of Pb^{2+} and Zn^{2+} from industrial effluent especially in the battery manufacturing, paints and dyes industries. This study also indicates that the pyridine modified bean husk could remove Hg^{2+} better than the formaldehyde modified bean husk in the printing and minting industrial effluent. @JASEM

The adsorption process with activated carbon has attracted interest in recent years because of its effectiveness for the removal of heavy metal ions at trace quantities, however it is very expensive. This makes the use of low cost material as sorbent for metals removal from wastewater to attract attention from many scientists (Adediran et al., 2000; Oyoh and Igbokwe, 2001; Egila and Okorie, 2003). More recently, great attempt has been made to develop new adsorbent from agricultural materials such as eucalyptus barks, rice-husks, and sugar cane waste (Saliba et al., 2000; Nagernaik et al., 2002; Krishnan and Anirudhan, 2003).

All these wastes cost little or nothing, abundantly available and there are possibilities of regeneration process.

In some studies carried out previously, chemical modification of cellulosic materials significantly enhanced their ion-binding properties, providing greater flexibility in their application to a wide range of heavy metals (Gardea-Torresdey et al., 1999; Abia et al., 2002; Horsfall Jr and Abia, 2003; Horsfall Jr and Spiff, 2005).

The entire modified agricultural wastes contain cellulose that possess some ion-exchange properties due to the presence of small number of carboxyl, hydroxyl, sulphur, cyano and or amino group in their structure. The chemical modification is expected to improve metal ion binding capacity of the materials. This work is aimed at using formaldehyde and pyridine for the modification of bean husks with the objective of utilizing them for removal of metal ions from aqueous solution.

To the best of our knowledge there is no reported works viz a viz the adsorption of metal ions on chemically modified bean husks. This work is interesting from industrial perspective as it could provide low cost technique that may be effective for removal of toxic metals from industrial effluents.

MATERIAL AND METHODS

Preparation of metal ions aqueous solution: The metal ions aqueous solution Pb(II), Zn(II), Hg(II), Cu(II) and Cd(II) were prepared from $Pb(NO_3)_2$, $CuSO_4.5H_2O$, $Cd(NO_3)_2.4H_2O$, $ZnSO_4.7H_2O$ and $Hg(NO_3)_2.2H_2O$. The pH of solutions was adjusted to 5 to prevent hydrolysis.

Preparation of adsorbent: All the chemicals used were of analytical grade and used without further purification. The bean husks were obtained at the Ilorin main market. The husks were air-dried, grinded with a grinder and sieved through a 100µm mesh screen. The portion retained on the mesh was further air-dried and divided into two parts, first portion for modified and the other half unmodified.

Modification of adsorbent with formaldehyde: The procedure described by Saliba et al., (2000) was adopted for the modification of bean husks. A mixture of 100g of the bean husks powder, 400ml of 39% v/v formaldehyde and 1600ml of 0.2M tetraoxosulphate (VI) acid was boiled at 50^0C for 2h. The mixture was filtered and washed, several times with deionised water until the pH of 7.0 was attained. The residue was dried in an oven at 50^0C for 24h.

Modification of adsorbent with pyridine: The modified procedure described by Saliba et al., (2000) was adopted. 100g of bean husks powder were homogenized with 1500ml of 7% aqueous tetraoxosulphate (VI) acid and heated at 65^0C for

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24h. The mixture was washed thoroughly with deionised water and dried at 50^0C in an oven. A mixture of 70g of substrate, 500ml pyridine and 80g of EDTA was heated at 70^0C for 3h. It was allowed to cool and later filtered. The modified substrate was washed several times with deionised water until a pH of 7.0 was attained.

Determination of contact time: The contact time experiment was conducted to obtain how long the adsorbent would take to absorb maximum amount of metal ions. 500mg of each of the modified adsorbents was weighed into conical flasks. Pb^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+} in solution (2.50mg in 50ml water) were added to the adsorbent. The flasks were then labeled for time intervals 30, 60, 90, 120, 150, 180, and 210 minutes. The flasks were tightly covered and shaken at the appropriate time interval. At the end of each time interval, the suspension was filtered and analyzed for metal ions concentrations. It was discovered that optimum adsorption of all the metals were achieved within the first 160-180mins and remained fairly stable thereafter. Therefore contact time of 3hr was chosen for the equilibrium sorption experiment.

Equilibrium sorption experiment: The batch adsorption of the metals ions by modified bean husks were carried out by shaking 1.0g of the substrate with 100ml of various concentration. ($10mg/dm^3$, $15mg/dm^3$, $25mg/dm^3$, $30mg/dm^3$, $45mg/dm^3$, and $55mg/dm^3$) of metal ions solution in a pyrex reagent bottles at room temperature (25 ± 1^0C) using an electrical shaker at predetermined contact time of 3h. The mixtures were then filtered and the filtrate analyzed for metal ions concentrations. Blank solutions were also shaken without adsorbent and the concentrations of the metal ions were determined using the Atomic absorption spectrophotometer. (SP-9, Unicam model). This was taken as initial concentration. The difference between initial and final metal ions concentrations was calculated to be the metal ions concentration adsorbed by the substrate.

Calculations of the degree of metal ions removal and equilibrium isotherms: : The amount of Pb^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, and Cu^{2+} removed by formaldehyde and pyridine modified bean husks during the series of batch investigations were determined by means of a mass balance expression as shown in Equation 1.

$$q_e = \frac{v}{m}(C_o - C_e) \qquad (1)$$

Here, q_e is the metal concentration of the substrate (mg/g) at equilibrium, C_e is the metal concentration in solution (mg/dm^3) at equilibrium, C_0 is the initial metal concentration in solution mg/dm^3. V is the volume (in dm^3) of initial metal solution used, and m represents the mass (in g) of the substrate used. The experiments were performed in triplicate, and the means were taken for each set of values.

Langmuir equation (L) was applied in the form (eqn 2) described by (Horsfall and Spiff, 2005)

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \qquad (2)$$

Here, K_L (in 1/g) is a constant related to the adsorption / desorption energy, and q_{max} is the maximum sorption upon complete saturation of the substrate surface. The linear plots of C_e/q_e Vs. C_e for both modified formaldehyde and pyridine bean husks were carried out to obtain Langmuir adsorption isotherm. The value of q_{max} and K_L were determined from the slopes and intercept of the plots and are reported in Table 1.

The Freundlich (F) model was chosen to estimate the adsorption intensity of the bean husks. Freundlich equation was applied in the form (Eqn. 3) described by Horsfall and Spiff, 2005.

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (3)$$

A plot of 1n C_e against 1n q_e was carried out to obtain a straight line which indicated Freundlich adsorption isotherm. The constants 1/n and 1n K_F can be determined from the slope and intercept, respectively.

RESULTS AND DISCUSSION

To estimate the sorption capacity, experimental data from various initial concentration experiments were fitted to Langmuir and Freundlich equilibrium adsorption Isotherms.

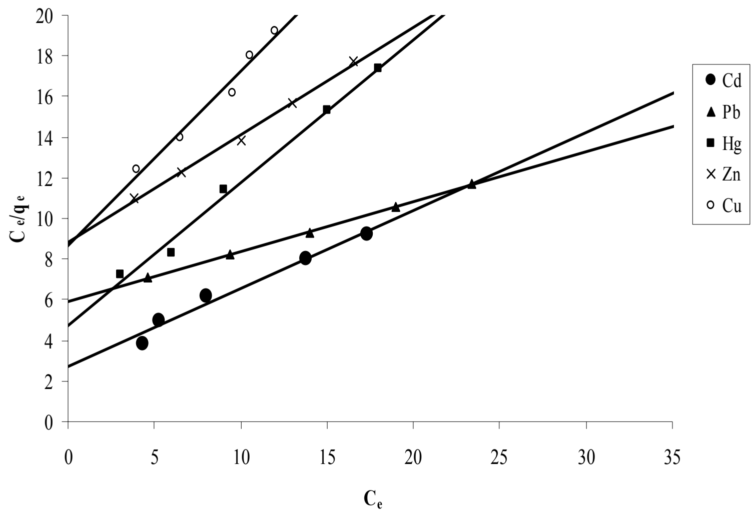

Fig 1: Linear Langmuir adsorption isotherm for formaldehyde modified bean husk

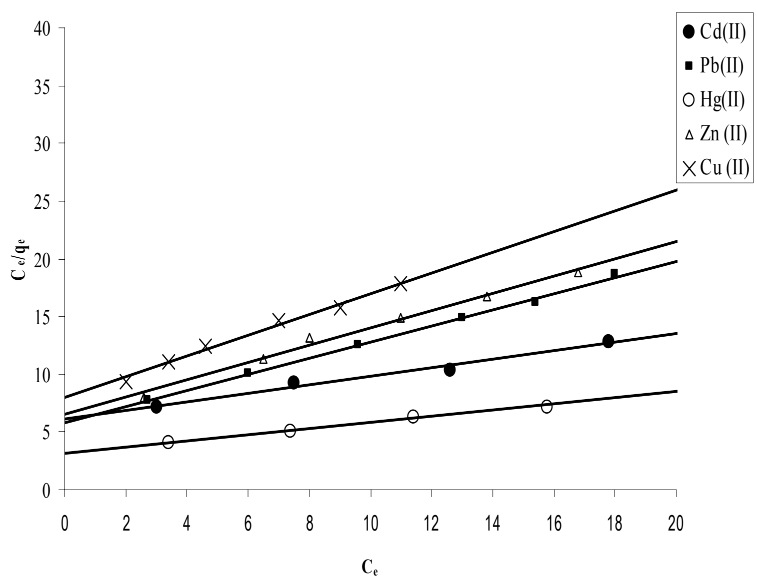

Fig 2: Linear Langmuir adsorption isotherm for pyridine modified bean husk

Fig 1 and 2 show the data linearized to fit the Langmuir equation. The plots of specific sorption C_e/q_e against equilibrium Concentration (C_e) gave the linear isotherm parameters q_{max} and K_L. The calculated values of K_L and q_{max} are shown in Table 1. The adsorption Coefficient K_L which is related to the apparent energy of sorption showed that formaldehyde bean husks has highest values of K_L for Cu^{2+} and lowest value of K_L for Pb^{2+}. This could mean that the energy of adsorption is not very favourable for Cu^{2+} than the rest of the metal ions. For pyridine modified bean husks, the highest value of K_L was also obtained for Cu^{2+} and the lowest value obtained for Hg^{2+}. This indicates that for both modified bean husks, not all binding sites may be available for Cu^{2+}. The value of sorption capacity q_{max}, which is a measure of the maximum adsorption capacity corresponding to complete monolayer, is showed in Table 1.

Table 1: Langmuir Adsorption parameters for formaldehyde and pyridine modified bean husks

	Formaldehyde		Pyridine	
Metal ions	K_L(1/g)	q_{max} (mg/g)	K_L (1/g)	q_{max} (mg/g)
Pb^{2+}	0.012	6.41	0.058	1.40
Cd^{2+}	0.030	4.76	0.041	1.82
Zn^{2+}	0.036	1.58	0.074	1.11
Hg^{2+}	0.060	1.51	0.030	4.76
Cu^{2+}	0.063	0.84	0.086	0.75

The q_{max} of 6.41, 4.76, 1.58, 1.51 and 0.84 mg/g for Pb^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+} and Cu^{2+} respectively showed that formaldehyde modified bean husks adsorbed most Pb^{2+} and least for Cu^{2+}. The trend in adsorption is in order of $Pb^{2+} > Cd^{2+} > Zn^{2+} > Hg^{2+} > Cu^{2+}$ which agreed with results of dynamic adsorption experiment. The results also conform to the report of Niagenaik et al (2002). The q_{max} value for pyridine modified bean husks has the values of 4.76, 1.82, 1.40, 1.11 and 0.75 mg/g for Hg^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} respectively. This shows that pyridine modified bean husk adsorbed most for Hg^{2+} and least for Cu^{2+}. The trend in adsorption as seen in Table 1, is in order of $Hg^{2+} > Cd^{2+} > Pb^{2+} > Zn^{2+} > Cu^{2+}$. This also agrees with results of dynamic sorption experiment. The adsorption Isotherm in figs 3 and 4 indicate that the sorption process of the metal ion on modified bean husks also obey the Freundlich Isotherm. The Freundlich equation parameter 1/n for all the metal ions were found to be less than unity, indicating that their isotherm can be characterized by a concave Freundlich Isotherm. This indicates that significant adsorption took place at low metal conc. The calculated Freundlich adsorption parameter K_F, which is an adsorption capacity, is shown in Table 2. The values are obtained from the graphs in figures 3 and 4.

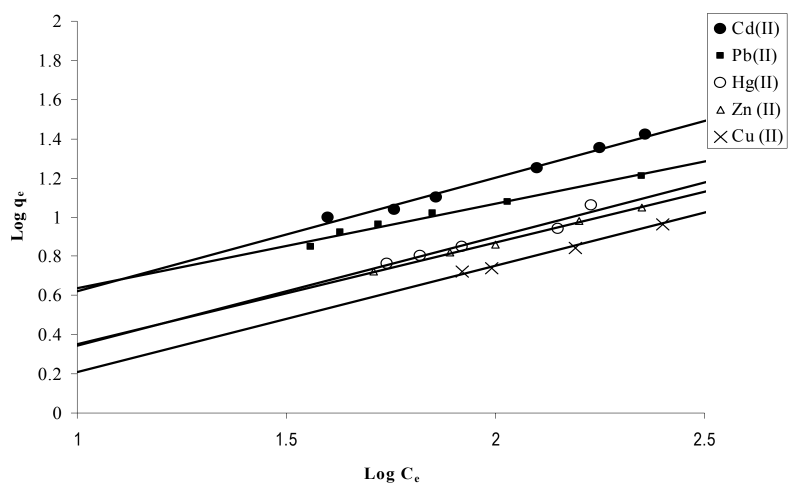

Fig 3: Linear Freundlich adsorption isotherm for formaldehyde modified bean husk

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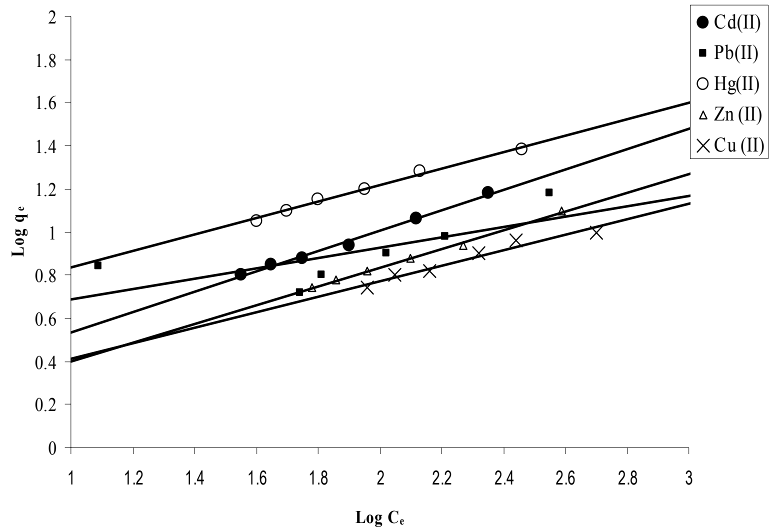

Fig 4: Linear Freundlich adsorption isotherm for pyridine modified bean husk

Adsorption capacities (K_F) for Pb^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, and Cu^{2+} using formaldehyde modified bean husks are 5.01, 3.63, 2.18, 1.82 and 1.58mg/g respectively while pyridine modified bean husks adsorption capacities gave 6.92, 3.63, 2.64, 2.48, 1.91 mg/g for Hg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} and Cu^{2+} respectively. These are in accordance with report made by investigation on other types of cellulosic materials (Gardea-Torresdey et al., 1999).

Table 2: Freundlich Adsorption parameters for formaldehyde and pyridine modified bean husks for metal ions

	Formaldehyde		Pyridine	
Metal ions	1/n	K_F(mg/g)	1/n	K_F(mg/g)
Pb^{2+}	0.40	5.01	0.47	2.64
Cd^{2+}	0.67	3.63	0.40	3.63
Zn^{2+}	0.53	2.18	0.50	2.48
Hg^{2+}	0.71	1.82	0.30	6.92
Cu^{2+}	0.60	1.58	0.45	1.91

It can be seen that the trend in adsorption as seen in table 2 is in order of $Pb^{2+} > Cd^{2+} > Zn^{2+} > Hg^{2+} > Cu^{2+}$ for formaldehyde modified bean husks, while that of pyridine modified bean husks is $Hg^{2+} > Cd^{2+} > Pb^{2+} > Zn^{2+} > Cu^{2+}$. This agrees with the trend obtained with Langmuir Adsorption isotherm and dynamic sorption. These results compared favorably with literature data (Adediran et al., 2000) and confirm that the modified bean husks can be used for removal of metal ion from aqueous solutions.

Conclusion: From the studies carried out in our laboratory on the modification of bean husks with formaldehyde and pyridine, it was observed that they have considerable potential for the removal of studied trace metal ion from aqueous solution. Our data revealed that formaldehyde modified bean husks showed highest removal rate for Pb^{2+} and pyridine modified bean husks showed the highest removal rate for Hg^{2+}.

Hence, not only is bean husks inexpensive and readily available, it also has the potential for metal removal from contaminated water, upon modification.

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