

Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk

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Abbreviations: EDTA: ethylenediamine tetra acetic acid

The mobilization of heavy metals in the environment due to industrial activities is of serious concern due to the toxicity of these metals in humans and other forms of life. The equilibrium adsorption isotherms of Cd(II), Pb(II) and Zn(II) ions, detoxification from waste water using unmodified and EDTA-modified maize husk have been studied. Maize husk was found to be an excellent adsorbent for the removal of these metal ions. The amount of these metal ions adsorbed increased as the initial concentration increased. Also, EDTA-modification enhanced the adsorption capacity of maize husk due to the chelating ability of ethylenediamine tetra acetic acid (EDTA). Among the three adsorption isotherms tested, Dubinin-Radushkevich isotherm gave the best fit with R^2 value ranging from 0.7646 to 0.9988 and an average value of 0.9321. This is followed by Freundlich and then Langmuir isotherms. The sorption process was found to be mostly a physisorption process as seen from the apparent energy of adsorption which ranged from 1.03 KJ/mol to 12.91 KJ/mol. Therefore, this study demonstrates that maize husk which is an environmental pollutant could be used to adsorb heavy metals and achieve environmental cleanliness.

The mobilization of heavy metals in the environment due to industrial activities is of serious concern due to the toxicity

of these metals in humans and other forms of life (Al-Garni, 2005). These metals tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, becoming a serious threat to the environment. These metals can be toxic to microbial population at sufficiently high concentration. However, some metals such as silver, mercury, cadmium and copper are markedly more toxic even at very low levels. Also, among these toxic heavy metals, mercury, lead and cadmium have been called "the big three" and are in the lime light due to their major impact on the environment (Volesky, 1994; Volesky and Holan, 1995). These heavy metal pollutants are also non-biodegradable.

Anthropogenic sources of these heavy metals include wastes from the electroplating and metal finishing industries, metallurgical industries, chemical manufacturing, tannery operations, mine drainage, battery manufacturing, and leachates from landfills and contaminated ground water from hazardous waste sites (Gallagher et al. 1990; Reed et al. 1994). Sources of human exposure to Cd include atmospheric, terrestrial and aquatic routes (Lopez et al. 1994), as well as phosphate fertilizer (McLaughlin et al. 1996). The most severe form of Cd toxicity in humans is "Itai-itai", a disease characterized by excruciating pain in the bone (Kasuya et al. 1992; Yasuda

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Table 1. Linear regression equations and coefficient of determination (R^2) for Freundlich, Langmuir and Dubinin-Radushkevich isotherm models for the metal ions adsorption on unmodified and modified maize husk of 450 μm and 850 μm particle sizes.

Metal ions	Unmodified		Modified	
	450 μm	850 μm	450 μm	850 μm
Freundlich Isotherm				
Cd	$Y = 2.6421 x - 5.3968$ ($R^2 = 0.9775$)	$Y = 1.6218 x - 2.5328$ ($R^2 = 0.9875$)	$Y = 0.2926 x + 2.0573$ ($R^2 = 0.9743$)	$Y = 0.9686 x + 0.0876$ ($R^2 = 0.9334$)
Pb	$Y = 1.8178 x - 3.178$ ($R^2 = 0.9748$)	$Y = 2.1734 x - 4.3554$ ($R^2 = 0.9932$)	$Y = 0.2506 x + 2.0689$ ($R^2 = 0.9609$)	$Y = 1.0631 x + 0.4862$ ($R^2 = 0.9952$)
Zn	$Y = 1.1595 x - 0.3138$ ($R^2 = 0.9846$)	$Y = 1.3107 x - 0.7849$ ($R^2 = 0.9846$)	$Y = 0.0245 x + 2.7883$ ($R^2 = 0.6279$)	$Y = 0.312 x + 1.977$ ($R^2 = 0.9768$)
Langmuir Isotherm				
Cd	$Y = -0.0066 x + 9.593$ ($R^2 = 0.9621$)	$Y = -0.003 x + 7.7867$ ($R^2 = 0.8345$)	$Y = 0.0012 x + 0.1344$ ($R^2 = 0.9795$)	$Y = 0.00008 x + 0.9488$ ($R^2 = 0.0233$)
Pb	$Y = -0.0046 x + 10.038$ ($R^2 = 0.8502$)	$Y = -0.007 x + 14.646$ ($R^2 = 0.9341$)	$Y = 0.0014 x + 0.1902$ ($R^2 = 0.9742$)	$Y = 0.00008 x + 2.0808$ ($R^2 = 0.1238$)
Zn	$Y = -0.0003 x + 0.9212$ ($R^2 = 0.6266$)	$Y = -0.0006 x + 1.208$ ($R^2 = 0.8414$)	$Y = 0.0013 x + 0.0339$ ($R^2 = 0.9966$)	$Y = 0.0012 x + 0.1655$ ($R^2 = 0.9887$)
Dubinin-Radushkevich Isotherm				
Cd	$Y = -0.9121 x + 8.138$ ($R^2 = 0.9654$)	$Y = -0.6514 x + 7.0375$ ($R^2 = 0.9988$)	$Y = -0.022 x + 6.6179$ ($R^2 = 0.8743$)	$Y = -0.1654 x + 7.079$ ($R^2 = 0.9121$)
Pb	$Y = -0.7767 x + 7.2452$ ($R^2 = 0.9765$)	$Y = -0.9387 x + 7.3686$ ($R^2 = 0.9876$)	$Y = -0.029 x + 6.473$ ($R^2 = 0.8875$)	$Y = -0.2879 x + 6.9124$ ($R^2 = 0.9943$)
Zn	$Y = -0.185 x + 7.4298$ ($R^2 = 0.9956$)	$Y = -0.249 x + 7.6253$ ($R^2 = 0.9693$)	$Y = -0.0051 x + 6.6113$ ($R^2 = 0.7646$)	$Y = -0.0267 x + 6.5972$ ($R^2 = 0.8597$)

et al. 1995). Other health implications of Cd in humans include kidney dysfunction, hepatic damage and hypertension (Klaassen, 2001). Zn is an essential element to man, being a cofactor for many enzyme systems. It has been reported to competitively inhibit Pb uptake in cells (Lou et al. 1991). Toxic levels of Pb in man have been associated with encephalopathy, seizures and mental retardation (Schumann, 1990).

Removal of toxic heavy metals from industrial waste waters is essential from the stand point of environmental pollution control (Puranik and Paknikar, 1999; Yan and Viraraghavan, 2003). Chemical oxidation, reduction, precipitation, solidification, electrolytic recovery and ion exchange are some of the physicochemical waste water treatment processes which are being used for metal removal. Application of such methods however, is sometimes restricted because of technical or economical constraints (Bossrez et al. 1997; Yu and Kaewsarn, 1999). Hence, more economical means such as biosorption for the removal of metals have been sought for. It is non-polluting,

and it can be highly selective, more efficient, easy to operate and hence cost effective. Also, adsorption using activated carbon have been reported (Ouki and Neufeld, 1997; Shim et al. 2001; Monser and Adhoum, 2002).

Various biomass materials and agricultural by-products have been utilized in the removal of toxic heavy metals from waste water, such as; sunflower stalks (Sun and Shi, 1998), coconut fibre and sawdust (Raji and Anirudhan, 1997; Igwe et al. 2005), maize cob (Abia et al. 2005), cassava waste (Abia et al. 2003), banana pith (Low et al. 1995) *medicago sativa* (Alfalfa) (Gardea-Torresdey et al. 1998), Sphagnum moss peat (Ho et al. 1995), Fungal, bacteria, algae (Kapoor and Viraraghavan, 1995; Puranik and Paknikar, 1999; Yang and Volesky, 1999; Davis et al. 2000; Figueira et al. 2000; Aksu, 2001; Hussein et al. 2003; Liu et al. 2004) and so on. The present article reports the feasibility of utilizing maize husk as a low cost adsorbent material for the removal of toxic heavy metal ions from waste water.

Maize husk is an example of plant residues. They are mainly composed of ligno-cellulose materials, have relatively large surface areas that can provide intrinsic adsorptive sites to many substrates and can inherently adsorb waste chemicals such as dyes and cations in water due to the columbic interaction and physical adsorption (Sun and Shi, 1998). They are renewable agricultural wastes available abundantly at little or no cost. Disposal of the agricultural biomasses form litters and constitute environmental pollution mostly in the south-eastern part of Nigeria and other nations that cultivate maize. This constitutes a major obstacle to sustainable environment.

Three heavy metal ions Cadmium(II) Lead(II) and Zinc(II) were selected and used in adsorption isotherm studies of maize husk. The effect of modifying the adsorbent using EDTA, a chelating agent was also investigated. Particle size of the adsorbent was also varied. The effects of pH and temperature on the sorptive capacity of the maize husk with these three heavy metal ions have previously been reported (Igwe and Abia, 2003), and the optimum temperature of 30°C and pH of 7.5 that was gotten, was used in this study.

MATERIALS AND METHODS

Materials

Maize (*zea mays*) husk was collected from a local farm in Uturu, Abia state, Nigeria. They were cut into small pieces, air- dried and powered in a grinder separately. 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 nitric acid solution (2% v/v) overnight, rinsed with deionized water and air-dried. All reagents used were analytical grades, purchased and used without further purification.

Methods

EDTA-modification. The activated and treated maize husk was EDTA-modified by a method previously reported (Abia et al. 2005). A 30 g sample of the husk was hydrolyzed with 500 ml of 7% (v/v) aqueous sulphuric acid for 18 hrs at 65°C. The mixture was filtered, washed with deionized water several times and dried at 50°C. 17 g of the hydrolyzed husk were refluxed in a mixture of 300 ml of pyridine and 56.7 g of EDTA for 3 hrs at 70°C. The mixture was cooled followed by addition of 300 ml of deionized water and then filtered. The filtered husk (EDTA-modified) was washed copiously with deionized water and dried at 50°C for 12 hrs. This was used as the modified adsorbent for the analysis. Another portion of the activated husk was left unmodified and also used for analysis.

Batch adsorption experiment

Equilibrium sorption of Cd(II), Pb(II) and Zn(II) ions on the husk was carried out using 100 mL of various concentrations (2000 mg/L-1000 mg/L) of metal ions at

Table 2. Freundlich, Langmuir and Dubinin-Radushkevich isotherm constants for the metal ions adsorption on unmodified and modified maize husk of 450 µm and 850 µm particle sizes.

Metal ions	Unmodified				Modified							
	450 µm		850 µm		450 µm		850 µm					
*F	K _F	n	K _F	n	K _F	n	K _F	n				
Cd Pb	4.0 x 10 ⁻⁶	0.38	2.93 x 10 ⁻³	0.62	114.10	3.42	1.22	1.03				
	6.64 x 10 ⁻⁴	0.55	4.41 x 10 ⁻⁵	0.46	117.19	3.99	3.06	0.94				
	0.49	0.86	0.16	0.76	614.11	40.82	94.84	3.21				
*L	As	K	As	K	As	K	As	K				
Cd	-151.51	-6.88 x 10 ⁻⁴	-3.33 x 10 ²	-3.86 x 10 ⁻⁴	833.33	8.93 x 10 ⁻³	1.25 x 10 ⁴	8.43 x 10 ⁻⁵				
Pb	-217.39	-4.58 x 10 ⁻⁴	-142.86	-4.78 x 10 ⁻⁴	714.29	7.36 x 10 ⁻³	1.25 x 10 ⁴	3.85 x 10 ⁻⁵				
Zn	-3.33 x 10 ³	-3.26 x 10 ⁻⁴	-166.67	-4.97 x 10 ⁻³	769.23	0.04	833.33	7.25 x 10 ⁻³				
*D-R	B _D	q _D	E	B _D	q _D	E	B _D	q _D	E	B _D	q _D	E
Cd	0.456	3422.07	1.05	0.326	1138.54	1.24	0.011	748.37	6.74	0.083	1186.78	2.45
Pb	0.388	1401.36	1.14	0.469	1585.41	1.03	0.015	647.42	5.77	0.144	1004.66	1.86
Zn	0.093	1685.47	2.32	0.125	2049.40	2.00	0.003	743.45	12.91	0.013	733.04	6.20

*F: Freundlich.

*L: Langmuir.

*D-R: Dubinin-Radushkevich isotherms.

constant metal ion-substrate contact period (1 hr), at 30°C and pH of 7.5. 2 g of husk was put into 100 mL of the metal ion solution of specified 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 spectrophotometer (FAAS) model 200A. The amount of metal ions adsorbed by the husk was taken as the difference between the initial and final ion concentration of the solutions. These were done for the unmodified and modified husk of two particle sizes.

RESULTS AND DISCUSSION

Sorption capacity

The differences in equilibrium sorption of Cd, Pb and Zn ions are illustrated as fractions of amount adsorbed (C_t/C_o) against initial concentration (C_o). The amount of the metal ions adsorbed at any time (t) is represented by C_t . The fraction of amount adsorbed against initial concentration for the adsorption of Cd(II) on modified and unmodified husk of two particle sizes is shown on Figure 1. The amount adsorbed on 450 μm modified was highest followed by 850 μm modified husk. The least was 450 μm unmodified husk. Figure 2 shows the fraction of amount adsorbed (C_t/C_o) against the initial concentration for Pb(II) ion on modified and unmodified husk of two particle sizes while Figure 3 shows that of the Zn(II) ion. For Pb(II) ion, the 850 μm modified was the highest, while for Zn(II) ion, the 450 μm modified was the highest. In all the three metal ions, the modified husk gave the highest adsorption capacity, showing that there was enhancement of adsorption by modifying with EDTA. Also comparing Figure 1, Figure 2 and Figure 3, it would be observed, that Zn(II) ion on modified husk gave the highest adsorption capacity and the least being Cd(II) ion on unmodified. It means generally, we can say that the trend of the sorption is $\text{Zn(II)} > \text{Pb(II)} > \text{Cd(II)}$. Comparing the adsorption capacities of the two sizes, for unmodified husk, Zn(II) on 850 μm size gave the highest adsorption followed by Zn(II) on 450 μm size. The same holds for the other two metal ions. For the unmodified husk, the trend changed for Zn(II) and Cd(II) that is, the 450 μm size was now higher than the 850 μm size in each case. That for the Pb(II) ion remained the same.

These trends could be explained based on the modes of adsorption on cellulosic materials. The adsorption of metal ions on cellulosic materials could be attributed to two main terms; intrinsic adsorption and columbic interaction (Sun and Shi, 1998). The columbic term results from the electrostatic energy of interactions between the adsorbents and the adsorbates. The charges on both substrates as well as softness or hardness of charge on both sides are mostly responsible for the intensity of the interaction. Columbic interaction can be observed from adsorption of cationic species versus anionic species on adsorbents (Sun and Shi, 1998). The intrinsic adsorption of the materials is determined by their surface areas, which can be observed

by the effect of different sizes of adsorbents. Also both factors could interact, that is, the micro porous adsorption and surface adsorption takes place at the same time.

All these results show that the amounts of the metal ions bound by the husk depend on the metal ion type, the concentration of the metal ion solution and the modification of the adsorbent. The differences in the uptake level of the metal ions can be explained in terms of the difference in the ionic sizes of the metal ions, the nature and distribution of active groups on the substrate and the mode of interaction between the metal ions and the substrate (Igwe and Abia, 2003). The ionic radii (Pauling) of the metal ions are Cd^{2+} (0.97 Å) Pb^{2+} (1.20 Å) and Zn^{2+} (0.74 Å). It has been noted that the smaller the ionic diameters, the higher the adsorption rate (Uzun and Guzel, 2000). From our study, Zn(II) ion which has the smallest ionic radius had the highest adsorption capacity. This is followed by Pb(II) and then Cd(II), against the trend of ionic radius. Thus, we reasoned that, the surface adsorption on constituent group on substrates plays a more vital contribution to adsorption capacity than the micro porous adsorption and this is more pronounced for the Pb(II) ion than the Cd(II) ion. Therefore, this makes the adsorption of Pb(II) ion higher than that of Cd(II) ion.

Sorption isotherms

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation (Muhamad et al. 1998; Jalali et al. 2002). These two isotherms and the Dubinin-Radushkevich isotherm model were used to assess the different isotherms and their ability to correlate experimental data.

The Freundlich isotherm. The Freundlich isotherm model was chosen to estimate the adsorption intensity of the sorbent towards the adsorbent. It is an empirical equation employed to describe the isotherm data given by:

$$Q_e = K_F (C_e)^{1/n} \quad [1]$$

Where, K_F and n are the Freundlich empirical constants (Teng and Hsieh, 1998). The linearized form of the Freundlich equation was used for analysis and it is given as;

$$\log Q_e = \log K_F + 1/n \log C_e \quad [2]$$

Where, C_e is the equilibrium liquid phase ion concentration (mg/L) and Q_e is the equilibrium solid phase ion concentration (mg/L).

Application of the Freundlich isotherm equation to analyze the equilibrium isotherms of the three ions gave linear plots, Figure 4 and Figure 5, for the unmodified and

modified husk respectively. The linear regression equations and the regression co-efficient (R^2) are shown on Table 1. The regression coefficient (R^2) ranges from 0.6279 for Zn(II) ion on unmodified husk of 450 μm particle size to 0.9952 for Pb(II) ion on unmodified husk of 450 μm particle size. Generally, this model gave very good fit to the experimental data.

The values of K_F , the binding constant and n , the exponent, are shown on Table 2. The values of K_F and n determine the steepness and curvature of the isotherm (Akgerman and Zardkoohi, 1996). The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration, even though it is not based on the theoretical background. Apart from 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 (Juang et al. 1996). 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 concentrations and vice versa (Teng and Hsieh, 1998). The values of $1/n$ less than unity were obtained mostly for the modified maize husk. Also, the higher the K_F value, the greater the adsorption intensity. Therefore, the K_F values which are higher for the modified husk confirms that the adsorption capacity of the modified husk was greater than that of the unmodified husk.

The Langmuir isotherm. The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The linearized Langmuir equation as reported by Eligwe et al. (1999), was used to analyze the data. The equation is given as:

$$C_e/Q_e = 1/K_As + C_e/As \quad [3]$$

where A_s (mg/g) is the sorbent binding capacity, that is, the maximum sorption upon complete saturation of adsorbent surface and K (dm^3/g) is the binding constant, that is, related to the adsorption/ desorption energy. It is well known that the Langmuir equation is intended for a homogeneous surface. A good fit of this equation reflects monolayer adsorption (Teng and Hsieh, 1998). The experimental data were fitted into Equation 3 for linearization by plotting C_e/Q_e against C_e , Figure 6 and Figure 7 for unmodified and modified maize husk respectively. The linear regression equations and coefficient of determination (R^2) generated are also shown on Table 1. The Langmuir constants are also shown on Table 2. The coefficients of regression (R^2) are very poor for the Langmuir isotherm. The values range from 0.0233 for Cd(II) ion on modified husk of 850 μm particle size to 0.9966 for Zn(II) on modified husk of 450 μm particle size. Generally most of the R^2 values fell below 85% and this means that the Langmuir model did not give a good fit to the sorption process when compared to the other isotherms tested. This is also confirmed from the negative values obtained for the Langmuir constants shown in Table 2.

The Dubinin-Radushkevich isotherm. This isotherm model was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The model is represented by the equation below:

$$q_e = q_D \exp(-B_D [RT \ln(1 + 1/C_e)]^2) \quad [4]$$

Where, B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the biomass 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 (Horsfall et al. 2004). The linear form of equation [4] is given as

$$\ln q_e = \ln q_D - 2B_D RT \ln(1 + 1/C_e) \quad [5]$$

Table 3. Comparison of the Regression Coefficients (R^2) for the three Isotherms.

Metal ions	Regression coefficient (R^2)			
	Unmodified		Modified	
	450 μm	850 μm	450 μm	850 μm
Freundlich Isotherm				
Cd	0.9405	0.6772	0.7478	0.9333
Langmuir Isotherm				
Cd	0.7067	0.8156	0.1902	0.8969
Dubinin-Radushkevich Isotherm				
Cd	0.9177	0.955	0.9114	0.9768

A plot of $\ln q_e$ against $RT \ln (1 + 1/C_e)$ (Figure 8 and Figure 9 for unmodified and modified maize husk respectively), yielded straight lines and indicates a good fit of the isotherm to the experimental data. The apparent energy (E) of adsorption from Dubinin-Radushkevich isotherm model can be computed using the relation given below (Horsfall et al. 2004).

$$E = 1/\sqrt{2B_D} \quad [6]$$

The regression equation and R^2 values for Dubinin-Radushkevich model is given on Table 1. From this table, it was observed that this isotherm also gave very good description of the sorption process, over the range of concentration studied. The apparent energy of adsorption and the Dubinin-Radushkevich isotherm constants are shown on Table 2. The high values of q_D shows high sorption capacity and these are higher for the unmodified than the modified. The values of the apparent energy of adsorption also depict physisorption process. This is similar to previous study (Horsfall et al. 2004). Therefore, the Dubinin-Radushkevich isotherm gave a very good fit to the sorption process.

A comparison of the coefficient of regression (R^2) for the three isotherms is shown on Table 3. For the Freundlich isotherm we have a range of 0.6297 to 0.9952 and an average value of 0.9476. The range for the Langmuir is 0.0233 to 0.9966 and the average is 0.7604. For the Dubinin-Radushkevich isotherm the range of R^2 values is 0.7646 to 0.9988 and an average value of 0.9321. Thus, 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 husk for removal of Cd(II), Pd(II) and Zn(II) ions, we can also, conclude from the values of R^2 that Dubinin-Radushkevich isotherm is the best followed by Freundlich isotherm. The Langmuir isotherm would be said as not giving a good fit to the sorption process.

CONCLUDING REMARKS

Maize husk which is an environmental pollutant have 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 by 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. The sorption process was found to be a physisorption process as seen from the apparent energy of adsorption. Other methods of modification are also being investigated.

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APPENDIX

FIGURES

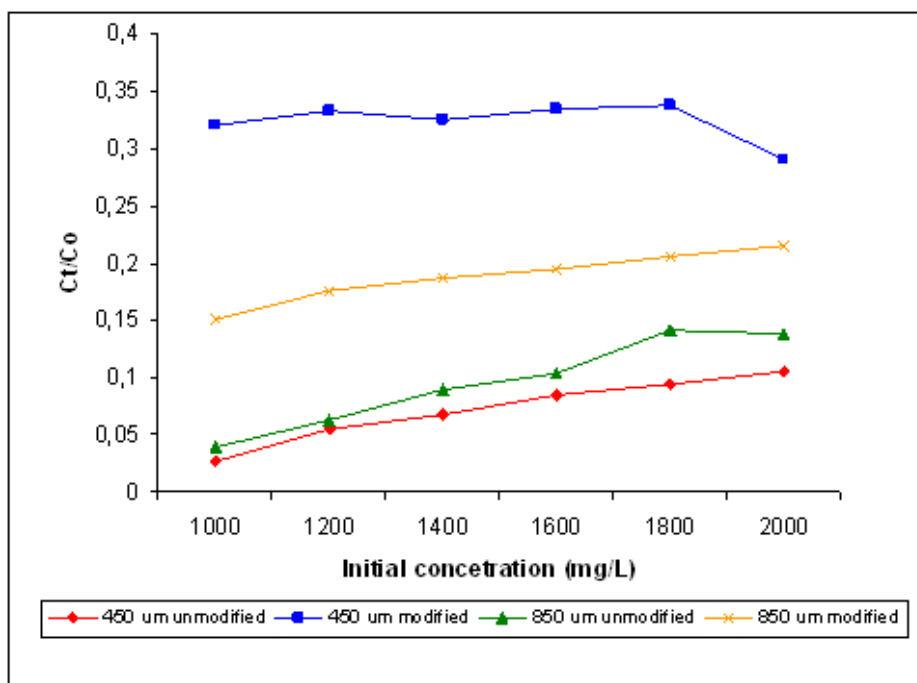


Figure 1. Fraction of amount adsorbed (C_t/C_o) against initial concentration (mg/L) for Cd(II) ion on modified and unmodified maize husk of two particle sizes of 450 µm and 850 µm.

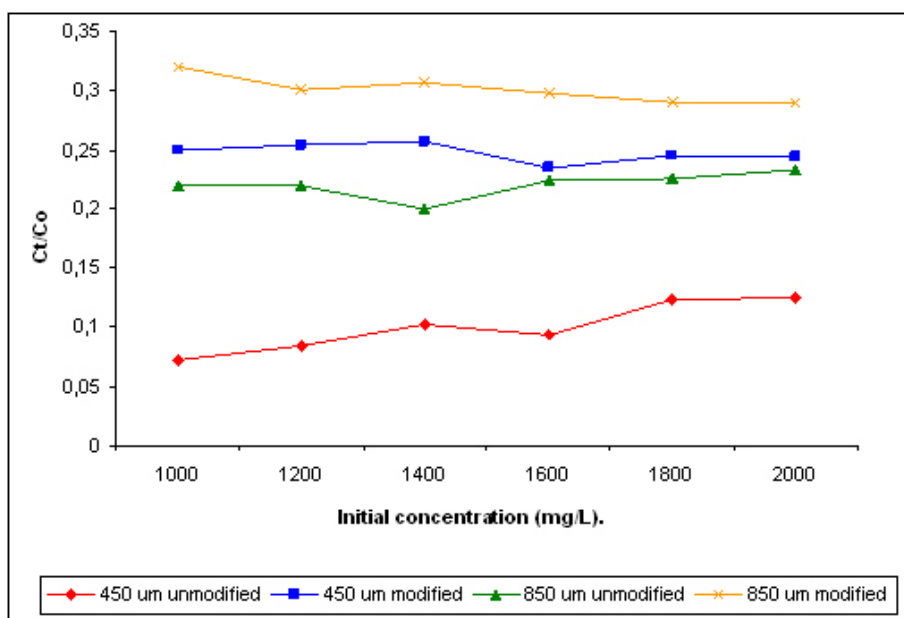


Figure 2. Fraction of amount adsorbed (C_t/C_o) against initial concentration (mg/L) for Pb(II) ion on modified and unmodified maize husk of two particle sizes of 450 µm and 850 µm.

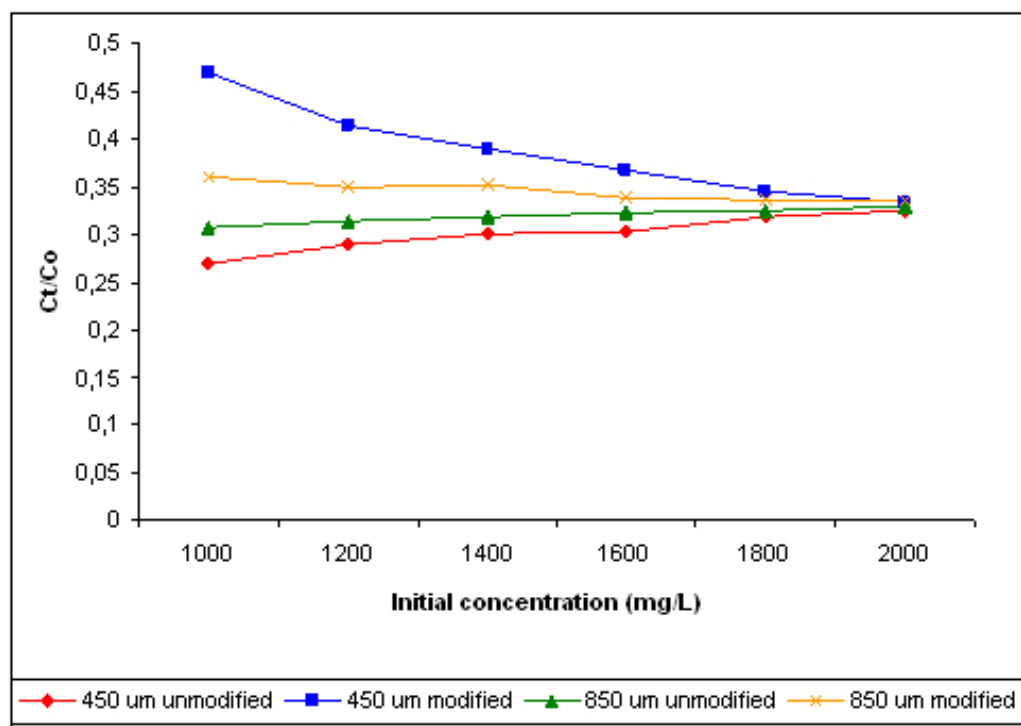


Figure 3. Fraction of amount adsorbed (C_t/C_o) against initial concentration (mg/L) for Zn(II) ion on modified and unmodified maize husk of two particle sizes of 450 µm and 850 µm.

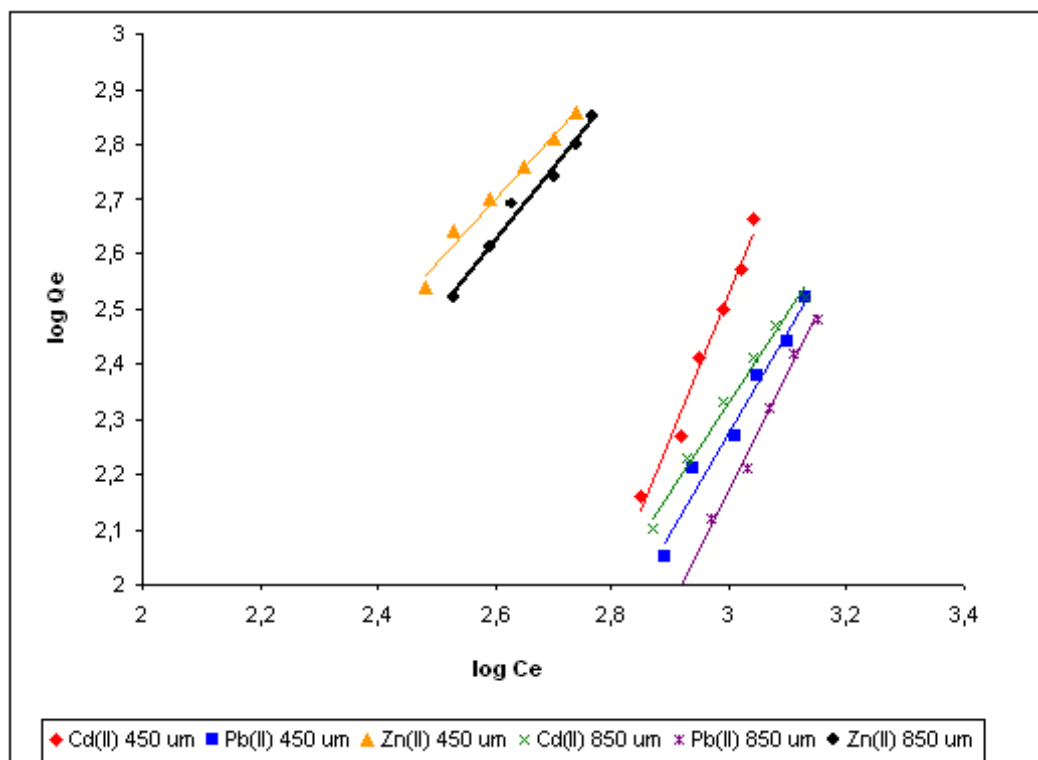


Figure 4. Freundlich isotherm plot for Cd(II), Pb(II) and Zn(II) ions on unmodified maize husk of 450 µm and 850 µm particle sizes.

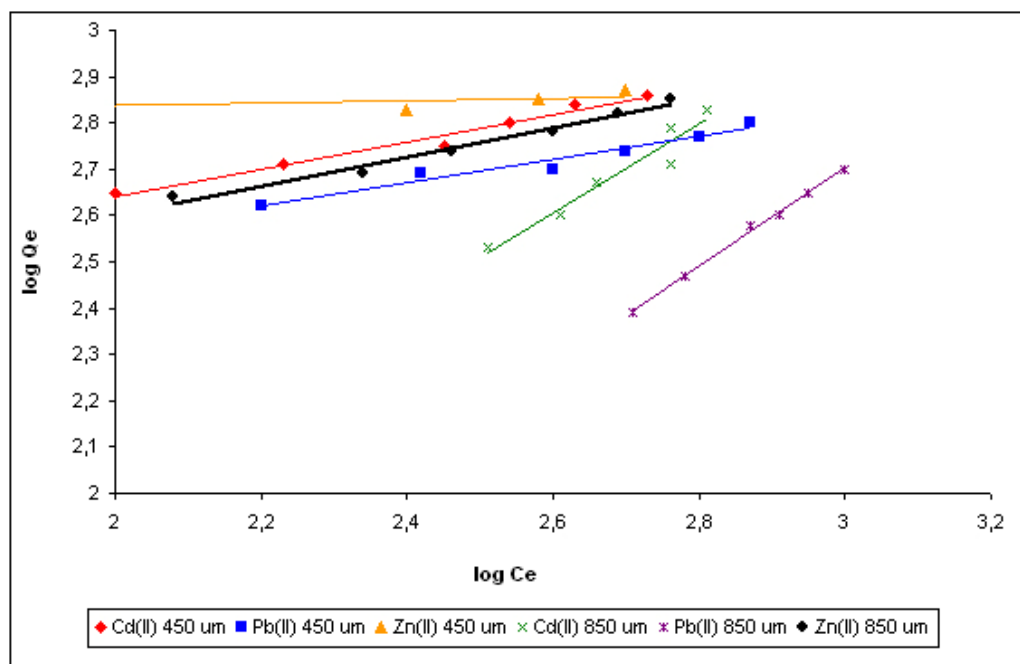


Figure 5. Freundlich isotherm plot for Cd(II), Pb(II) and Zn(II) ions on modified maize husk of 450 um and 850 um particle sizes.

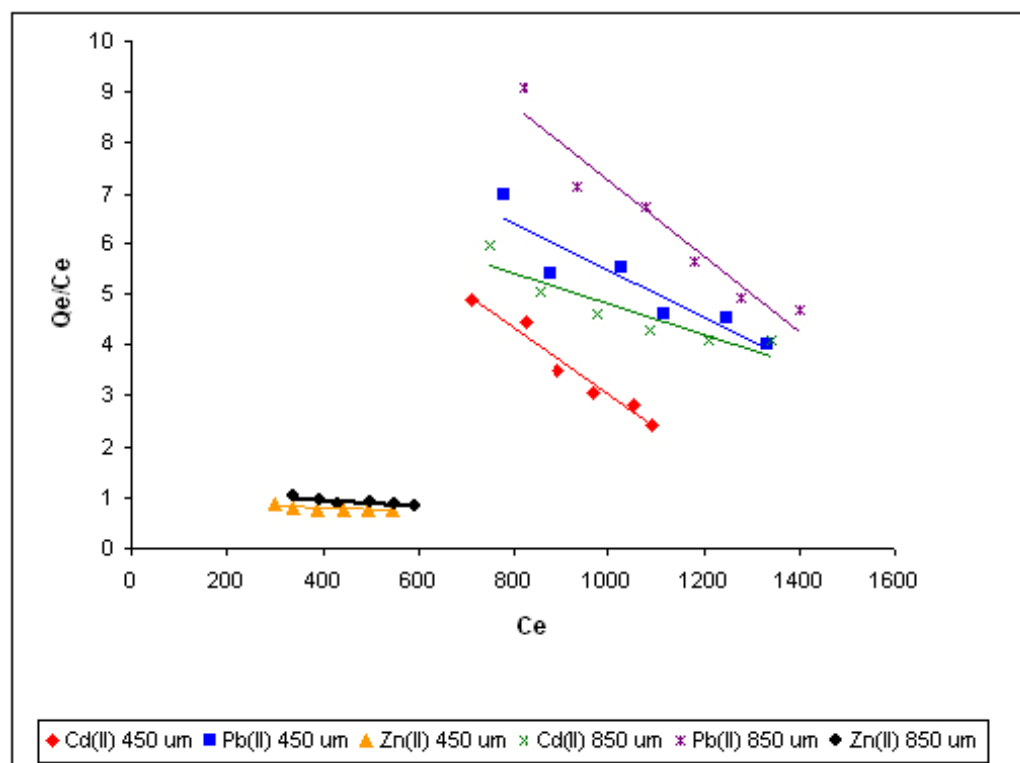


Figure 6. Langmuir isotherm plot for Cd(II), Pb(II) and Zn(II) ions on unmodified maize husk of 450 um and 850 um particle sizes.

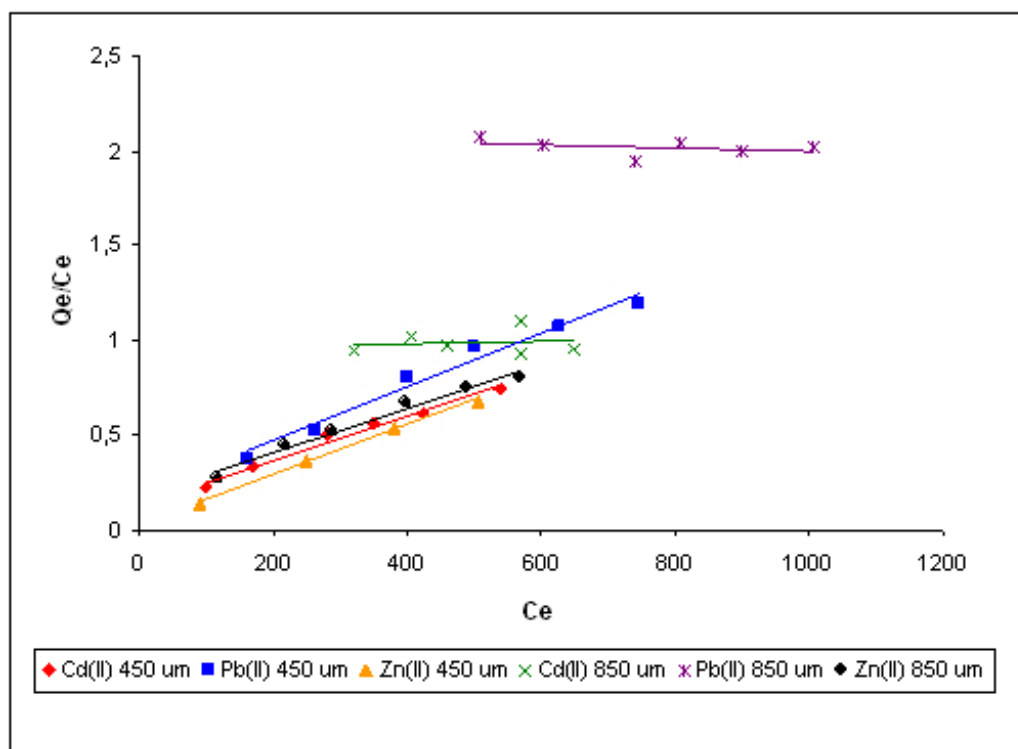


Figure 7. Langmuir isotherm plot for Cd(II), Pb(II) and Zn(II) ions on modified maize husk of 450 μm and 850 μm particle sizes.

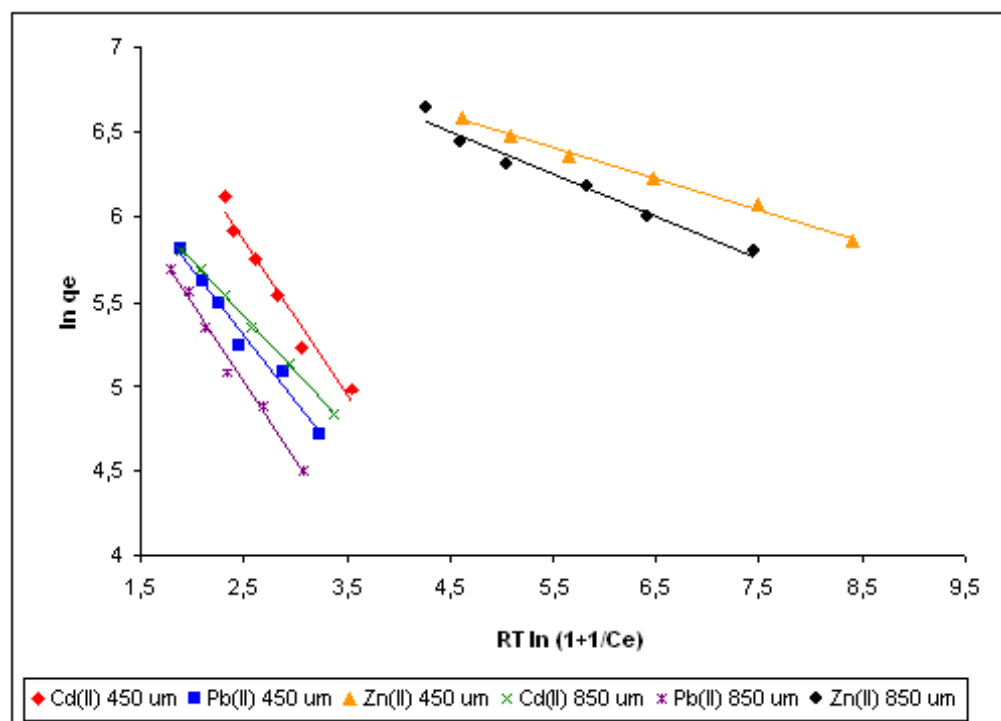


Figure 8. Dubinin-Radushkevich isotherm plot for Cd(II), Pb(II) and Zn(II) ions on unmodified maize husk of 450 μm and 850 μm particle sizes.

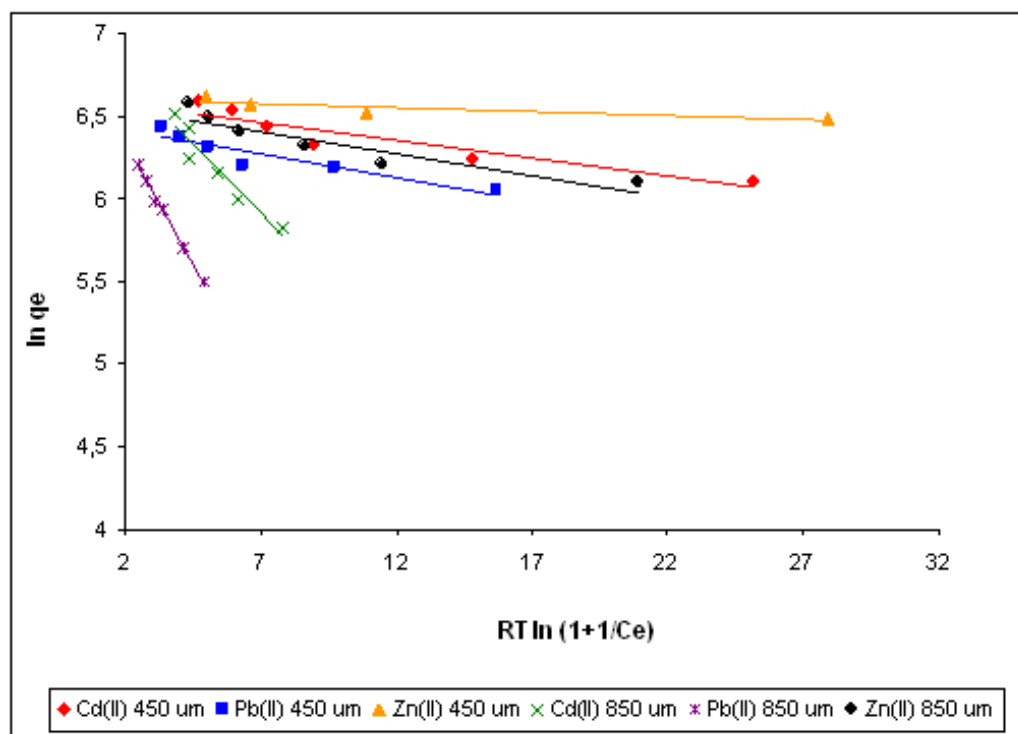


Figure 9. Dubinin-Radushkevich isotherm plot for Cd(II), Pb(II) and Zn(II) ions on modified maize husk of 450 um and 850 um particle sizes.