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Full Length Research Paper

Equilibrium and kinetics studies of metal ion adsorption on dyed coconut pollens

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Batch equilibration studies were conducted to determine the nature of adsorption of Zn (II) and Cu (II) onto dyed coconut pollens. The nature of adsorption of metal ions was explained using the Langmuir equation. The calculated values of equilibrium parameter indicated favourable adsorption by the adsorbents. Also the calculated values of fractional attainment of equilibrium α, the intraparticle diffusion rate constant, K_a show that adsorption of metal ions is particle diffusion controlled. The adsorbent produced from coconut fibre can be used to remove heavy metals from aqueous solution with high efficiency.

Key words: Adsorption dynamics, fractional attianment of equilibrium, intraparticle diffusion.

INTRODUCTION

Several studies have been carried on the use of modified agricultural products for adsorption of heavy metal from aqueous solution such as activated carbon (Koshima and Onishi, 1986), natural particles and coarse colloids (Lead et al., 1999), modified chitosan (Saucedo et al., 1993), walnut waste (Randall et al., 1974), peanut skin (Randall et al., 1975, 1975a), cotton (Kumar and Dara, 1982), coffee grounds (Macchi et al., 1986), apple waste (Maranon and Sastre, 1991), wool fibre (Balkose and Baltacioglu, 1992), green algae and rice hull (Rey et al., 1993), cotton seed hulls (Marshall and Champagne, 1995), linseed flax straw (Taylor et al., 1994), bark and other cellulosic materials. Recently, great effort has been contributed to develop new adsorbents and improve existing ones like chitosan (Karthikeyan et al., 2005) and *Caladium bicolor* (Wild Cocoyam) biomass (Horsfall and Spiff, 2005).

The fractional attainment of equilibrium is the ratio of the amounts of metal ion removed from solution after a certain time to that removed when sorption equilibrium is attained (Okieimen et al., 1990). A great deal of information is obtained from the fractional attainment of equilibrium. The rate of attainment of equilibrium may be either film-diffusion controlled or particle-diffusion controlled, even though these two different mechanisms cannot be sharply demarcated (Okieimen et al., 1987).

In this study the rate of adsorption of Cu(II) and Zn(II) ions onto dyed coconut pollens was investigated at pH of 3.0 and temperature of 30°C. The effect of contact time between the adsorbent and the metal ions is investigated and reaction rate constant determined. Langmuir isotherm was used to determine extent of metal ion adsorption.

MATERIALS AND METHODS

Coconut pollens utilized for this study were obtained from coconut trees in Effurun, Nigeria. The pollens obtained were dried by air for seven days and ground using a manual hand grinding mills. The resultant cream coloured product was sieved through 0.40, 0.63 and 0.80 mm (ASTM sieve) and stored in plastic containers, ready for use. The sample was labeled as undyed coconut pollen (UDCP). About 20 g each of these were dyed with a reactive dye (2,7-napthalene disulphonic acid-5-[(4,6-dichloro1,3,5-triazine-2-yl) amino]-4-hydroxyl-(1,3-disulpho-7-napthalenyl) azo tetrasodium salt (Sueimitsu et al.,1986) and labeled as dyed coconut pollen grain (DCPI, DCPII, and DCPIII, respectively).

To determine the effect of contact time, 1.0 g sample of the dyed coconut pollen was placed into a 50 ml solution of the Cu(II) and Zn(II) of initial concentration of 20 mg/ l. The different samples were shaken in vibratory shaker at 200 rev/min for a given time interval of 10, 20, 30, 40, and 50 min. The samples were filtered rapidly through a glass wool and the metal content of the filtrates determi-

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Table 1. Experiment data of Cu (II) adsorption on dyed coconut pollen.

Time (min)	DCP I, Particle size,0.40mm				DCP II, Particle size, 0.63mm			
	C_t	α	ln(1-α)	-ln(1-α^2)	C_t	α	ln(1-α)	-ln(1-α^2)
0	0.00	0.000	0.00	0.000	0.00	0.000	0.000	0.000
5	0.62	0.989	-4.59	3.897	1.18	0.993	-5.067	4.377
10	0.60	0.991	-4.69	4.311	1.16	0.994	-5.240	4.891
15	0.45	0.999	-6.50	5.609	1.08	0.999	-6.812	6.120
20	0.44	0.999	-6.91	6.215	1.06	1	∞	∞
25	0.42	1	∞	∞	1.06	1	∞	∞
30	0.42	1	∞	∞	1.06	1	∞	∞

Initial concentration of Cu(II) ions = 20 mg/l, adsorbent dose = 1.0 g.

Table 2 Experiment Data of Cu (II) Adsorption on Dyed Coconut Pollen

Time (min)	DCP III, Particle size,0.80mm				UDCP, 0.40mm			
	C_t	α	ln(1-α)	-ln(1-α^2)	C_t	α	ln(1-α)	-ln(1-α^2)
0	0.00	0.000	0.000	0.000	0.00	0.000	0.000	0.000
5	2.40	0.925	-2.108	1.939	7.34	0.915	-2.463	-1.812
10	1.83	0.955	-3.108	2.437	6.37	0.913	-2.437	-1.789
15	1.80	0.957	-3.142	2.471	6.37	0.913	-2.437	-1.789
20	0.98	1	∞	∞	6.16	1	∞	∞
25	0.98	1	∞	∞	6.16	1	∞	∞
30	0.98	1	∞	∞	6.16	1	∞	∞

Initial concentration of Cu (II) ions = 20mg/l, adsorbent dose = 1.0g

ned by a buck scientific Flame Atomic Absorption Spectrometer (FAAS) model 200 A. The amounts of the metal ions adsorbed were calculated from the difference between initial concentration and concentration at preset time interval. The intraparticulate diffusivity and the fractional attainment of equilibrium were then calculated.

RESULTS AND DISCUSSION

Kinetics of metal ions adsorption on undyed and dyed coconut pollen

The kinetics of the metal ions adsorption was studied over 30 min for different particle sizes. The values of fractional attainment of equilibrium, α calculated from α = C_i -C_t /C_i -C_t are shown in Tables 3 and 4, where the fractional attainment of equilibrium, α, is the ratio of the amounts of metal ion removed from solution after a certain time to that removed when sorption equilibrium is attained. C_i denotes the initial concentration of metal ions, C_t, the concentration of metal ions at the preset time intervals, and C_{eq}, the equilibrium concentration. As can be seen from Tables 1 and 2 the values of α increased with contact time which means that more of metal ions is taken up by the dyed coconut pollen. And in less than 20 min, maximum amount of the metal ions has been removed from the aqueous solution. This demonstrates that for smaller particles, the time for equilibrium is not much quicker for the initially larger surfaces area as more of the metal ions are expected to be adsorbed compared to larger particles. However, both the smaller and larger particles reach 0.97 of equilibrium at the same time probably due to a limited amount of dyed coconut Tables 5 and 6.

A linear driving force concept earlier developed (Vinod and Amirudhan, 2001), for rate equation was used to obtain the fractional attainment. The equation is expressed as: 1n (1 - ∝) = - $K_a t$ where α is the fractional attainment of equilibrium, and K_a is the overall rate constant or diffusion time constant. The plots of 1n (1 - α) against time for the amounts of metal ions adsorbed on undyed and dyed coconut pollen grains are shown in (Figures 1 and 2). K_a is the rate coefficient for particle-controlled processes corresponding to particle size of the adsorbent (Vinod and Amirudhan, 2001). The values of K_a determined from the slope of the plots for Cu(II) were 0.1745, 0.1594 and 0.1035 min^{-1} and Zn(II) were 0.3349, 0.1601 and 0.0724 min^{-1} for DCPI, DCPII and DCPIII, respectively. This indicates that metal ion is removed from aqueous solution at a fast rate. It was observed that metal ion uptake were faster for DCP I (0.40 mm) than others. The results show the rate of removal of metal ion from aqueous solution is particle-diffusion controlled, and diffusivity of the metal ion would be independent of the extent of sorption (Okieimen et al., 1990).

Table 3. Experiment Data of Zn (II) Adsorption on Dyed Coconut Pollen.

Time (min)	DCP I, Particle size,0.40mm				DCP II, Particle size, 0.63mm			
	C_t	α	1n(1-α)	-1n(1-α^2)	C_t	α	ln(1-α)	-ln(1-α^2)
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.34	0.98	-4.10	3.42	1.49	0.93	-2.63	1.97
10	0.20	0.99	-4.66	3.97	0.43	0.98	-3.94	3.25
15	0.17	0.99	-4.83	4.14	0.33	0.99	-4.23	3.55
20	0.01	1	∞	∞	0.04	1	∞	∞
25	0.01	1	∞	∞	0.04	1	∞	∞
30	0.01	1	∞	∞	0.04	1	∞	∞

Initial concentration of Zn (II) ions = 20mg/l, adsorbent dose =1.0g

Table 4. Experiment Data of Zn (II) Adsorption on Undyed and Dyed Coconut Pollen

Time (min)	DCP III, Particle size,0.80mm				UDCP, 0.40mm			
	C_t	α	1n(1-α)	-1n (1-α^2)	C_t	α	1n(1-α)	-1n(1-α^2)
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	1.99	0.93	-2.71	2.05	2.57	0.98	-4.11	3.43
10	0.95	0.94	-2.74	2.08	2.58	0.98	-4.08	3.39
15	0.71	1	∞	∞	2.30	0.99	-6.81	6.12
20	0.71	1	∞	∞	2.39	0.99	-5.08	4.39
25	0.71	1	∞	∞	2.28	1	∞	∞
30	0.71	1	∞	∞	2.28	1	∞	∞

Initial concentration of Zn (II) ions = 20mg/l, adsorbent dose =1.0g

Table 5. Equilibrium study Data of Cu (II) adsorption on Undyed and Dyed coconut pollen

UDCP(0.40mm)			DCP I (0.40mm)			DCP II (0.63mm)			DCP III (0.80mm)		
C_t mg/l	q_e mg/g	C_t/q_e	C_t mg/l	q_e mg/g	C_t/q_e	C_t mg/l	q_e mg/g	C_t/q_e	C_t mg/l	q_e mg/g	C_t/q_e
0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7.34	0.633	11.60	1.18	0.941	1.25	2.40	0.880	2.73	0.62	0.969	0.640
6.37	0.682	9.347	1.20	0.940	1.28	1.83	0.909	2.01	0.60	0.970	0.619
6.37	0.682	9.347	1.08	0.946	1.14	1.80	0.910	1.98	0.45	0.978	0.460
6.16	0.692	8.902	1.06	0.947	1.12	0.98	0.951	1.03	0.44	0.978	0.460
6.16	0.692	8.902	1.06	0.947	1.12	0.98	0.951	1.03	0.42	0.979	0.429
6.16	0.692	8.902	1.06	0.947	1.12	0.98	0.951	1.03	0.42	0.979	0.429

Initial concentration of Cu (II) ions = 20mg/l, adsorbent dose =1.0g

Langmuir isotherm

The adsorption capacity, q_e, was computed using $q_e = (C_i - C_t)$ V/m. The Langmuir Isotherm model is given as $q_e = q_{max} C_t / k_1 + C_t$ and rearranged into the form of y = mx + C as $C_t / q_e = K_1 / q_{max} + (1 / q_{max}) C_t$ where q_e = the amount of heavy metals sorbed onto adsorbent (mg/g), C_t = concentration of metal ion in solution after adsorption at time, t, (mg/l) q_{max} = maximum adsorption capacity (mg/l) k_1 = Langmuir constant (Lmg^{-1}). Plots of C_t/q_e versus C_t give a straight line graph with a gradient of $1/q_{max}$ and an interception of K_1/q_{max} on the y axis. Thus the maximum amount of Cu (II) adsorbed per gram of the adsorbent and the Langmuir constant for the adsorption determined were 1.09, 4.15, 3.81 and 2.26 Lmg^{-1} respectively. The linear relationship was obtained from the plots of C_t/q_e versus C_t (Figures 3 and 4) and the maximal amount of copper adsorbed on UDCP, DCP I, DCPII and DCP III were: 0.1280, 0.9376, 0.8902 and 0.8449 mg/g, respectively. The linear relationship was obtained from the plots of C_t/q_e versus C_t (Figures 5 and 6) and the maximal amount of zinc adsorbed on UDCP.

Table 6 Equilibrium study Data of Zn (II) adsorption on Undyed and Dyed coconut pollen.

UDCP(0.40mm)			DCP I (0.40mm)			DCP II (0.63mm)			DCP III (0.80mm)		
C_t mg/l	q_e mg/g	C_t/q_e	C_t mg/l	q_e mg/g	C_t/q_e	C_t mg/l	q_e mg/g	C_t/q_e	C_t mg/l	q_e mg/g	C_t/q_e
2.57	0.872	2.95	0.34	0.983	0.346	1.49	0.926	1.610	1.99	0.901	2.210
2.58	0.871	2.62	0.20	0.990	0.202	0.43	0.979	0.439	0.95	0.903	1.053
2.30	0.999	2.30	0.17	0.992	0.172	0.33	0.984	0.336	0.71	0965	0.786
2.39	0.881	2.71	0.01	0.999	0.010	0.04	0.998	0.040	0.71	0.965	0.786
2.28	0.886	2.57	0.01	0.999	0.010	0.04	0.998	0.040	0.71	0.965	0.786
2.28	0.886	2.57	0.01	0.999	0.010	0.04	0.998	0.040	0.71	0.965	0.786

Initial concentration of Zn (II) ions = 20mg/l, adsorbent dose =1.0g

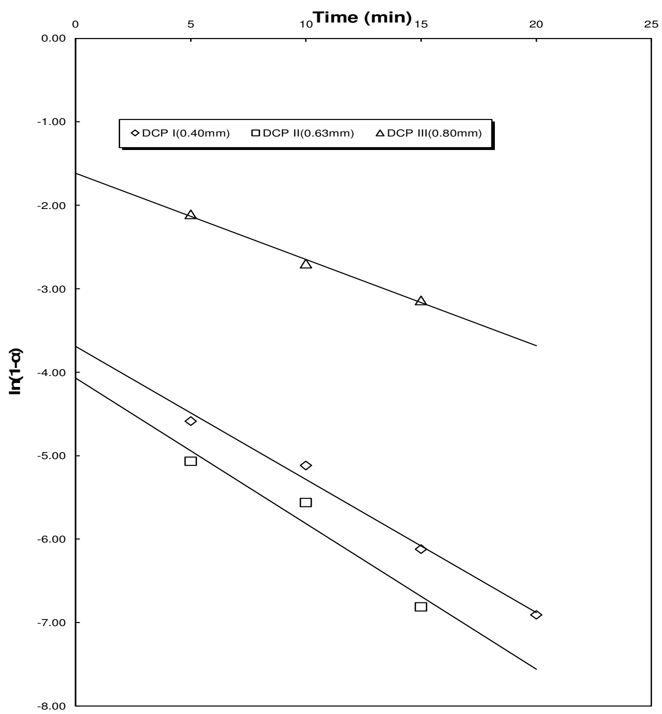

Figure 1. A plot of particle diffusivity 1n (1-α) against time (min) of Cu (II) adsorbed on DCP I, II and III.

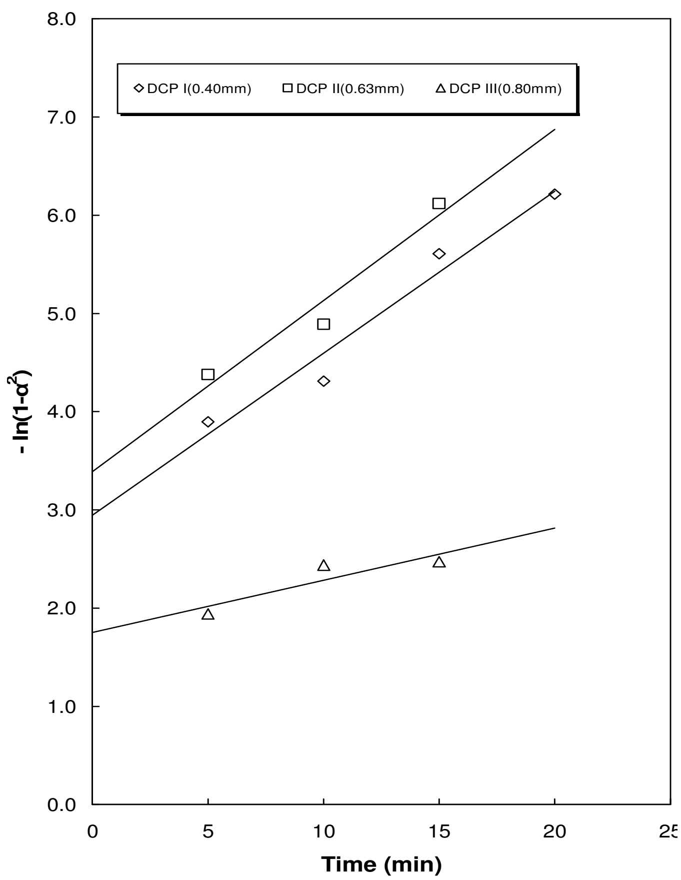

Figure 2. A plot of particle diffusivity -In (1-α^2) against time (t) of Cu (II) Adsorbed on DCP I, II, I II.

DCP I, DCPII and DCP III were 0.1280, 0.9376, 0.8902 and 0.8449 mg/g, respectively. This indicated the applicability of Langmuir adsorption isotherm on the adsorption process occurring through monolayer coverage and the binding at the adsorbent surface can be considered as adsorption (Campbell and Davies, 1995). The Langmuir isotherm therefore proved that the metal ion bound at the surface of the dyed coconut pollen is due to adsorption as it is used to describe monomolecular adsorption. The underlying removal mechanism is therefore fast ion-exchange and adsorption.

Equilibrium parameter

The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor or equilibrium parameter, S_f = 1/1+ k_1C_i (Karthikeyan et al., 2004) where C_i = initial concentration and k_1 = Langmuir constant. These values indicate the shape of the isotherm to be either unfavourable (S_f > 1), linear coconut pollen system were: 0.0439, 0.0119, 0.0129 and 0.0216 respectively. The S_f values, for 20 mg/l copper ions in the solution were between 0 and 1, indicated favourable adsorption.

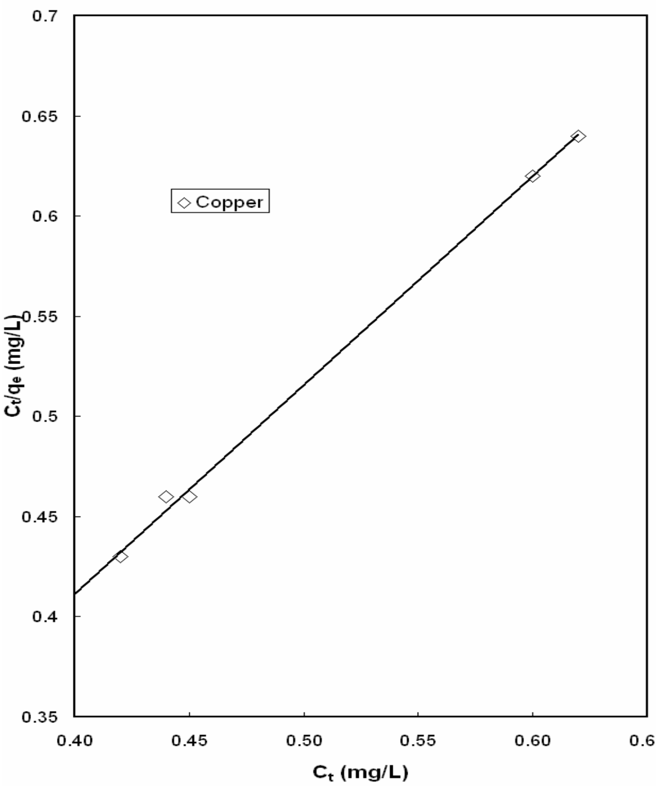

Figure 3. Langmuir Plot of copper ion adsorption on dyed coconut Pollen (DCP I).

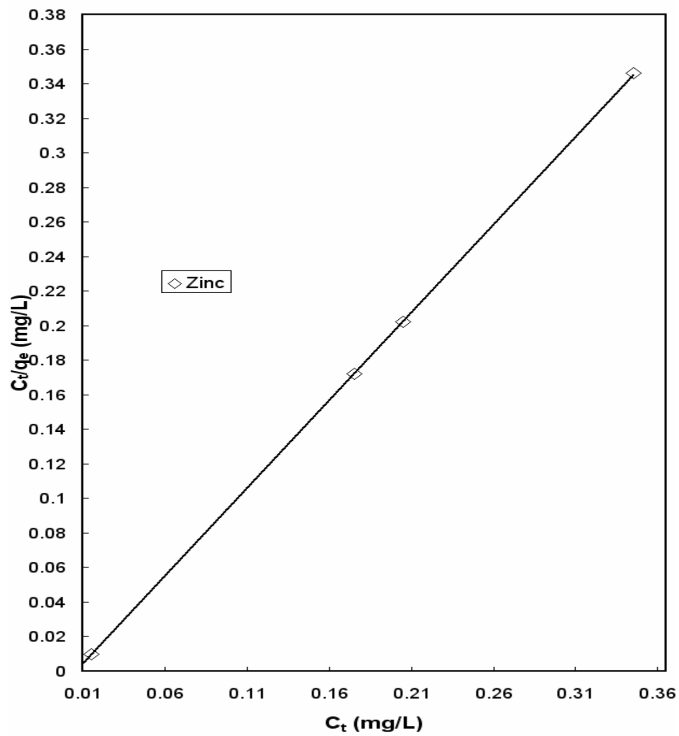

Figure 5. Langmuir Plot of zinc ion adsorption on dyed coconut pollen (DCPI)

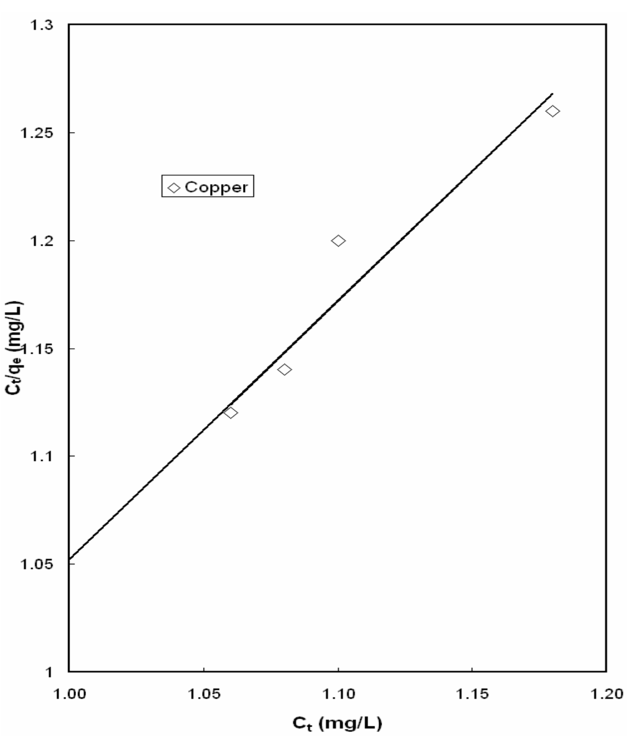

Figure 4. Langmuir Plot of copper ion adsorption on dyed coconut Pollen (DCPII).

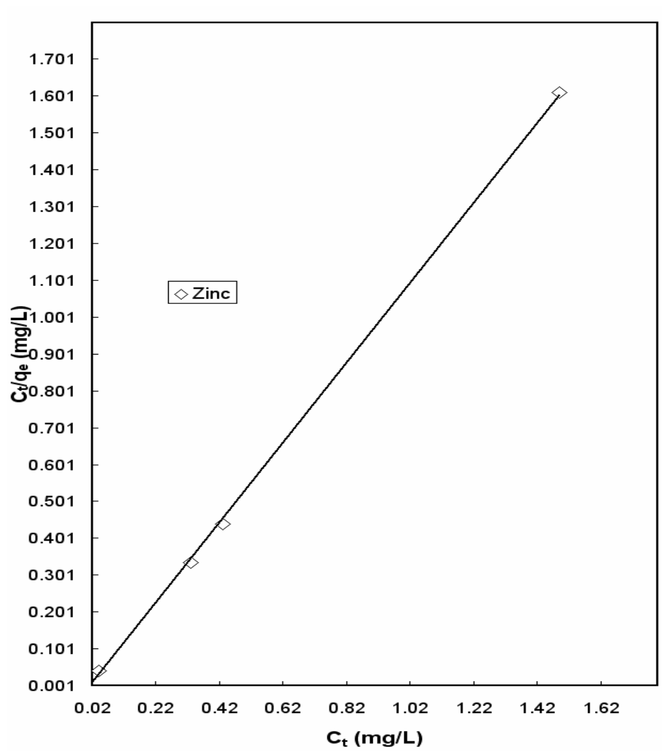

Figure 6. Langmuir Plot of zinc ion adsorption on dyed coconut pollen (DCPII).

Conclusion

The percentage adsorption of metal ions increases with decrease in particle size. The intraparticle diffusion rate constant, k_a is found to be high for smaller particle size. The adsorption mechanism obeys Langmuir equations indicating beneficial adsorption occurring through a monolayer mechanism.

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