BIOSORPTION OF CADMIUM, COPPER AND ZINC FROM SINGLE AND TERNARY METAL SOLUTIONS BY SAWDUST OF DANIELLIA OLLIVERI

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Abstract- This research investigated the adsorption of Copper, Zinc and Cadmium from their aqueous solutions using the sawdust of Danielliaolliveri as an adsorbent. The adsorbent was characterised by determining its functional group, Surface morphology and elemental composition using FTIR, SEM and EDX respectively. Batch adsorption was employed in studying the effect of experimental conditions (contact time, adsorbent dose, initial metal concentration, pH and temperature) on the adsorption of the metals in single and ternary systems. Thermodynamics parameters such as Enthalpy, Entropy and Free energy changes of the process were evaluated. The data obtained from equilibrium experiments were analysed using the Langmuir, Freundlich and Temkin isotherm models while the adsorption kinetics was elucidated with Pseudo- first order, Pseudo second order and intra particle diffusion models. The data were well fitted to Langmuir isotherm and Pseudo second order kinetics models. The adsorption was thermodynamically feasible and exothermic; the maximum monolayer coverage of the adsorbent by the cadmium and zinc was negatively affected by competitive adsorption in the ternary system.

Keyword-Danielliaoliveri, Adsorption,Biosorption, Sawdust, Heavy metals, Ternary system, Copper, Cadmium, Zinc,

I. INTRODUCTION

Heavy metal contamination has been a serious concern throughout the world [1]. The primary source of heavy metal contamination is industrial activities such as energy and fuel production, mining and smelting of metaliferous ores, and post production processes that contains wastes [2]. Some metals have harmful effects on life [3]; they are not biodegradable and tend to accumulate along the food chain, where human being is the last in the link, causing various diseases and disorders[4]. Generally, water bodies are major sites of heavy metal deposits due to the fact that streams and rivers flow through agricultural areas where pesticides and fungicides may have been used, and through industrial districts where there may have been many metal waste deposits and direct discharge of effluents into these water bodies [5]. Adsorption is one of the most popular methods for the removal of pollutants from effluents being very efficient. Efforts are on-going to search for cheaper sources of adsorbents from agricultural wastes such as coconut shell, orange peel, rice husk, coconut husk and sawdust as adsorbents to remove heavy metals from wastewater [6 - 8].As a contribution, this study aims at elucidating the adsorption characteristics of Danielliaoliverisawdust in the removal of heavy metal mixture from contaminated water.

II. METHODS

Preparation and characterization of adsorbent: Danielliaoliverasawdust was collected at a local sawmill, sun dried for 7 days prior tosieving, washed with de-ionised water, and dried at 105^0Cfor 24 hours.It was then stored in an air-tight container and labelled DS. Thesurface morphology, elemental composition and surface functional groups of the adsorbent weredetermined.

Adsorbate preparation: Analytical grade of Cu, Zn and Cd in their sulphate form were used all through this work. A 1000 mg/L solution of each of them was prepared as stock solution from which other working concentrations were prepared.

Batch Adsorption Studies: Batch adsorption experiments were carried out to determine the effects of factors such as contact time, pH, initial metal concentration, adsorbent dose and temperature in single and ternary metal systems.The adsorbent was separated from solution by filtration and the residual concentrations in filtrate samples were analyzed using Bulk Scientific 200 Atomic Absorption Spectrophotometer. The adsorption capacity of the adsorbent and the percentage removal of the metals were calculated using the following equations:

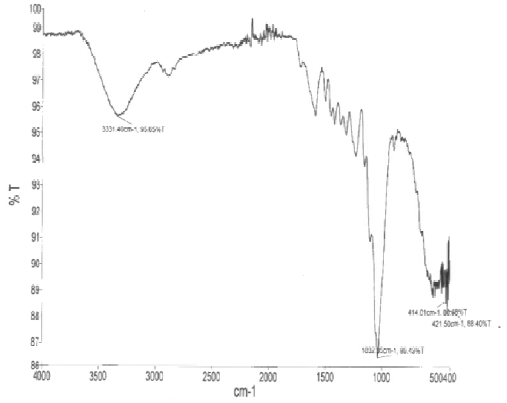
Adsorption capacity (q_e)= $\frac{(C_o - C_e)V}{W}$ (1)

Percentage removal (%R) = $\frac{C_o - C_e}{C_o} X\ 100$ (2)

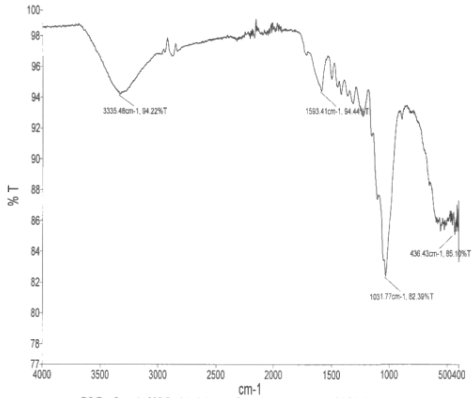
Where $q_e$is the amount of metal ion per unit mass of adsorbent at equilibrium (mg/g), C_o represents the initial concentrations of metal ion solutions (mg/L), C_e is the equilibrium concentration of metal (mg/L),V denotes the volume of metal solution (L) and Wis the weight of adsorbent (g).

III. RESULTS AND DISCUSSION

Characterization of the Adsorbents



(a)



(b)

Figure 1 FTIR spectra of DS (a) before adsorption and (b) after metal adsorption

The FTIR spectra of DS, after adsorption of the metals shows a shift in the positions of O–H peak from 3331cm^{-1} to 3335 cm^{-1}, C –O band from 1032 cm^{-1} to 1031 cm^{-1}, and the appearance of a band at 1593 cm^{-1} suggesting a C=C stretching vibration of an aromatic ring (Figure 1). Figure 3 shows the SEM micrograph with magnified image of the cavities and pores on the adsorbents prior adsorption of the metal ions. After adsorption, all the pores had been filled up with the metal ions. The EDX result showed DS to contain 62.40% of carbon, 36.44% of oxygen and trace amount of Calcium.

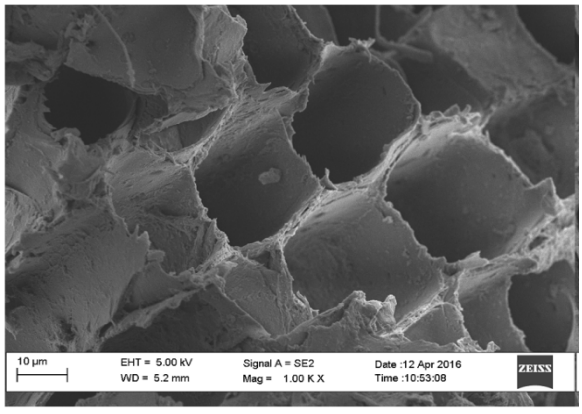


Figure 3: SEM imageof DSbefore

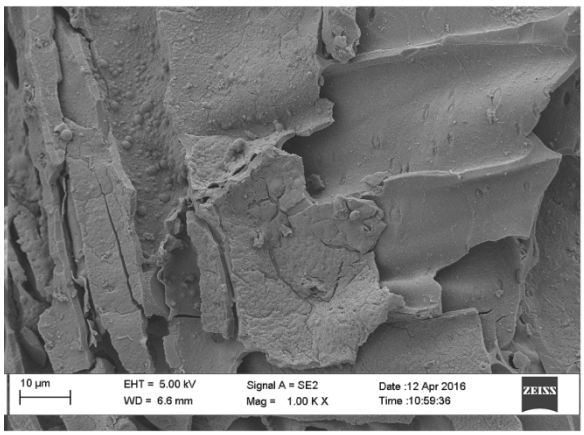


Figure 4: SEM image of DS after adsorption (1.00KX) adsorption (1.00kX)

Effect of Contact time and Kinetics: Figure5 shows the relationship between contact time and percentage removal of Cu, Zn and Cd with 1.25 g of the adsorbent. The result showed that the percentage removal increases with the increase in contact time. The fast initial uptakein the first 60 min was due to the accumulation of metal ions on the surface of adsorbent which is a rapid step.This may be attributed to the highly porous structure of adsorbent and the particle size, which provide large surface area for the sorption of metals on the binding sites[9]. Pseudo-second order kinetic model gives a better fit for the adsorption of Zinc, Copper and Cadmium. The model gives a perfect linearity compared to other models. From Table 2, it was observed that there exist a significant agreement between the experimental and calculated values of q_e for the pseudo-second order kinetic model compared to the pseudo-first order model which show no significant agreement between the q_e experimental and q_e calculated. This suggests that the process is chemisorpion whereby the metals stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface [10]. Intra-particle diffusion, though not the sole rate-controlling step, contributes significantly to the sorption process [11], as is evident in the high R^2 obtained from the plots (Table 2).

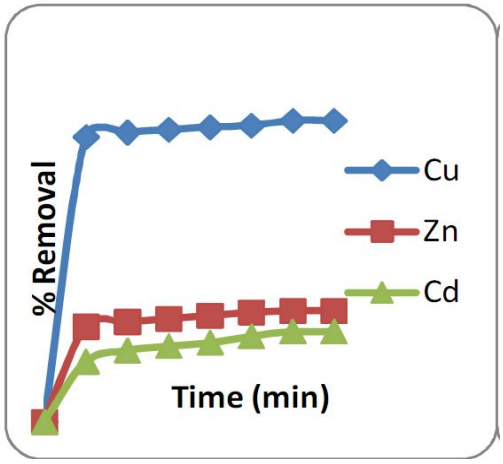


Figure 5: Effect of contact time.

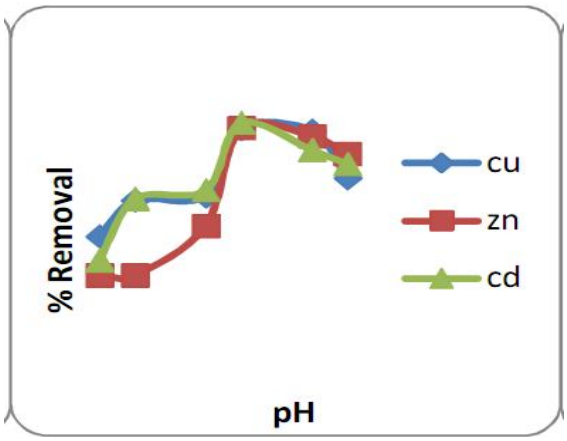


Figure 6: Effect of pH

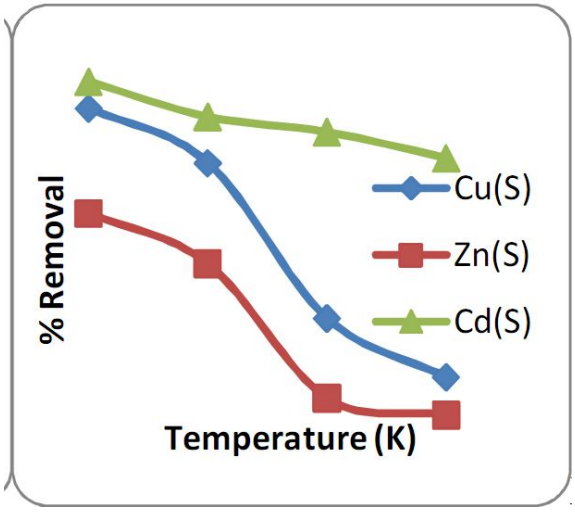


Figure 7: Effect of temperature

Effect of pH: The percentage removal of the metal ions increased as the pH increased till the optimum pH was reached between pH 6 and 8, after which the adsorption decreased (Fig. 6). The low adsorption percentage at low pH may be due to the higher concentration and high motility of H^+, which then competes with the metal ions for the adsorption sites [12].

Effect of temperature and thermodynamics: The results of the process at four different temperatures ranging from 303 K to 333 K show that adsorption decreases with increasing temperature (Fig. 7). The values of thermodynamics parameters obtained are given in Table 4.

The enthalpy change, ΔH for the adsorption of the three metals are negative, indicating the exothermic nature of the processes. Their entropy changes (ΔS)are also negative in both systems, implying a decreased randomness at the interface between the metals and DS. In the adsorption of the metals in single system, the adsorption Zinc was only spontaneous(negative ΔG values) at lower temperature whereas the process was spontaneous at all temperatures for Cadmiumand Copper.

Table 2: Kinetic Parameters for the adsorption Cu, Zn and Cd byDanielliaoliveri

Kinetic parameters	Cu	Zn	Cd
$q_{e(experimental)}$	9.5	3.5	2.85
Pseudo first order:			
K_1	0.230	0.203	0.293
q_e	0.680	0.971	1.503
R^2	0.998	0.927	0.946
Pseudo 2nd order:			
K_1	9.455	3.425	1.193
q_e	9.615	3.650	3.175
R^2	0.999	0.999	0.995
Intraparticle diffusion:			
K_3	0.326	0.350	0.622
C	0.841	2.694	1.309
R^2	0.977	0.997	0.985

Table 4: Thermodynamic parameters for Cu, Zn and Cd ontoDanielliaoliverisawdust

Thermodynamic parameters	300K	313K	323K		303K	313K	323K
	Single system				Ternary mixture		
Cu							
ΔG^0(J/mol)		-1.96	-0.97	-0.02	-0.60	0.12	0.24
ΔS^0(J/mol.K)	-99.19			-35.78			
ΔH^0(kJ/mol)	-32.03			-11.50			
Zn							
ΔG^0(J/mol)		-0.54	0.01	0.66	6.41	6.65	7.17
ΔS^0(J/mol.K)	-59.96			-51.88			
ΔH^0(kJ/mol)	-18.71			-9.59			
Cd							
ΔG^0(J/mol)		-2.36	-1.20	-1.63	6.58	6.86	7.14
ΔS^0(J/mol.K)	-36.65			-28.26			
ΔH^0(kJ/mol)	-13.47			-1.99			

Effect of adsorbent dose:The results in figure 8 and 9 showed the availability and accessibility of the adsorption sites on the adsorbents. The adsorption of the metal ions was studied by varying the adsorbent dosage from 0.1 g to 1.25 while keeping metal ion concentration (100 ppm) constant. Increase in the dose decreases the adsorption capacity due to availability of constant amount of exchangeable metal ion with increasing number of available adsorption site [13]. As more sites are been created there are limited amount of metal ion to fill them up.It can be observed that the adsorption capacity of the adsorbent dropped when there was more than one metal in the solution. Adsorption capacity for Cu in the ternary mixture slightly changes while other metals showed a significant reduction in adsorption. This suggests that there existsa competition between the metal ions for the adsorption sites on the adsorbent and Cu ion exerts an inhibitory effect on Zn and Cd.

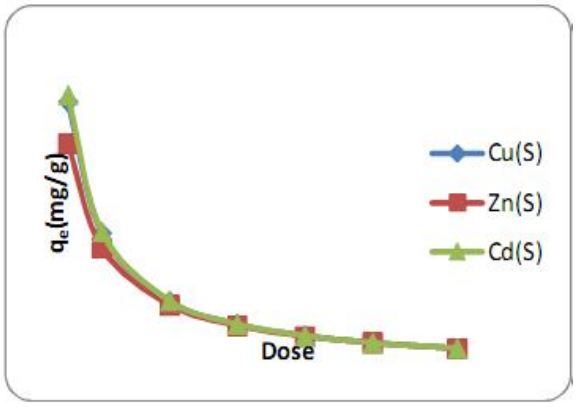


Figure 9: Effect of DS dose on the adsorption of

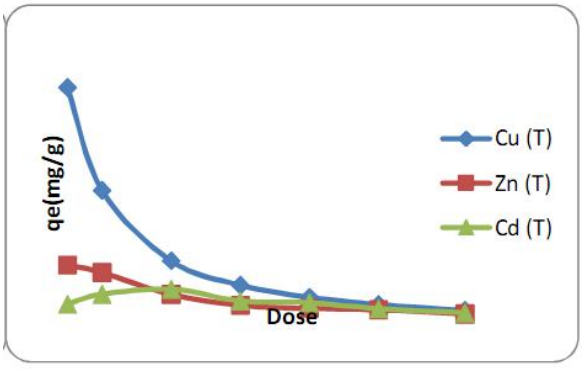


Figure 10: Effect of DS dose on the adsorption of Cu, Zn and Cd in Single system Cu, Zn and Cd in ternary system

Adsorption Isotherm studies: The results of the adsorption of Zn, Cu and Cd from aqueous solution are shown in Table 5.Langmuir isotherm gives a better fitting for the adsorption of Zn, Cu and Cd in single metal systems due to the high correlation coefficient obtained experimental data. This could be due to a small surface area for metal adsorption causing a monolayer adsorption occurring on the surface of the adsorbent [14].

Table 5: Isotherm parameters for the adsorption of Cu, Zn and Cd on RS in single and ternary systems

Isotherm parameters	Cu	Zn	Cd
single metal system)			
Langmuir			
b(L/mg)	0.376	0.185	0.431
q_0	8.333	7.752	8.365
R^2	0.993	0.995	0.986
Freundlich			
N	*3.021*	3.012	3.610
K_f	2.518	1.982	3.012
R^2	0.950	0.977	0.959
Tempkin			
b_t	1817	2171	2016
A_t	8.334	4.001	15.17
R^2	0.987	0.990	0.984
Ternary mixture			
Langmuir			
b(L/mg)	0.291	0.157	0.124
q_0	8.333	0.594	0.491
R^2	0.980	0.732	0.713
Freundlich			
N	2.985	7.519	14.49
K_f	2.427	2.009	1.945
R^2	0.957	0.893	0.425
Tempkin			
b_t	3670	4150	3976
A_t	0.095	3.787	3.166
R^2	0.927	0.890	0.881

CONCLUSION

Cadmium, copper and zinc were adsorbed fromsingle-solute and ternary-solute aqueous solutions onto sawdust of Danielliaoliveri.The biosorption process in the single systems followed Langmuir isotherm model with the monolayer coverage of the range 7.75 – 8.36 mg/g. The monolayer coverage for cadmium and zinc got reduced in the ternary metal system. Adsorption was generally more sponteineousin the single systems

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