



Scholars Research Library

Archives of Applied Science Research, 2012, 4 (2):809-819
(<http://scholarsresearchlibrary.com/archive.html>)



Biosorption of zinc from aqueous solution using coconut (*Cocos nucifera* L) coir dust

U. Israel and *U. M. Eduok

Department of Chemistry, Faculty of Science, University of Uyo, Uyo, Akwa Ibom State, Nigeria

ABSTRACT

The ability of coconut (*Cocos nucifera* L) coir dust to remove Zn(II) ions from aqueous solution by adsorption was studied. The extent of removal of Zn (II) was found to be dependent on contact time, pH and particle size of the adsorbent. The optimum time, pH and particle size was found to be 60 mins, 7.5 and 50 microns respectively. The adsorption studies include both equilibrium adsorption isotherms and kinetics. Several isotherm models were investigated and the adsorption isotherm data were best represented by the Freundlich isotherm. The kinetic data were well described by the pseudo- second order kinetic model. The mechanism of adsorption process was determined from the intraparticle diffusion model. The results indicate that coir dust could be employed as a low-cost alternative for the removal of Zn (II) ions from solution.

Keywords: Adsorption, coir dust, isotherm, kinetics, Zn (II).

INTRODUCTION

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased influx of metallic substances into the aquatic environment. Most heavy metals are extremely toxic, non-biodegradable and tend to accumulate as metalloorganic complexes in living systems. Trace concentration of zinc (Zn) are important for the physiological function of living tissue and regulate many biochemical process. However, trace amounts of free zinc ions can cause heavy damage to the environment and kill organisms. When zinc is discharged into natural waters at increased concentrations in sewage, industrial wastewater or from mining operations, it can have severe toxicological effects on both humans and aquatic ecosystems [1]. Hence, it is essential to remove zinc from industrial wastewaters before transport and cycling into the natural environment. A number of technologies such as coagulation/flocculation, precipitation, ion-exchange, electrochemical processes and membrane technology have been utilized for zinc removal from industrial wastewaters.

Recently, several studies on the removal of zinc from effluents using low cost agricultural materials have been reported [2,3,4]. In most cases, zinc uptake capacities are quite low and the adsorbents are susceptible to degradations at low pH acid regeneration. Nowadays, the most popular removal materials are bioadsorbents whereby zinc can exchange preferentially with other ions such as H^+ , Na^+ , Ca^{2+} [5,6,7]. In this study, coconut coir dust, an agricultural waste material has been tested for the removal of zinc ions from aqueous solution. The objective of this work is to investigate the effect of pH, particle size variation, initial ion concentration, effect of time during the treatment of zinc ion in aqueous solutions.

MATERIALS AND METHODS

Experimental details

Batch Equilibrium Adsorption Studies

The ion exchange of Zn (II) on coconut coir dust was carried out using the batch method. Batch adsorption experiments were conducted using 0.5g of adsorbent with 100ml of solutions containing Zn (II) ions of desired concentration at constant temperature of 29.6 °C in 250ml conical flasks. The particle size of the sample (coir dust) was 50microns, and the flask containing the adsorbate was shaken for 3hr, the solution containing the residual metal ions were filtered through a whatman filter paper (No.41). The exact concentration of metal ions and filterable metal concentration were determined by AAS (Pye Unicam 919 Atomic Absorption Spectrophotometer). The flame type was air acetylene and absorption wavelength was 213.9nm for Zn (II) ions. The percent adsorption (%) was calculated using the equation:

$$\%Adsorption = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

where C_o and C_f are the concentrations of metal ion in initial and final solution respectively.

RESULTS AND DISCUSSION

3.1 Characterization and Properties

The physicochemical and elemental analysis of coir dust is presented in Tables 1 and 2. This study showed that coir dust contain light metals such as Na (463.20), K (711.60), Ca (227.40) and Mg (172.00) which are exchangeable with heavy metal ions such as Pb, Cd, Zn, Fe in aqueous solution.

The elemental composition of coir dust as shown in table 2 fitted with those reported in literature [8,9,10]. It is believed that the ion exchange properties are due to its ability to take up heavy metal ions from solution in exchange for cation of light metals such as Na, Mg and Ca [11]. Heavy metals easily form multidentate stable complexes with the functional groups (COO⁻, OH) present in coir dust than light metals [12]. For coir dust, the content of lignin (35.5%) is relatively high compared to other non-wood fibre species, e.g flax (2.9%) hemp (3.0%), sisal (12.7%), jute (13.7%) and bagasse (19.9%) and comparable to hardwood (18 – 34%) and softwood (28 – 40%) [13], while the cellulose content (36%) is higher compared to other fibre specie e.g bagasse (28-32%), jute (16 -22%), hardwood (19 -26%) [14]. The carboxylate and phenolic groups of lignin, pectin and hemicellulose are known as the main sites for metal binding, resulting in bonds of more or less covalent character. Due to the structure and composition of the coir dust, it is reasonable to suggest that more than one component within the network of lignin and hemicellulose is responsible for the bonding. The exchange/ sorption properties of coconut coir dust is due to the presence of some functional groups such as carboxylic, hydroxyl, phenolic and lactone groups which have a high affinity for metal ions [15]. Other investigations have been carried out to determine the ion-exchange properties of coir related materials such as coconut shell, activated carbon from coir dust and modified coir dust [16,17,18,19].

3.2 Effect of Contact Time

The adsorption data for the uptake of metal ions versus contact time for a fixed adsorbent dose of 0.5 gL⁻¹ and with initial concentration of 50mg/L, particle size of 50µm at pH 7.0 is shown in Fig. 1. The sorption curve exhibit initially a short linear portion, followed by a plateau region showing that there is no appreciable change in the remaining metal ion concentration after 60 mins. This time represent the equilibrium time at which an equilibrium metal concentration (C_e) is presumed to have been attained. An empirically found functional relationship common to most adsorption process is that the metal uptake varies almost proportionally with $t^{1/2}$ rather than the contact time, t [20]. Therefore, in Fig. 9, plot of metal ion adsorbed q_t vs $t^{1/2}$ is presented for Zn (II) ions for the particle size of 500µm. It is evident that the adsorption of Zn (II) ions onto coir dust followed two phases, a linear phase of adsorption and then an almost flat plateau section. This may be attributed to the instantaneous utilization of the most readily available adsorbing site on the adsorbent surface.

3.3 Effect of pH

The adsorption of zinc ions onto coconut coir dust was studied over a pH range of 2 – 12 for a fixed adsorbent dose of 0.5g/L⁻¹ at particle size of 50µm (Fig 2). The pH was adjusted using dilute hydrochloric acid and sodium hydroxide solutions. A general increase in adsorption with increasing pH of the solution was observed for the metal ion up to a pH value of 7.5 as maximum, which also decreased at lower and higher pH. This increase in zinc removal with increasing pH has also been shown by Jain and Ram [20, 21,22], using sand sediments and fungal biomass respectively. The pH dependence of metal uptake could be related to the functional groups of the adsorbent and also the solution chemistry of the metal ions. At pH values less than 4, the metal is in the free ionic form (Zn²⁺) and as such, there is decrease in metal uptake at low pH values. This led to the hypothesis that the functional groups in the adsorbent and their associated ionic state are responsible for the extent of adsorption. Biosorbent materials

such as coir dust contain weak acidic and sometimes basic functional groups [23]. From the theory of acid – base equilibria in the pH range 2.5 – 5.0, binding of heavy metal cations is determined primarily by the degree of dissociation of the weak acidic groups. Carboxylic acid groups (–COOH) is one of the important functional group for the uptake of metal ions by the adsorbent [24]. The ionic state of a bioadsorbent can be used to explain the pH dependence of bioadsorption. Low pH conditions allow hydrogen and hydronium ions to compete with zinc ions for metal binding sites uptake. At higher pH values, there are lower numbers of competing hydrogen ions and more ligands are exposed with negatives, resulting in greater zinc sorption.

3.4 Effect of Particle Size

The plot between percent adsorption of metal ions at equilibrium versus adsorbent size reveals that for a fixed adsorbent dose of 0.5gL⁻¹, the metal ion adsorbed was higher the smaller adsorbent size (Fig 3). This is because, adsorption being a surface phenomenon, the smaller particle sizes offered comparatively larger surface area and hence higher adsorption takes place. High adsorption of adsorbate by smaller particle sizes of adsorbent has been attributed to availability of more specific surface area on the adsorbent [24].

3.5 Isotherm Models

The sorption data have been subjected to different sorption isotherms, namely Langmuir, Freundlich, Flory-Huggins, and Dubinin – Kaganer- Radushkevich (DKR). The equilibrium data for the metal ion over the concentration range from 5 to 200mg/l at 30°C have been correlated with the Langmuir isotherm [25]

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (2)$$

where C_e is the equilibrium concentration of metal ions in solution, q_e is the equilibrium quantity of metal ion sorbed onto adsorbent at equilibrium, Q_o and b are Langmuir constants related to sorption capacity and sorption energy respectively. Maximum sorption capacity (Q_o) represents monolayer coverage of sorbent with sorbate and b represents enthalpy of sorption and should vary with temperature. A linear plot is obtained when C_e/q_e is plotted against C_e over the entire concentration of the metal ion investigated (Fig. 4). The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Tables 3 and 4 with $Q_o = 17.857\text{mg/g}$, $b = 0.143(\text{L/mg})$ respectively. The Langmuir model did not effectively describe the sorption data as the correlation value R^2 had a value of 0.921 which was not as high as that from the Freundlich isotherm ($R^2 = 0.976$).

The Freundlich sorption isotherm, one of the most widely used mathematical description of adsorption, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich isotherm was also applied to the removal of Zn (II) ions onto coconut coir dust (Fig.5).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where C_e is the equilibrium concentration in mg/l and q_e shows that the adsorption seems to follow the Freundlich isotherm model as well as the Langmuir isotherm. The constants K and n were calculated for the metal cation and found to be $K_f = 3.656\text{mg/g}$ and $n = 0.26\text{g}$ respectively (Table 3). K_f is a parameter related to the temperature and n is a characteristic constant for the adsorption system under study. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentration. This isotherm does not predict any saturation of the sorbent by the sorbate, thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface.

The Flory –Huggins model has been used to describe the sorption of adsorbates on adsorbents. This model which helps to account for the degree of surface coverage as characteristics of the adsorbate on the adsorbent is expressed in the linear form as:

$$\log \left(\frac{\theta}{C} \right) = \log K_{FH} + \alpha_{FH} \log (1 - \theta) \quad (4)$$

where θ is the surface coverage of the adsorbent by the adsorbate. $\theta = (1 - C_e/C_o)$, where C_o and C_e are the initial and equilibrium Zn (II) concentrations respectively. The plot of $\log \theta/C_o$ versus $\log (1 - \theta)$ is linear (Fig. 6) if the adsorption conforms to this model and the equilibrium constants K_{FH} and α_{FH} can be obtained from the intercept and slope of the plot as 6.266mg/g and 0.220 respectively (Table 3).

The equilibrium constant K_{FH} from the Flory- Huggins is related to the Gibbs – free energy by the equation:

$$\Delta G^{\circ} = RT \ln K_{FH} \quad (5)$$

where R is the universal gas constant = 8.314J/mol; T is the absolute temperature ($^{\circ}\text{K}$) and K_{FH} is the Flory – Huggins equilibrium constant. The ΔG° for Zn (II) adsorption onto coir dust in this study was computed to be - 4.66kJ/mol. The negative value of ΔG° indicates that the adsorption of Zn (II) by coir dust is spontaneous and exothermic reaction. Sekar *et al.* [26] reported exothermic reaction for the adsorption of Pb(II) onto activated carbon prepared from coconut shell. The Flory –Huggins isotherm is also important in adsorption studies since the degree of surface coverage is related to the sticking probability of the adsorbate on the adsorbent by the relationship:

$$S^* = (1 - \theta) \exp \frac{-E_a}{RT} \quad (6)$$

where S^* = sticking probability, E_a = activation energy, R = universal gas constant 8.314J/mol,

T is the temperature.

This sticking probability which is a function of the type of adsorbate/adsorbent system gives the potential of an adsorbate to remain on the adsorbent indefinitely [27].

The Dubinin – Kaganer – Radushkevich (DKR) was chosen to estimate the characteristic porosity and the apparent free energy of adsorption. The DKR equation has the form:

$$\ln q_e = \ln q_D - \beta_D RT \left[\ln \left(1 + \frac{1}{C_e} \right) \right] \quad (7)$$

where q_e is the maximum number of metal ions adsorbed per unit mass of adsorbent (mg/g), q_D is the maximum sorption capacity, β_D is the porosity factor which is related to the mean sorption energy, and $RT \ln \left(1 + 1/C_e \right)^2 = \epsilon^2$, ϵ being the Polanyi potential. The plot of $\ln q_e$ versus ϵ^2 should be linear which gives β_D (mol^2/J^2) as slope and $\ln q_D$ as the intercept. This plot is presented in Fig 7 and isotherm parameters were $\ln q_D$ (83.5) and β_D (0.683) respectively (Table 3). The porosity factor was found to be less than unity, indicating that the sorption of Zn (II) ions onto coir dust may require less number of cycles to reduce the concentration of this metal ion to below regulatory levels. The sorption energy (E) can also be worked out using the following relationship:

$$E = \frac{1}{\sqrt{2\beta_D}} \quad (8)$$

The DKR parameters are calculated from the slope of the line in Fig 7 and listed in Table 3. As shown in Table 4, the E_s (sorption energy) value is 8.55kJ/mole for Zn^{2+} on coir dust. This energy value fall in the range for ion exchange mechanism, in which the sorption energy lies within (8 – 16) kJ/mol. The sorption capacity, q_D in the DKR equation was found to be 83.46 mol/kg for Zn (II).

3.6 Kinetic Studies

Table 4 present the values of constants of kinetic models like pseudo – first order, pseudo – second order, and Elovich equation for sorption of Zn (II) onto coconut coir dust. The kinetic rate constants k_1 , k_2 , β_E and α_E are 0.3501(g/mg/min), 1.8491(g/mg/min), 6.643(g/mg/min) and 0.8826 which are shown in Table 4 for the sorption of Zn (II) ions by coir dust. The result showed a low correlation coefficient for pseudo – first order $R^2 = 0.544$, and $R^2 = 0.919$ for Elovich model respectively. These results indicate that these models are not necessarily applicable in the present case.

This suggests that this biosorption system is not a pseudo-first order reaction. The applicability of the pseudo-first order (Lagergren Model) suggests the formation of monolayer onto the surface of adsorbent, hence it suggest a multilayer sorption as also suggested by Freundlich isotherm being the best fit for this reaction. The sorption rate constant k_2 , initial sorption rate, h , and equilibrium sorption capacity, q_e of the pseudo – second order model is shown in Table 4 and Fig. 8. These results show a very good compliance with the pseudo – second order equation with high correlation coefficient ($R^2 = 0.972$). Thus, the pseudo – second order model proves suitable to describe the adsorption of kinetic data in the present study. The pseudo – second order model has been widely used to describe non – chemical equilibrium [28] and non physical equilibrium [29]. This model assumes that two reactions are occurring, the first one is fast and reaches equilibrium quickly and the second is a slower reaction that can continue for a long period of time. The reaction can occur either in series or in parallel [30]. The initial sorption rate, h , has been widely used for evaluation of the sorption rates [31]. In the present study, the value of $h=0.785$ and $k_2=1.8491$ (g/mg/min). This confirms that there is more than one mechanism involved in the adsorption process.

Some studies published in literature also reported pseudo- second order kinetics as suitable for sorption of Zn (II) ions on bone char and biosolids [32].

The intraparticle diffusion coefficient for the adsorption of Zn (II) was calculated from the slope of the plot between amounts of Zn (II) adsorbed q_e (mg/g) versus $t^{1/2}$ ($\text{min}^{1/2}$). Based on this plot (Fig. 9), it was concluded that the sorption process of Zn (II) is comprised of two phases, suggesting that intraparticle diffusion mechanism is not the rate limiting step for the whole reaction [33]. The initial portion of the plot indicated an external mass transfer whereas the second linear portion is due to intraparticle or pore diffusion. The intercept of the plot which was determined to be 33.31 provides an estimation of the thickness of the boundary layer, i.e, the larger the intercept value, the greater is the boundary layer effect [34]. The slope of the second linear portion of the plot has been identified as the intraparticle diffusion parameter K_p ($\text{mg/gmin}^{0.5}$). The two phases in the intraparticle diffusion plot suggest that the adsorption of Zn (II) ions by the adsorbent proceed by surface sorption and intraparticle diffusion.

Table1: Characterization of coir dust

Parameter	% content in coir dust
Moisture content	25.5
Ash content	9.0
Water extractive	28.2
Acid (Dil HCl) extractive	41.3
Swelling in water	
1 hr	65.7
5hr	70.8
10hr	77.7
24hrs	85.7
Swelling in acetone	0.934
Swelling in dil. HCl	3.229
pH of coir dust in water	6.40
Cellulose	35.99
Lignin	53.5
Alkali soluble (1%NaOH) solution	27.5
Alkali soluble (18% NaOH) solution	41.3
Cation exchange capacity (mmolg^{-1})	2.39

Table2 : Multielemental contents in the coir (based on air dried weight)

Metal	$\mu\text{g metal/g coir dust}$ present study	$\mu\text{g metal/g coir dust}$ literature study[10]
Na	463.20	861.0
K	711.60	3630
Ca	227.40	564
Mg	172.00	474
Pb	0.180	0.175
Cu	1.60	3.12
Cd	0.04	0.020
Cr	0.20	0.238
Zn	4.286	4.32
Fe	285.20	121.0
Mn	1.094	5.94
Mo	0.020	0.035
Co	0.060	0.054
Ni	1.00	0.715
As	ND	ND
Hg	ND	ND
V	ND	ND

*pH = 7.0; temp = 29.6 °C ; dose 500mg/50ml solution; ND = not detected
particle size = 50 μm ; colour of coir dust = brown to light brown.*

Table 3: Isotherm constant for adsorption studies

Metal				
Zn(II)	Langmuir	$Q_o(\text{mg/g})$	$b(\text{L/mg})$	R^2
		17.857	0.1436	0.921
	Freundlich	$K_F(\text{mg/g})$	$1/n$	n
		3.656	3.378	0.269
	Flory – Huggins	$K_{FH}(\text{mg/g})$	α_{FH}	
		6.266	0.220	0.969
	Dubinin – Radushkevich	β_D	q_D	$E_s(\text{KJ/mol})$
		0.683	834.64	0.855

Table 4: Kinetic model for adsorption of Zn(II) unto coconut coir dust

Metal	Pseudo first order				Pseudo second order				Elovich				Intraparticle diffusion		
	$q_{e.exp}$	K_1 (g/mgmin)	$q_{e.cal}$ (mg/g)	r^2	K_2 (g/mgmin)	$q_{e.cal}$ (mg/g)	H	r^2	β	$1/\beta$	α (mg/gmin)	r^2	K_{id}	C	r^2
Zn(II)	39.00	0.3501	4.186	0.553	1.8491	1.205	0.785	0.969	0.8826	1.133	6.643	0.633	1.133	33.31	0.733

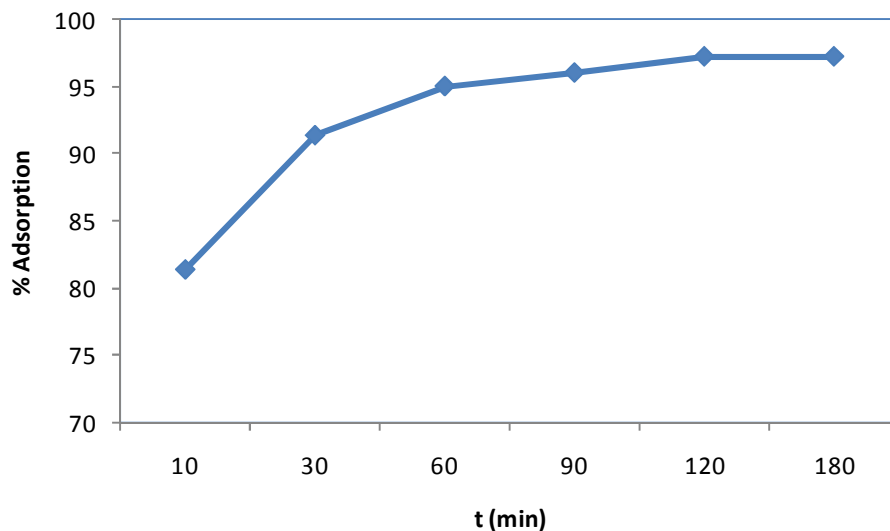


Fig. 1. Plot of % adsorption versus contact time of Zn (II) on coir dust.

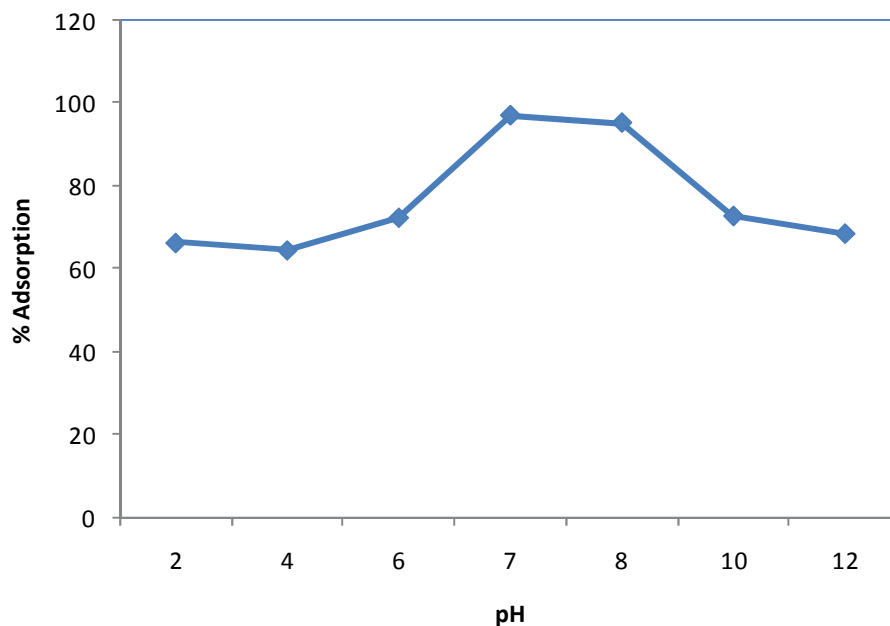


Fig. 2. Plot of % adsorption versus pH for Zn (II) on coir dust.

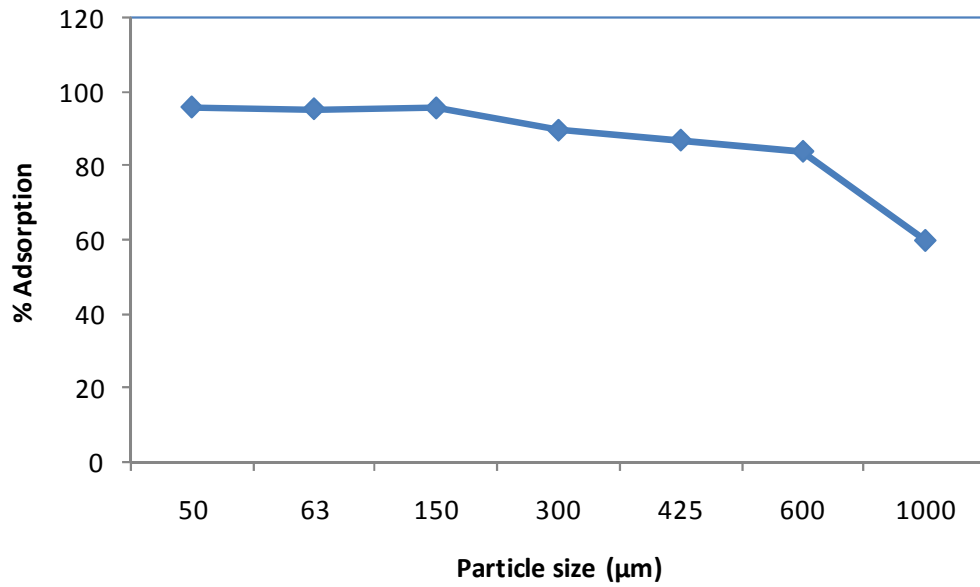


Fig. 3. Plot of % adsorption versus particle size for Zn (II) on coir dust.

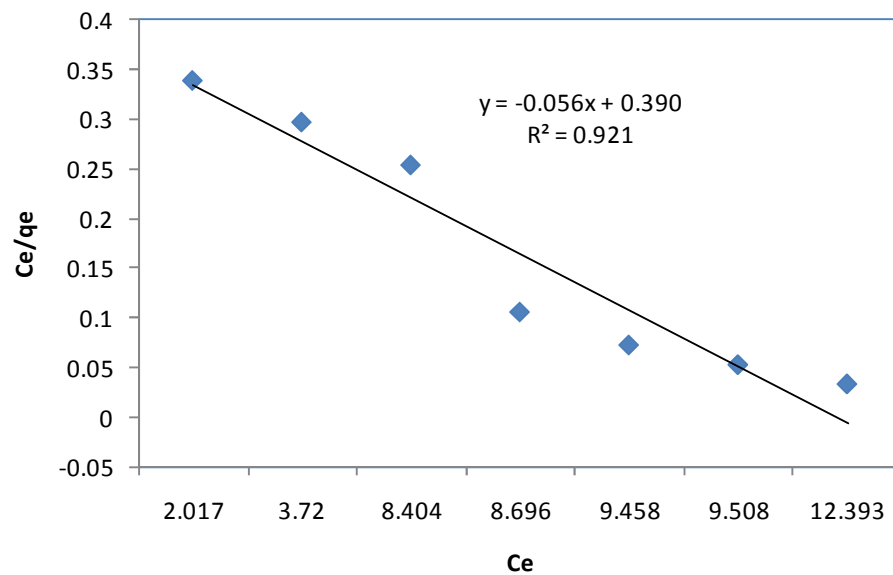


Fig. 4. Langmuir adsorption isotherm plot for Zn (II) on coir dust.

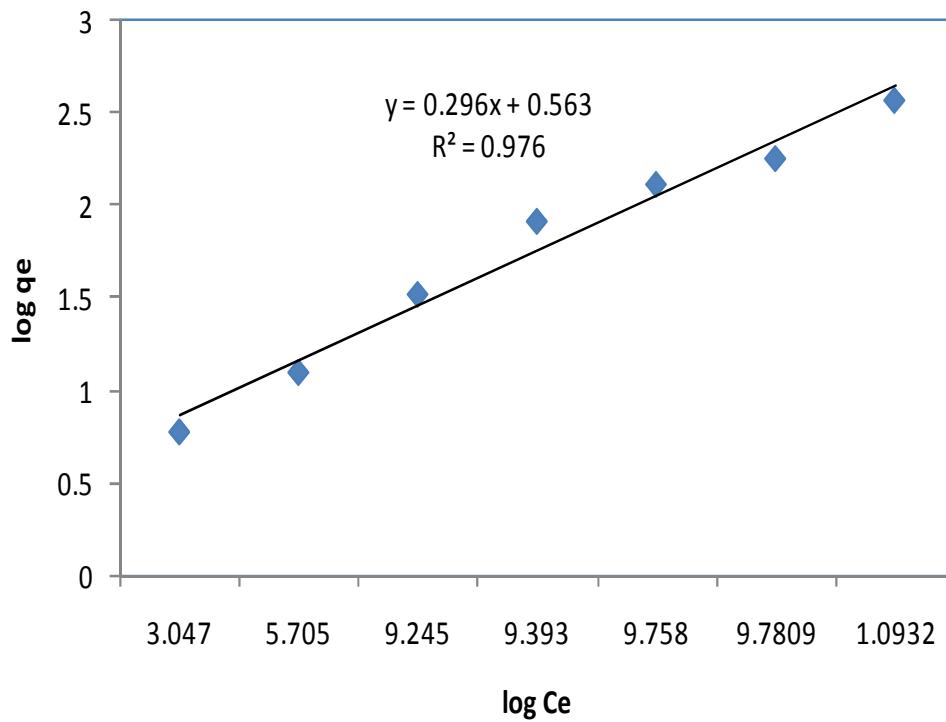


Fig. 5. Freundlich adsorption isotherm plot for Zn (II) on coir dust.

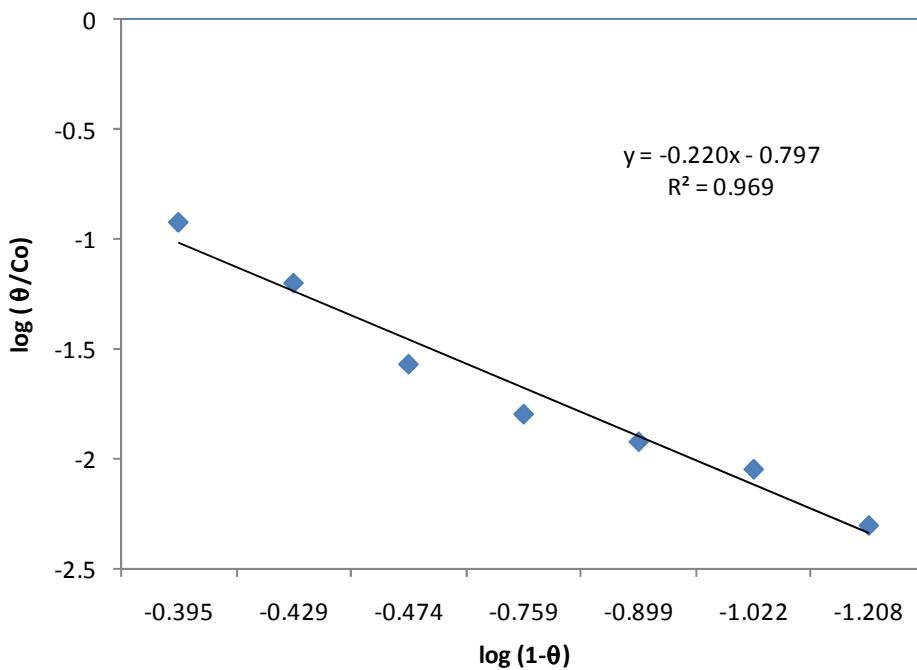


Fig. 6. Flory-Huggins adsorption isotherm plot for Zn (II) on coir dust.

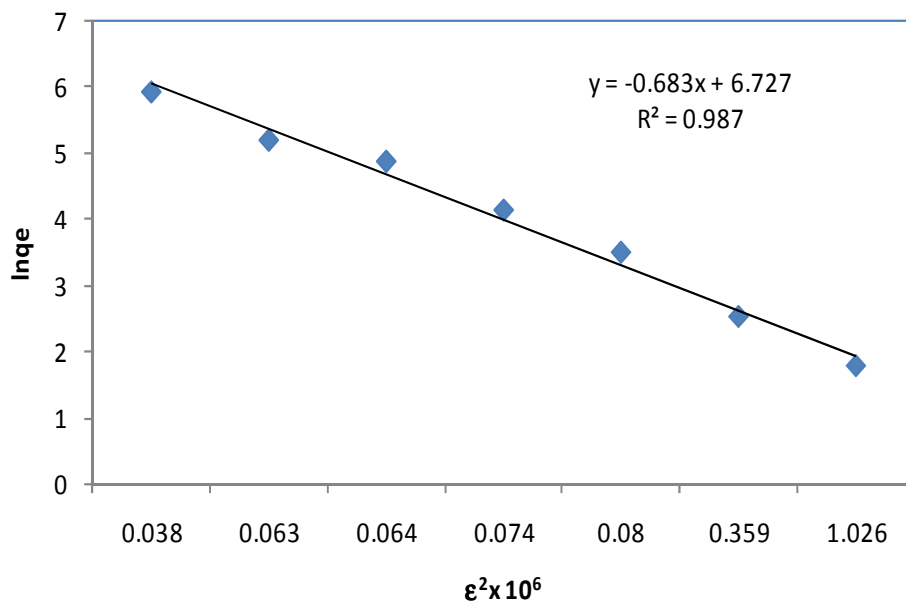


Fig. 7 . Dubinin-Radushkevich adsorption isotherm plot for Zn (II) on coir dust.

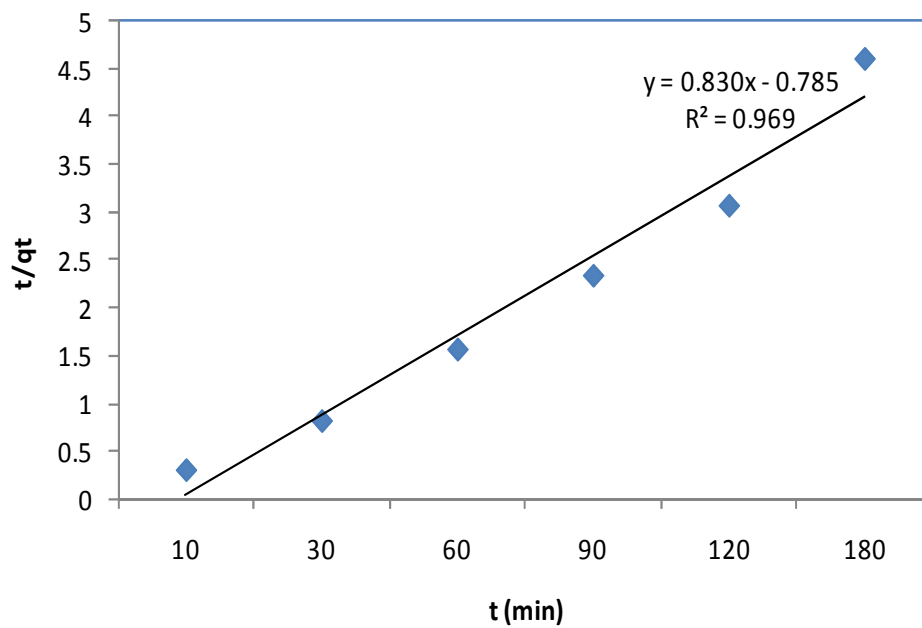


Fig. 8. Pseudo-second order kinetic plot for Zn (II) adsorption on coir dust.

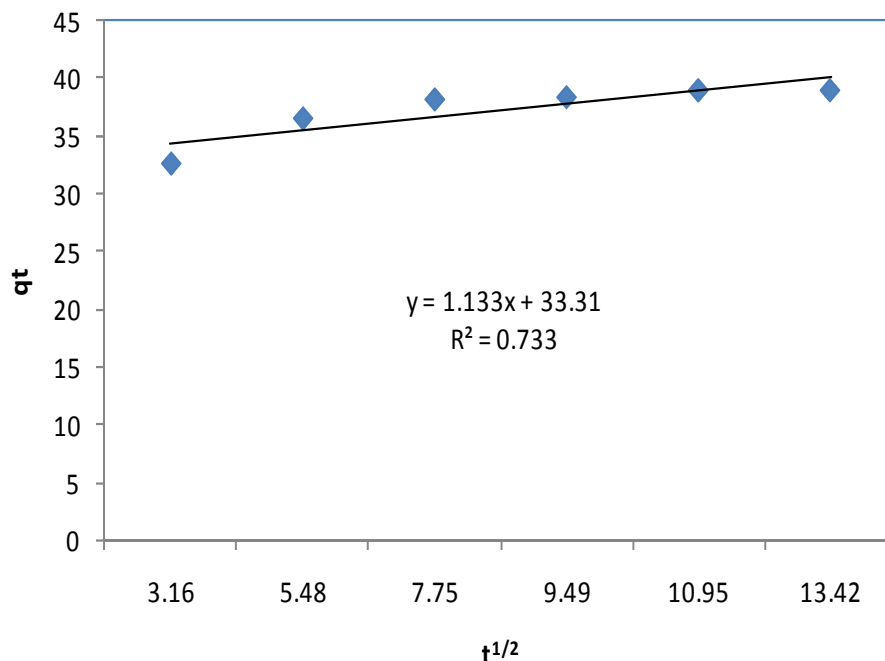


Fig. 9. Intraparticle diffusion plot for Zn (II) adsorption on coir dust.

CONCLUSION

- (1) The results obtained showed that coconut coir dust is an efficient adsorbent for Zn (II) ions in aqueous media.
- (2) The adsorptivity of the metal ions increased with increasing pH, contact time and initial concentration of ions.
- (3) The adsorption also increased with decreasing particle sizes of the coir dust.
- (4) Zn (II) ions adsorption followed the pseudo-second-order model and Intraparticle diffusion model.
- (5) The Freundlich adsorption isotherm model best fit the adsorption behavior of Zn (II) ions than other models tested.
- (6) The negative value of ΔG_{ads} shows the spontaneous adsorption of Zn (II) ions on the surface of the adsorbent.

REFERENCES

- [1] L. Norton, K. Baskaran, T. Mckenzie, *Adv. Environ. Res.*, **2004**, 8, 629.
- [2] R. J. E. Martin, R Pardo, R. A. R. Boaventura, *Water Res.*, **2004**, 38, 693.
- [3] D. Mohan, K. P. Singh, *Water Res.*, **2002**, 36, 2364.
- [4] S. Tunali, T. Akar, *J.Hazard Mater.*, **2006**, 13, 137.
- [5] E. Chockalingam, S. Subramanian, *Chemosphere*, **2004**, 62, 699-708.
- [6] J.S. Kwon, S.T. Yun, S.O. Kim, B. Meyer, I. Hutcheon, *Chemosphere*, **2005**, 65 1416.
- [7] P. Miretzyky, A. Saralegui, A. F. Cirelli, *Chemosphere*, **2007**, 57, 997.
- [8] S. Balce, A survey of Potential Industrial Products of the Coconut. Paper read at the symposium on problem of coconut plantation/industry. 8th pacific science congress, Nov. 1953, Quezon city, Australia, **1956**, 23.
- [9] F. C. Francia, E.U. Escolano, J.A. Same, *The Philippines Lumberman*, **1973**,19, 1.
- [10] K. Conrad, H. C.B. Hansen, *Biores. Technol.* **2007**, 98, 89.
- [11] D. Kratochvil, B. Volesky, G. Demopoulos, *Water Res.*, **1997**, 31, 2327.
- [12] A.U. Baes, S.J.P. Umali, P. Marcedo, *Water Sci.*,**1996**, 34, 193.
- [13] J.S. Han, R.M. Rowell, Chemical composition of fibres. In: Rowell, R. M., Young, R. A. and Rowell, J. K. (eds). Paper and composites from Agrobased resources. CRC Press. Inc. New York, **1997**, 5.
- [14] W.T. Han, S.T. Ooi, C.K. Lee, *Environ. Technol.*, **1993**, 14, 277.
- [15] S. Babel, D. Kurniawan, *Chemosphere*, **2004**, 54, 951.
- [16] K. Kadirvelu, K. Namasivayam, *Adv. In Env. Research.*, **2003**, 7, 1471.
- [17] A.E. Manas, S. Romana, A. Torres, Utilization of coconut coir dust for wastewater treatment and recovery of heavy metals. *Terminal report*. **1990** FORD PC87/03/05.
- [18] S. Anirudhan, M.R. Unnithan, *Chemosphere*, **2006**, 66, 60.
- [19] J. Weber, J.C. Morris, *Sanit. Eng. Div. Am. Soc. Cir. Eng.*,**1963**, 89, 31.

- [20] K. Jain, D. Ram, *J. de. Sciences Hydrologiques*, **1997**, 42, 713.
- [21] T. Mathieckal, Q. Yu, *Water Sci. Technol.*, **1996**, 34, 1.
- [22] D. Kratochvil, B. Volesky, *Water Res.*, **1998**, 3, 2760.
- [23] P. R. Puranik, K.M. Packnikar, *J. Biotechnol.* **1997**, 55, 113.
- [24] G. Karthikeyan, K. Anbalagan, N. Muthulakshmi, *J. Chem. Sci.*, **2004**, 116, 119.
- [25] I. Langmuir, *J. AM. Chem. Soc.*, **1916**, 38, 221.
- [26] M. Sekar, V. Sakhi, S. Rengaraj, *J. Colloid and interface Sci.*, **2004**, 279, 307.
- [27] S. Meenakshi, N. Viswanathan, *J. Colloid and Interface Sci.*, **2007**, 308, 438.
- [28] L. S. Lee, P.S.C. Rao, M.I. Brusseau, R.A. Ogwade, *Environ. Toxicol. Chem.* **1988**, 7, 779.
- [29] M.L. Brusseau, P.S.C. Rao, *Environ. Control*: **1984**, 19, 33.
- [30] A. Benhamiou, A. Yaacoubi, L. Nibou, B. Tanouti, *J. Hazard mater.*, **2005**, 117, 243.
- [31] C.K. Ko, C.W. Cheng, K.K. Chog, J.F. Porter, G. McKay, *Chemosphere*, **2004**, 54, 273.
- [32] Y.S. Ho, A.E. Ofomaja, *Biochem. Eng. J.*, **2006**, 30, 117.
- [33] C.H. Weng, C.Z. Tsai, S.H. Chu, Y.C. Sharma, *Technol.*, **2007**, 54, 187.
- [34] S. Arivoli, M. Hema, M. Karuppaiah, S. Saravanam, *Chemosphere*, **2008**, 5, 820.