

Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob

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Abstract: The need to clean-up heavy metal contaminated environment can not be over emphasized. This paper describes the adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions from aqueous solution using unmodified and EDTA-modified maize cob. Maize cob was found to be an excellent adsorbent for the removal of these metal ions. The amount of metal ions adsorbed increased as the initial concentration increased. Also, EDTA - modification enhanced the adsorption capacity of maize cob probably due to the chelating ability of EDTA. Among the three adsorption isotherm tested, Dubinin-Radushkevich gave the best fit with R² value ranging from 0.9539 to 0.9973 and an average value of 0.9819. This is followed by Freundlich isotherm (Ave. 0.9783) and then the Langmuir isotherm (Ave. 0.7637). The sorption process was found to be a physiosorption process as seen from the apparent energy of adsorption which ranged from 2.05KJ/mol to 4.56KJ/mol. Therefore, this study demonstrates that maize cob which is an environmental pollutant could be used to adsorb heavy metals and achieve cleanliness thereby abating environmental nuisance caused by the maize cob.

Keywords: Adsorption isotherm; heavy metal; maize cob; waste water; EDTA.

Introduction

The impact of heavy metal release into our environment is increasing as a result of population explosion, haphazard rapid urbanization, industrial and technological expansion, increased energy utilization and waste generation from domestic and industrial sources. These have rendered many waters unwholesome and hazardous to man and other living resources [1]. The release of these heavy metals poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature [2]. Metallic effluents can lead to increased nutrient load in water bodies especially

if they are essential metals [3]. Also, these metals in effluent may increase fertility of the sediment and water column and consequently lead to eutrophication, which in open waters can progressively lead to oxygen deficiency, algal bloom and death of aquatic life [3].

Water contaminated with metallic effluent can cause several health problems. Lead for instance, can interfere with enzyme activities and formation of red blood cells. It can affect nerves and brain at low concentration. Heavy metals such as mercury, cadmium and chromium can bioaccumulate and through the food chain to toxic levels in man. Cadmium is responsible for kidney tubular impairment and osteomalacia [3].

Cadmium, zinc and manganese are reported to affect ion regulation if present in sufficient concentrations [4]. Cadmium and manganese are also known to affect calcium metabolism, development and skeletal calcification as well as long term effect and spawning and recruitment of fish and other aquatic lives. Any changes in pH of water bodies as a result of influx of effluent can cause serious change in water chemistry which can affect resources especially around the coastal areas.

The menace of these heavy metals has resulted in their urgent and effective removal. A number of technologies have been developed over the years to remove heavy metals from industrial wastewater, which include coagulation/flocculation process, membrane filtration, oxidation process, activated carbon adsorption, reverse osmosis, ion exchange, solvent extraction [5-7]. These processes may be ineffective or expensive especially when the heavy metal ions are in solutions containing in the order of 1-100 mg dissolved heavy metal ions/L [8]. These processes are also complicated, time consuming and require skilled personnel [1]. The high cost of coal based activated carbons has stimulated the search for cheaper alternatives. Recently, non-conventional and low cost agricultural by-products have been employed. This includes nut shells, wood, bone, peat processed into activated carbons [9-19]; maize cob and husk [20-23]; cassava waste [24]; sawdust and coconut fibre [25]; and so on. Biomasses such as *Aspergillus terreus* [26]; *Pseudomonas* sp. [27]; *Rhizopus arrhizus* [28]; have been reported to be important adsorbents for the removal of metals and organics from municipal and industrial wastewater.

In order to estimate practical or dynamic adsorption capacity, however, it is essential first of all to have enough information on adsorption equilibrium. Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Several adsorption isotherms exists. In this paper, we report the results of the adsorption isotherm studies for the bioremediation of Cd (II), Pb (II) and Zn (II) ions on unmodified and EDTA modified maize cob. Freundlich,

Langmuir and Dubinin-Radushkevich isotherms were used to analyze the experimental data. The effect of EDTA modification on the adsorbent was also investigated.

Experimental details

Material

Maize (zea mays) cob was collected from a local farm in Uturu, Abia state, Nigeria. They were cut into small pieces, air-dried and powdered in a grinder. The meal obtained was air-dried and first sieved through a 1000 μm mesh and then through an 850 μm and 450 μm mesh. The meal retained on the 850 μm and 450 μm mesh was used. It was soaked in dilute acid solution (HNO_3 , 2% v/v) for 24 hrs at room temperature, rinsed with deionized water and air-dried then stored for use. All reagents used were analytical grades, purchased and used without further purification.

Methods.

EDTA-Modification.

The activated and treated maize cob was EDTA-modified by a modified method previously reported [22]. A 30 g sample of the cob was hydrolyzed with 500 mL of 7% (v/v) aqueous sulphuric acid for 18 hours at 65°C. The mixture was filtered, washed with deionized water several times and dried at 50 °C. 17 g of the hydrolyzed cob was refluxed in a mixture of 300 mL of pyridine and 56.7 g of EDTA for 3 hours at 70 °C. The mixture was cooled followed by addition of 300ml of deionized water and then filtered. The filtered cob (EDTA – modified) was washed copiously with deionized water and dried at 50 °C for 12 hours. This was used as the modified adsorbent for the analysis. Another portion of the activated cob was left unmodified and also used for the analysis.

Batch Adsorption Experiment

Equilibrium adsorption of Cd (II), Pd (II) and Zn (II) ions on the maize cob was carried out using 100ml of various concentrations (1000 mg L^{-1} -2000 mg L^{-1}) of metal ions at constant metal ions-substrate contact time (1 hour), at tempera-

ture of 30 °C and pH of 7.5, 2 grams of the cob was put into 100ml of the metal ion solution of known concentration. At the end of the given contact time, the mixture was filtered rapidly. The metal ion concentration in the filtrate was determined by Flame Atomic Absorption Spectrometry (FAAS) model 200A. The amount of metal ion adsorbed by the cob was gotten as the difference between the initial and final ion concentration of the solutions. These were done for the unmodified and modified cob of two particle sizes.

Results and Discussion

The activation of the maize cob with 2% (v/v) nitric acid was to open-up the micro pores of the maize cob and make them ready for adsorption. Ethylenediamine tetracetic acid (EDTA) is a chelating agent. Therefore, the modification of the maize cob with EDTA was to change the surface characteristics of the adsorbent and then, to find out the effect this will have on the sorption process.

Adsorption Capacity

The results of the experimental runs for the adsorption of Cd (II), Pb (II) and Zn (II) ions on modified and unmodified maize cob of two particle sizes are thus presented. These results are presented as fraction of amount adsorbed (C_t/C_0) against initial concentration (C_0). The amount of metal ions adsorbed at time t is represented by C_t . Figure 1 shows the fraction of amount adsorbed against initial concentration for the adsorption of Cd (II) ion on modified and unmodified maize cob of two particle sizes. The amount adsorbed on 450 μm modified cob was highest followed by modified 850 μm , then followed by unmodified 450 μm and lastly unmodified 850 μm . Figure 2 shows the fraction of amount adsorbed (C_t/C_0) against initial concentration (C_0) for Pb (II) ion on modified and unmodified cob of two particle sizes while, Figure 3, shows that of the Zn (II) ion. The same trend seen in Figure 1, i.e., 450 μm modified > 850 μm modified > 450 μm unmodified > 850 μm unmodified, still obtains for Figure 2 and 3.

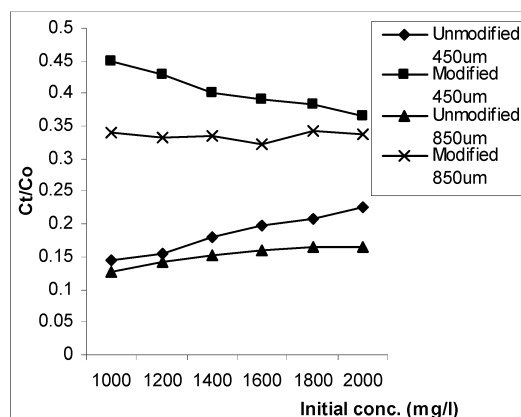


Figure 1. Fraction of amount adsorbed (C_t/C_0) against initial concentration (Mg/L) for Cd (II) ion on modified and unmodified maize cob of two particle sizes.

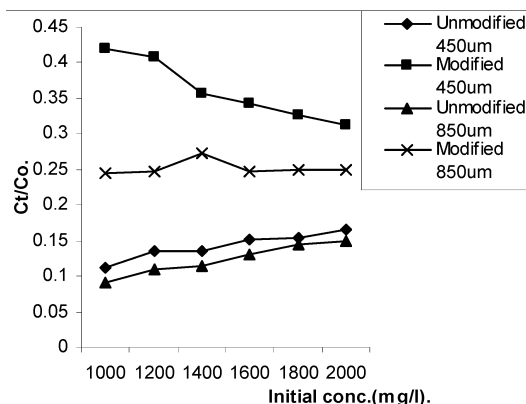


Figure 2. Fraction of amount adsorbed (C_t/C_0) against initial concentration (Mg/L) for Pb (II) ion on modified and unmodified maize cob of two particle sizes.

In all the three metal ions, the modified cob gave the highest adsorption capacity, showing that there was enhancement of adsorption by modifying with EDTA.

Figure 4, shows the fraction of amount adsorbed for the three metal ions on one size of 450 μm modified and unmodified maize cob. From this figure, we can see that Zn (II) ion on modified cob had the highest adsorption capacity and the least being Pb (II) ion on unmodified maize cob. The fraction of amount adsorbed for the three metal

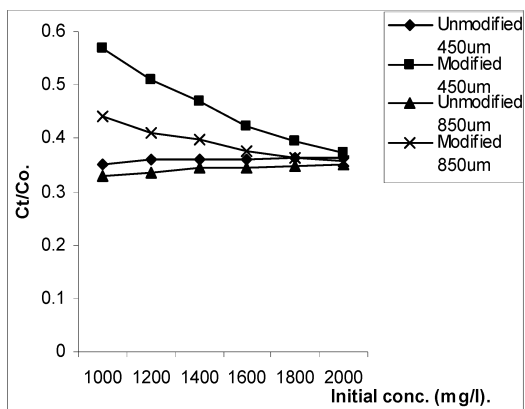


Figure 3. Fraction of amount adsorbed (C_t/C_o) against initial concentration (Mg/L) for Zn (II) ion on modified and unmodified maize cob of two particle sizes.

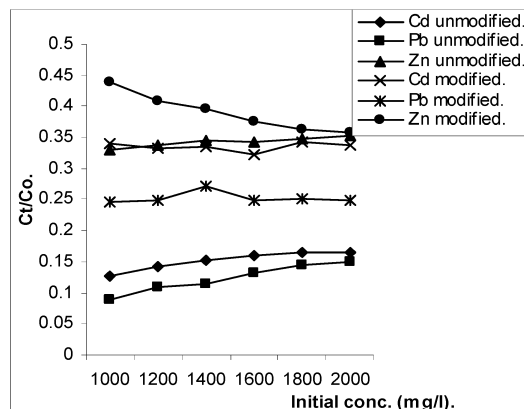


Figure 5. Fraction of amount adsorbed (C_t/C_o) against initial concentration (Mg/L) for the three metal ions on 850um modified and unmodified maize cob.

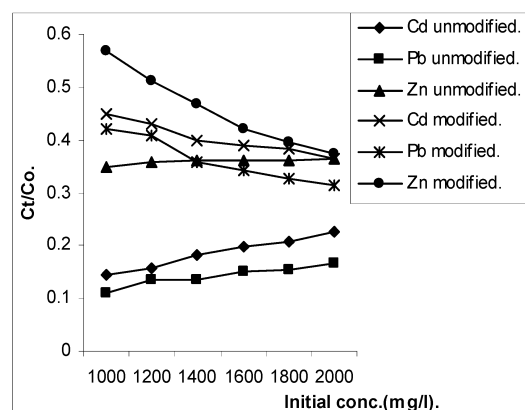


Figure 4. Fraction of amount adsorbed (C_t/C_o) against initial concentration (Mg/L) for the three metal ions on 450um modified and unmodified maize cob.

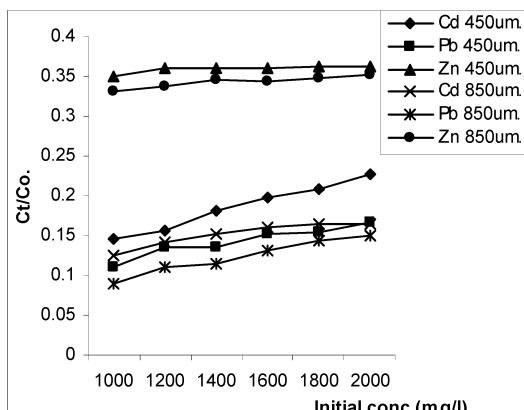


Figure 6. Fraction of amount adsorbed (C_t/C_o) against initial concentration (Mg/L) for the three metal ions on unmodified maize cob of two sizes.

ions on modified and unmodified maize cob of particle size 850 μm is shown on Figure 5. From this figure, we can also see that Zn (II) ion on modified had the highest and Pb (II) ion on unmodified had the lowest adsorption capacity. Therefore, we can put the trend of sorption as Zn (II) > Cd (II) > Pb (II). To compare vividly, the adsorption capacities of the two sizes, the fraction of amount adsorbed for the three metal ions on unmodified cob for the two sizes is shown on Figure 6, while that for modified cob is shown on

Figure 7. In each case, Zn (II) ion on 450 μm always had the highest value while Pb (II) on 850 μm always had the lowest value. This definitely means that, in addition to our previously proposed trends, the 450 μm size gave a better sorption capacity whether modified or unmodified than the larger particle size of 850mm.

These trends of sorption could be explained based on the ionic radius of the metal ions. The ionic radii (Pauling) of the metal ions are Cd^{2+} (0.97 \AA), Pb^{2+} (1.20 \AA), and Zn^{2+} (0.74 \AA).

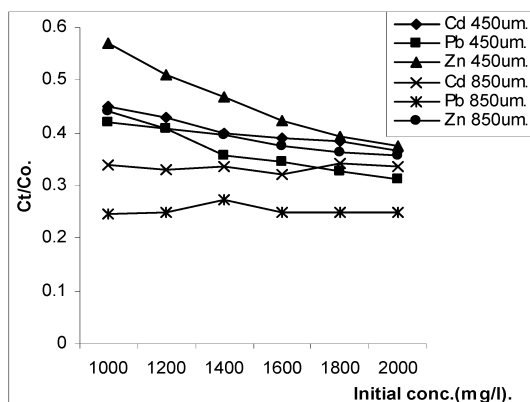
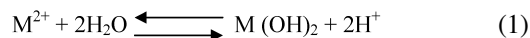


Figure 7. Fraction of amount adsorbed (C_t/C_0) against initial concentration (Mg/L) for the three metal ions on modified maize cob of two particle sizes.

This means that the smaller the ionic radius of a metal ion, the higher the adsorption rate. It has been noted that the smaller the ionic diameter, the higher the adsorption rate [29]. Thus, from our study, Zn (II) ion which has the smallest ionic radii had the highest adsorption capacity, followed by Cd (II) and Pb (II) ions. Therefore, the trend of ionic radii is in opposite direction to the trend of adsorption capacity.

This trend of adsorption can also be explained based on the trend of hydration energies of the metal ions (ΔH_{hyd}), which is given as $-2044 \text{ KJ mol}^{-1}$ for Zn^{2+} ; $-1806 \text{ KJ mol}^{-1}$ for Cd^{2+} and $-1480 \text{ KJ mol}^{-1}$ for Pb^{2+} [30]. It could be seen that the trend of the adsorption process also follows the trend of the hydration enthalpies of the metal ions. Also, the hydrolysis reaction of the metal ions could be represented by the equation below;



The above equation is an overall equation for a reaction that essentially takes place in two steps which may be given as;



This means that in aqueous solutions, these reactions will occur, and then followed by

the adsorption of the metal ions on the adsorbent. Thus, the heavy metal that becomes more hydrolyzed will be the least adsorbed. Giving by the hydration enthalpies of the metal ions given above, we expect that Pb^{2+} will be hydrolyzed more than Cd^{2+} and then Zn^{2+} , hence, Pb^{2+} is the least adsorbed and Zn^{2+} is adsorbed more than the other metal ions.

Adsorption Isotherm

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. The earliest and simplest known relationships describing the adsorption equation are the Freundlich and the Langmuir isotherms [31]. These two isotherms and the Dubinin-Radushkerich isotherm model were used to access the different isotherms and their ability to correlate the experimental data.

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm.

$$q = (q_{\max} b C_{eq}) / (1 + b C_{eq}) \quad (4)$$

where q is milligrams of metal accumulated per gram of the biosorbent material; C_{eq} is the metal residual concentration in solution at equilibrium, q_{\max} , is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates [32]. The Langmuir isotherm is based on these assumptions [33]. metal ions are chemically adsorbed at a fixed number of well defined sites; each site can hold only one ion; all sites are energetically equivalent and; there is no interaction between the ions.

When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and it's equated by the following equation.

$$C_{eq}/q = 1/q_{\max} b + C_{eq}/q_{\max} \quad (5)$$

From the linear plots of C_{eq}/q vs C_{eq} (not shown), we calculated the linear regression equations for the Langmuir isotherm for the sorption process shown on Table 1. From these regression equations and the linear plots, the values of the Langmuir constants were calculated and are shown on Table 2. q_{max} and b were obtained from the slope and intercept of the plots.

The essential characteristic of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined as [34];

$$R_L = 1/(1 + b C_0) \quad (6)$$

Where b is the Langmuir constant and C_0 is the initial concentration of the metal ions. The R_L value indicates the shape of the isotherm. According to McKay et al (1982), R_L values between 0 and 1 indicate favourable absorption. Also R_L values equal to 0 indicate irreversible absorption, $R_L = 1$ is linear and $R_L > 1$ is unfavourable. From our study, R_L values for Cd (II), Pb (II) and Zn (II) ions adsorption ranged from 0.0011 to 0.0476. This is for initial concentra-

tion of 1000-2000 mg L⁻¹ of the metal ions. Therefore, the adsorption process is favourable.

The Freundlich isotherm was chosen to estimate the adsorption intensity of the adsorbent towards the adsorbate. It is represented by the equation [36].

$$q = K_F C_{eq}^{1/n} \quad (7)$$

Where C_{eq} is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and K_F and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The linearised form of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as [34].

$$\ln q = \ln K_F + 1/n \ln C_{eq} \quad (8)$$

The Linear regression equation for the Freundlich adsorption isotherm is shown on Table 3. The values of K_F and n were calculated from the intercepts and slopes of the Freundlich plots respectively and are shown on Table 4. According to Kadrueln and Namasivayam (2000) [37], n

Table 1. Linear regression equation's of Langmuir Isotherm for adsorption of Cd (II), Pb (II) and Zn (II) on two particle sizes of unmodified and modified maize cob.

| Unmodified | | |
|------------------|-----------------------|-----------------------|
| Metal ions | 450µm | 850µm |
| Cd ²⁺ | y = 0.5051x + 1.752 | y = 0.3583x + 3.4193 |
| Pb ²⁺ | y = 0.5294x + 3.3187 | y = 0.8543x + 3.37 |
| Zn ²⁺ | y = 0.0174x + 0.7207 | y = 0.0329x + 0.8033 |
| Modified | | |
| Metal ions | 450µm | 850µm |
| Cd ²⁺ | y = -0.1x + 0.8433 | y = -0.0011x + 0.986 |
| Pb ²⁺ | y = -0.1669x + 1.4073 | y = -0.0069x + 1.9927 |
| Zn ²⁺ | y = -0.179x + 0.88 | y = -0.1066x + 0.948 |

Table 2. Langmuir isotherm constants for adsorption of Cd (II), Pb (II) and Zn (II) on two particle sizes of unmodified and modified maize cob.

| Metal ions | Unmodified | | | | Modified | | | |
|------------------|----------------|------------|-----------|-------|-----------|-------|-----------|-------|
| | 450µm | | 850µm | | 450µm | | 850µm | |
| | q_{max} mg/g | K_L L/mg | q_{max} | K_L | q_{max} | K_L | q_{max} | K_L |
| Cd ²⁺ | 1.98 | 0.29 | 2.79 | 0.10 | -10.0 | -0.12 | 909.09 | 1.12 |
| Pb ²⁺ | 1.89 | 1.66 | 1.17 | 0.25 | -5.99 | -0.12 | 144.93 | 6.95 |
| Zn ²⁺ | 57.47 | 0.02 | 30.40 | 0.04 | -5.59 | -0.20 | -9.38 | -0.11 |

Table 3. Linear regression equations of Freundlich isotherm for adsorption of Cd (II), Pb (II) and Zn (II) on two particle sizes of unmodified and modified maize cob.

| Unmodified | | |
|------------------|-----------------------|-----------------------|
| Metal ions | 450µm | 850µm |
| Cd ²⁺ | y = -0.0997x + 2.7773 | y = -0.0829x + 2.6333 |
| Pb ²⁺ | y = -0.09x + 2.6267 | y = -0.1031x + 2.6127 |
| Zn ²⁺ | y = -0.062x + 2.9353 | y = -0.0649x + 2.9287 |
| Modified | | |
| Metal ions | 450µm | 850µm |
| Cd ²⁺ | y = -0.0426x + 2.9173 | y = -0.0603x + 2.8993 |
| Pb ²⁺ | y = -0.0337x + 2.838 | y = -0.0603x + 2.776 |
| Zn ²⁺ | y = -0.017x + 2.885 | y = -0.0423x + 2.9013 |

Table 4. Freundlich isotherm constants for adsorption of Cd (II), Pb (II) and Zn (II) on two particle sizes of unmodified and modified maize cob.

| Metal ions | Unmodified | | | | Modified | | | |
|------------------|----------------|--------|----------------|--------|----------------|--------|----------------|--------|
| | 450µm | | 850µm | | 450µm | | 850µm | |
| | K _F | n | K _F | n | K _F | n | K _F | n |
| Cd ²⁺ | 598.8 | -10.03 | 429.8 | -12.06 | 826.6 | -23.47 | 793.1 | -16.58 |
| Pb ²⁺ | 423.4 | -11.11 | 409.9 | -9.70 | 688.6 | -29.67 | 597.0 | -16.58 |
| Zn ²⁺ | 861.6 | -16.13 | 848.6 | -15.41 | 767.4 | -58.82 | 796.7 | -23.64 |

values between 1 and 10 represents beneficial adsorption. Also, Akgerman and Zardkoochi (1996) [38], states that the values of k_F and n determine the steepness and curvature of the isotherm. The Freundlich equation frequently gives n adequate description of adsorption data over a restricted range of concentration, even though it is not based on any theoretical background. Apart from a homogeneous surface, the Freundlich equation is also suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau, indicating a multi-layer adsorption [39]. The values of $1/n$, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa [40].

The magnitude of K_F and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity. The value of n , which is related to the distribution of bonded ions on the adsorbent surface is found to be negative for the three metal ions adsorption on the two adsorbent types this indicates unfavourable adsorption. Also,

the higher the K_F value, the greater the adsorption intensity. Therefore, the K_F values which are higher for the modified cob confirms that the adsorption capacity of the modified cob was greater than that of the unmodified cob.

The Dubinin – Radushkevish isotherm was chosen to estimate the characteristics porosity of the biomass and the apparent energy of adsorption. The model is represented as [41].

$$q_e = q_D \exp(-BD [RT L_n (1 + 1/C_{eq})]^2) \quad (9)$$

Where, B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution and q_D is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface. The Linear form of equation (9) is given as:

$$\ln q_e = \ln q_D - 2B_D RT \ln(1 + 1/C_e) \quad (10)$$

The plots of $\ln q_e$ against $RT \ln(1 + 1/C_e)$ (not shown), yielded straight lines and indicates a

Table 5. Linear regression equations of Dubinin-Radushkevich isotherm for adsorption of Cd (II), Pb (II) and Zn (II) on two particle sizes of unmodified and modified maize cob.

| Unmodified | | |
|------------------|-----------------------|-----------------------|
| Metal ions | 450 μ m | 850 μ m |
| Cd ²⁺ | y = -0.2283x + 6.3907 | y = -0.1911x + 6.0607 |
| Pb ²⁺ | y = -0.2097x + 6.0607 | y = -0.2374x + 6.0093 |
| Zn ²⁺ | y = -0.1431x + 6.766 | y = -0.15x + 6.74 |
| Modified | | |
| Metal ions | 450 μ m | 850 μ m |
| Cd ²⁺ | y = -0.0966x + 6.7113 | y = -0.11366x + 6.668 |
| Pb ²⁺ | y = -0.0754x + 6.524 | y = -0.1377x + 6.3887 |
| Zn ²⁺ | y = -0.047x + 6.665 | y = -0.0949x + 6.6753 |

Table 6. Dubinin-Radushkevich isotherm constants for adsorption of Cd (II), Pb (II) and Zn (II) on two particle sizes of unmodified and modified maize cob.

| Metal ions | Unmodified | | | | | | Modified | | | | | |
|------------------|----------------|----------------|------|----------------|----------------|------|----------------|----------------|------|----------------|----------------|------|
| | 450 μ m | | | 850 μ m | | | 450 μ m | | | 850 μ m | | |
| | q _D | B _D | E | q _D | B _D | E | q _D | B _D | E | q _D | B _D | E |
| Cd ²⁺ | 596.3 | 0.114 | 2.09 | 428.7 | 0.096 | 2.28 | 821.6 | 0.048 | 3.23 | 786.8 | 0.068 | 2.71 |
| Pb ²⁺ | 428.7 | 0.105 | 2.18 | 407.2 | 0.119 | 2.05 | 681.3 | 0.038 | 3.63 | 595.1 | 0.069 | 2.69 |
| Zn ²⁺ | 867.8 | 0.072 | 2.64 | 845.6 | 0.075 | 2.58 | 784.50 | 0.024 | 4.56 | 792.6 | 0.048 | 3.23 |

Table 7. Comparison of regression coefficients (R₂) for Freundlich, Langmuir and Dubinin-Radushkevich isotherms for the adsorption process

| Metal ions | Unmodified | | Modified | |
|-------------------------------|-------------|-------------|-------------|-------------|
| | 450 μ m | 850 μ m | 450 μ m | 850 μ m |
| Freundlich isotherm | | | | |
| Cd ²⁺ | 0.9871 | 0.9694 | 0.9824 | 0.9925 |
| Pb ²⁺ | 0.9770 | 0.9836 | 0.9656 | 0.9557 |
| Zn ²⁺ | 0.9823 | 0.9857 | 0.9797 | 0.9923 |
| Langmuir isotherm | | | | |
| Cd ²⁺ | 0.9626 | 0.8530 | 0.9704 | 0.001 |
| Pb ²⁺ | 0.8735 | 0.9308 | 0.9746 | 0.0845 |
| Zn ²⁺ | 0.6745 | 0.8794 | 0.9872 | 0.9717 |
| Dubinin-Radushkevich isotherm | | | | |
| Cd ²⁺ | 0.9882 | 0.9713 | 0.9885 | 0.9921 |
| Pb ²⁺ | 0.9741 | 0.9806 | 0.9685 | 0.9539 |
| Zn ²⁺ | 0.9847 | 0.9885 | 0.9973 | 0.9932 |

good fit of the isotherm to the experimental data. The linear regressions are shown on Table 5. The values of q_D and B_D calculated from the intercepts slopes of the plots respectively are shown on Table 6. Also shown on the same table 6 is the

apparent energy (E) of adsorption from the Dubinin-Radushkevich isotherm, which was calculated using equation (11)

$$E = 1/(2B_D)^{1/2} \quad (11)$$

The higher the values of q_D , the higher the adsorption capacity. The values of q_D from Table 6 are seen to be higher for the modified than the unmodified cob, showing that the modified cob exhibited higher adsorption capacity than the unmodified cob. The values of the apparent energy of adsorption shown on Table 6 depict physiosorption process [41]. This means that the Dubinin-Radushkevich isotherm gave a very good fit to the adsorption process. This is similar to results from previous studies [41].

A comparison of the coefficient of regression (R^2) for the three isotherms is shown on Table 7. For the Freundlich isotherm we have a range of 0.9557 to 0.9925 with an average value of 0.9783. The range for the Langmuir isotherm is 0.001 to 0.9872 with an average value of 0.7637. For the Dubinin-Radushkevich isotherm, the range of R^2 value is 0.9539 to 0.9973, with an average value of 0.9819. Therefore, in as much as one can say that the isotherms are appropriate in their own merits in describing the potential of unmodified and EDTA – modified maize cob for removal of Cd (II), Pb (II) and Zn (II) ions, we can also conclude from the average values of R^2 that the Dubinin-Radushkevich isotherm is the best followed by the Freundlich isotherm and then the Langmuir isotherm.

Conclusions

Maize cob is an agricultural by product and constitutes an environmental nuisance when littered all over the place due to foul odour on decomposition. In this study, it has been found to be a good adsorbent for the removal of Cd (II), Pb (II) and Zn (II) ions from aqueous solutions. The modification of the adsorbent using EDTA has been shown to enhance the adsorption capacity. Among the three adsorption isotherms tested, Dubinin-Radushkevich isotherm gave the best fit, followed by the Freundlich isotherm and then the Langmuir isotherm. From the values of the apparent energy of adsorption, the adsorption process was found to be a physiosorption process.

The recovery of the metal ions and the regeneration of the adsorbent is our next research focus. This will help to reduce the discharge of

the metal loaded adsorbent into the environment and also, maximize the process efficiency and minimize the cost of the remediation process. This is also very essential especially in the case of the modified adsorbent which may generate some harmful degradation by-products because of the modification process. Therefore, the research into the desorption of the metal ions from the loaded adsorbent probably by the use of some solvents is a good focus. This will help to regenerate the adsorbent. Again, other methods of modification are also being investigated.

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