Usefulness of *Telfairia occidentalis* Waste for the Adsorption of Toxic Heavy Metals from Simulated Effluent

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Abstract: ***Exploitation of unmodified and thioglycolic acid modified waste as a low-cost adsorbent for the adsorption of $Cd^{2+}Ni^{2+}$ and Pb^{2+} from simulated aqueous solutions was investigated. The results clearly demonstrate the effect of particle size and contact time as important experimental parameters on the adsorption process in batch experiments. The maximum evaluated particle size concentration and time concentration for Cd^{2+}, Ni^{2+} and Pb^{2+} uptake onto unmodified and modified Telfairia occidentalis waste biomass were 99.68 mg/g Cd^{2+}, 99.99 mg/g Ni^{2+}, 99.75 mg/g Pb^{2+}at 250 µm for the unmodified and 98.78 mg/g Cd^{2+}, 98.88 mg/g Ni^{2+} at 250µm and 98.52 mg/g Pb^{2+} at 125 µm for the modified waste. 99.99 Cd^{2+}, 99.99 mg/g Ni^{2+} and 99.89 mg/g Pb^{2+} at 10 minutes for the unmodified waste and 99.45 mg/g Cd^{2+} at 60 minutes, 99.73 mg/g Ni^{2+} at 90 minutes, 88.80 mg/g Cd^{2+}at 90 minutes for the modified. The kinetic of metal ions adsorption on Telfairia occidentials waste biomass has also been studied by fitting the data in Lagergren's first-order, Ho-Mckay's pseudo-second-order kinetics hypothesis and Elovich adsorption model. It was observed that the removal of metal ions over the waste biomass showed a better fit with the pseudo-second-order process and Elovich adsorption model than the pseudo -first-order.***

Keywords: Adsorption kinetics, contact time, heavy metal ions, particle size, Telfairia occidentalis coat.

1. Introduction

The mobilization of heavy metals in the environment through industrial activities is of serious concern because of the toxicity of these metals to the environment [1]. However, some metals such as cadmium, nickel and lead are markedly very toxic, even at very low concentrations [2]. Thus their removal is vital from the stand point of environmental pollution control [3 – 4]. Several physico-chemical processes for the removal and recovery of heavy metals from effluents exist out of which the adsorption is one of the most effective as the important aspect of adsorption process is easy regenerability and cost effective [5].

Adsorption principle and techniques have proven successful in the treatment of metal contaminated effluents from industries and other sources. Aksu and co-workers [6-15] have made substantial contributions in this area. According to literature *Telfairia occidentalis* waste has been a good adsorbent in heavy metal removal from industrial wastewaters [16]. This waste is generated during the processing of the *Telfairia occidentalis*. It has been reported that this waste serves as livestock meal but its digestibility is considered poor due to its anti-nutritional factors [17]. The proximate composition of *Telfairia occidentalis* coat has been given [18] and as a result of this composition, it has been classified as a lignocellulosic material, hence the interest in finding out its feasibility of adsorbing toxic metals from solutions. In this present study, *Telfairia occidentalis* coat has been utilized as an adsorbent for the removal of Cd^{2+}, Ni^{2+} and Pb^{2+} from simulated aqueous solutions. During this study, the effect of particle size and period of contact have been observed on the adsorption of the metal ions over the *Telfairia occidentalis* coat. The kinetics of adsorption has been studied to determine the efficiency of the adsorption process.

2. Materials and Method

All reagents used were analytical grade, purchased and used without further purification. The waste biomass was gotten by removing the coat of the *Telfairia occidentalis* which was obtained from Umuahia main Market, Abia State. The coat was crushed in a mill, washed with deionized water and over dried at 50^0C for 12hrs. This was sieved to obtain different sizes (125, 250, 375, 600, 625, 850) µm and activated with 2% (v/v) nitric acid overnight, washed with deionized water and finally oven-dried at 105^0C for 6hrs. The activated samples represented the unmodified sample. About 5 g portion of the activated 250 µm particle size of the sample were taken from the bulk of the activated sample and modified [19] by soaking the sample into 1000 cm^3 of 0.3M thioglycollic acid at 25 ^{0}C for 24hrs. The mixture was filtered, washed with de-ionized water and then with methanol. It was finally washed with de-ionized water and dried at 50 ^{0}C. The thiolated sample represented the modified samples for the experiment.

3. Experimental Procedure

Stock solution of 1000 mg/l of Cd^{2+}, Ni^{2+} and Pb^{2+} as a synthetic wastewater, was prepared by dissolving 1 g of each salt in 1000cm^3 of de-ionized water and made up to the mark of the volumetric flask. Each of these solutions represented the metal ion solution of 1000 mg/l concentration. From the stock solutions of 1000 mg/l, 5$cm^3$of each of the solution was pipetted into beakers and made up to the mark of 50ml volume with deionized water to give a concentration of 100 mg/l which was used for the adsorption process. The adsorption studies were conducted using a batch technique at 25 ^{0}C and pH of 7.5. 1g of the various sizes (125, 250, 375, 600, 625, 850) µm of both unmodified and modified samples were put into a 250cm^3 conical flasks containing 50 cm^3 i.e. (5 ml aliquot of 1000 mg/l stock solutions + 45 cm^3 de-ionized water) portion of the test solutions and allowed to stand for 1 hr with intermittently shake. The solutions were filtered and the filtrates were analyzed for residual metals using atomic absorption spectrophotometer (Buck model 200 A). For the time effect, 50 cm^3 of each of the metal ion solutions of 100 mg/l were placed into various flasks containing 1g (250 µm) size of the sample. The flasks were agitated for various time intervals of 10, 30, 60, 90 and 120 minutes, after which the mixtures were filtered and the filtrates were analyzed for residual metal using AAS (Buck model 200A). Triplicate analysis were made and the amounts of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed during the series of batch investigations were determined using a simplified mass balance ($Qe = C_o - C_e$), where Q_e = amount adsorbed (mg/g) by the adsorbents at equilibrium or metal ion concentration on adsorbent at equilibrium, C_e = metal ion concentration (mg/l) (final concentration) in the solution (of the filtrate) at equilibrium while C_o = initial metal ion concentration (mg/l) in solution used.

4. Results and Discussion

Table 1: Amount of heavy metal ions adsorbed by various sizes of *Telfairia occidentalis* waste from aqueous solution at 298 K

	Unmodified *Telfairia occidentalis* coat			Modified *Telfairia occidentalis* coat		
Particle size(µm)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+}(mg/g)	Cd^{2+}(mg/g)	Ni^{2+}(mg/g)	Pb^{2+} (mg/g)
125	99.589± 0.017	99.999±0.018	99.661±0.007	98.619±0.241	98.601± 0.173	98.520± 0.414
250	99.675± 0.018	99.999 ±0.018	99.746 ±0.042	98.777 ±0.305	98.699 ± 0.212	97.423 ± 0.033
375	99.670± 0.016	99.999 ±0.018	99.700 ±0.023	97.676 ±0.144	97.507 ± 0.274	97.411 ± 0.038
600	99.655± 0.010	99.999 ±0.018	99.562 ±0.033	97.702 ±0.133	98.880 ± 0.286	97.351 ± 0.053
625	99.600± 0.012	99.872 ±0.034	99.600 ±0.018	97.799 ±0.094	97.709 ± 0.192	97.325 ± 0.073
850	99.589± 0.017	99.860 ±0.039	99.589 ±0.022	97.601 ±0.175	97.676 ± 0.205	97.000 ± 0.206

Table 1 shows concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by various sizes of unmodified and modified *Telfairia occidentalis* waste from aqueous solutions. The data generally revealed that the adsorption capacity of the *Telfairia occidentalis* waste increases with decrease in particle size indicating that the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by *Telfairia occidentalis* waste increases with increase in the surface area of contact. The breaking of larger particles tend to open tiny cracks and channels on the particle size surface of the material resulting in more accessibility to better diffusion, owing to the smaller particle size [20]. Slight difference was observed between the adsorption capacities of unmodified and modified samples of *Telfairia occidentalis* waste. Modification was found to decrease the adsorption capacity of the adsorbent and equally showed irregular pattern of adsorption unlike in the unmodified sample [Fig 1]. Adsorption capacity of the unmodified adsorbent was best for Ni^{2+} followed by Pb^{2+} and least for Cd $^{2+}$ while Ni^{2+} followed by Cd^{2+} and least for Pb^{2+} was the order of adsorption for the modified adsorbent. Maximum concentrations were given as follows: 99.99 Ni^{2+}, 99.75 Pb^{2+} and 99.68 Cd^{2+} mg/g for the unmodified sample, 98.88 Ni^{2+}, 98.78 $Cd^{2+}$and 98.52 Pb^{2+} for the modified waste sample. Therefore the different particle sizes have different removal abilities as 250 µm showed highest removal ability for metal ions than other particle sizes.

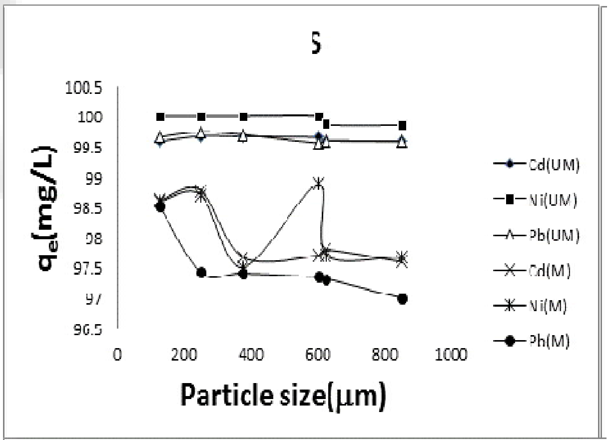

Figure 1: Effect of particle size on the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Telfairia occidentalis* waste

5. Time Dependency

Table 2: Concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by *Telfairia occidentalis* waste from aqueous solutions at various temperatures.

	Unmodified *Telfairia occidentalis* coat			Modified *Telfairia occidentalis* coat		
T (K)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)
303	99.986±0.018	99.999±0.023	99.872±0.088	99.833±0.486	99.879±0.156	99.008±3.094
323	99.962±0.006	99.979±0.023	99.720±0.020	98.934±0.084	99.520±0.005	90.695±0.624
343	99.953±0.003	99.972±0.020	99.641±0.015	98.766±0.009	99.487±0.152	90.527±0.700
363	99.931±0.001	99.869±0.026	99.587±0.039	98.190±0.248	99.450±0.036	90.198±0.846
383	99.902±0.020	99.821±0.048	99.555±0.054	98.004±0.332	99.320±0.094	90.025±0.924

Table 2 shows the variation of the concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by *Telfairia occidentalis* waste from aqueous solutions at various time intervals. Unlike the modified waste sample that showed longer time with irregular pattern of adsorption of the metal ions, adsorption of the metal ions by the unmodified waste samples was found to increase at a shorter time (10 min). Maximum concentrations were given as 99.99 Cd^{2+}, 99.99 Ni^{2+} and

99.89 Pb^{2+} mg/g. Irregular adsorption with modified waste sample indicated that modification had effects on the adsorption capacity of this adsorbent.

6. Kinetic Studies

Pseudo-first-order, pseudo-second-order and Elovich adsorption model were used to describe the adsorption of the on-going process. The pseudo-first-order model did not give any correlation with the data hence plot is not shown. The pseudo-second-order model as developed by [21] was plotted using equation below. A pseudo-second-order adsorption rate equation can be expressed as follows,

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (1)$$

where k_2 is the rate constant of pseudo-second-order adsorption ($gmg^{-1}min^{-1}$), q_e and q_t are the adsorption capacity at equilibrium and at time, t, respectively. Introducing boundary conditions to equation 1, i.e. t = 0 to t=t and q_e = 0 to q_t = q_t, integrated form of equation 1 was obtained (equation 2) and upon simplification, equations 3 and 4 were obtained.

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_t} + k_2 t \quad (2)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (3)$$

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e}(t) \quad (4)$$

The implication of equation 4 is that a plot of $1/q_t$ versus t should be linear with slope and intercept equal to q_e and $\frac{1}{h}$ (h = $k_2 q_e^2$) respectively. Fig. 2 shows pseudo-second-order kinetic plots for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Telfairia occidentalis* wastes respectively. Adsorption parameters obtained from the plots are presented in Table 3.

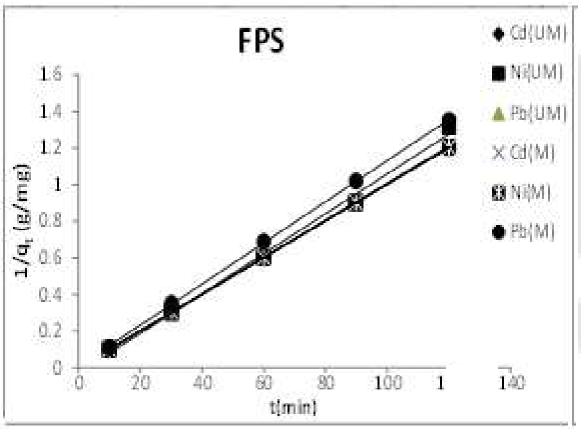

Figure 2: Variation of $1/q_t$ with t (pseudo-second-order kinetic) for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Telfairia occidentalis* waste

Table 3: Pseudo-second-order adsorption parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Telfairia occidentalis* waste

System	*Ions*	*Slope*	q_e	*h*	k_2	R^2
T.o	Cd(UM)	0.01	-4.00E-	-2.50E+15	-2.50E+11	1
	Ni(UM)	0.0109	-0.0303	-3.30E+01	-3.92E-03	0.9945
	Pb(UM)	0.01	-0.0001	-1.00E+04	-1.00E+00	1
	Cd(M)	0.0101	-0.0004	-2.50E+03	-2.55E-01	1
	Ni(UM)	0.01	0.003	3.33E+02	3.33E-02	1
	Pb(M)	0.0112	0.0074	1.35E+02	1.70E-02	0.9998

From the results obtained, it can be seen that values of R^2 are very close to unity indicating the application of a pseudo-second-order model to the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Telfairia occidentalis* wastes. It is also evident from the results that values of k_2 calculated from the plots are relatively low. It was also observed that h and k_2 values for the adsorption of Ni^{2+} and Pb^{2+} by modified *Telfairia occidentalis* adsorbent were higher than those obtained from the unmodified adsorbent. The reverse was however observed for the adsorption of Cd^{2+} by *Telfairia occidentalis* waste. According to Sharma and Goya (2009), a pseudo-first and -second order kinetics cannot reveal the mechanism of adsorption therefore, a model of Elovich was also used to test for the adsorption mechanism of the studied adsorbates. Elovich adsorption model can be expressed as follows (Chien and Clayton, 1980; Sparks, 1986):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (5)$$

where α is the initial adsorption rate ($mgg^{-1}min^{-1}$) and β is the desorption constant (gmg^{-1}) during any one experiment. Chien and Clayton (1980) had proposed that αβt>>t and if the boundary conditions are applied (i.e. t=0 and q_t = q_t at t = t), the Elovich equation becomes,

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (6)$$

The implication of equation 6 is that a plot of q_t versus ln(t) should be linear with slope and intercept equal to $\frac{1}{\beta}$ and $\frac{1}{\beta}ln(\alpha\beta)$ respectively. Fig. 4 shows Elovich plots for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Telfairia occidentalis* waste. Values of Elovich constants deduced from the plots are presented in Table 4. From the results obtained, it can be seen that the adsorption of the heavy metal ions by *Telfairia occidentalis* waste fitted the Elovich adsorption model excellently.

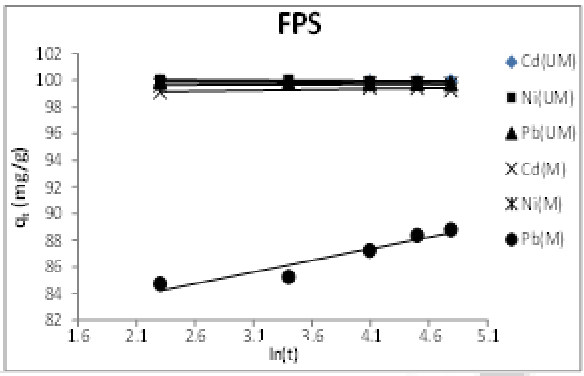

Figure 3: Variation of q_t with ln(t) (Elovich adsorption model) for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Telfairiaoccidentalis*waste

Table 4: Elovich parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Telfairiaoccidentlis* waste

System	*Metal ion*	*Slope*	*Intercept (I)*	*β*	*Iβ*	*α*	R^2
T.o	Cd(UM)	-	100.06	-39.5257	-3954.94	0	0.906
	Ni(UM)	-	100.14	-17.6367	-1766.14	0	0.8047
	Pb(UM)	-	100	-18.7617	-1876.17	0	0.947
	Cd(M)	0.1045	98.915	9.5694	946.55	-	0.5493
	Ni(M)	0.0299	99.57	33.4448	3330.1	-	0.7729
	Pb(M)	1.742	80.22	0.5741	46.05	1.74E+20	0.9064

7. Conclusion

Telfairia occidentalis coat as a cheap natural waste has been proven as a good adsorbent for toxic heavy metals removal in wastewater especially when unmodified at 250 µm, pH of 7.5, temperature of 25 ^{0}C, concentration of 100 mg/l and period of 30 minutes contact. Almost 100% heavy metals removal was achieved. Kinetically, Elovich adsorption model gave better fit for the data than pseudo-first and pseudo-second order models. Hence, there is need to investigate the probable changes of adsorption efficiency in conditions of encountering the various metals in actual wastewaters using *Telfairia occidentalis* coat.

8. Future Scope

The impact of this study to the society involves the use of low cost adsorbents in maintaining pollution free environment since it involves waste management and detoxification of toxic pollutants. Moreover this study gives an insight for the upcoming researchers to adopt this method in different areas such as in agricultural research i.e. a situation where this adsorbent will be mixed with fertilizers before application in order to minimize its leaching to the environment.

References

[1] S. M. Al-Garni, "Biosorption of lead by gram-ve capsulated and non-capsulated bacteria," Water SA, XXX1, pp 345-349, (2005).
[2] B.Volesky, Z. R. Holan, "Biosorption of heavy metals," Biotechnology progress, X1 (3), pp 235-250, (1995).
[3] P. R. Puranik, K. M. Paknikar, "Biosorption of lead, cadmium and zinc by *Citrobacter strain* MCM B-181, Characterization studies," Biotechnology progress, XV (2), pp 228-237, (1999).
[4] G. Yan, T. Viraraghavan, "Heavy metals removal from aqueous solution by fungus *Mucorrouxii*," Water research, XXXVII (18), pp 4486-449, (2003).
[5] D. Kratochvil, B. Volesky, "Advances in the biosorption trends,"Biotechnology XVI (7): pp 291-300, (1998).
[6] Z. Aksu, "Equilibrium and kinetic modeling of cadmium(11) biosorption by *C. vulgaris* in batch system effect of temperature, Sep. Purif. Tech. CXXI: pp, 285-294, (2001).
[7] K. Bhattacharya, C. Venkobachar, "Removal of cadmium by low cost adsorbent," Journal of Envi. Eng. Division (ASCE), CX, pp, 110-123, (1984).
[8] N. Chubar, J. R. Carvacho, C. M. J. Neiva, "Cork biomass as biosorbent for Cu(11), Zn(11) and Ni(11)," Colloids Surf. A: Physico-chem. Eng. Asp. CCXXX, pp. 57-65, (2003).
[9] Cabuk, S. Ilhan, C. Filik, F. Caliskan, "Pb^{2+} biosorption by pretreated fungal biomass" Turk. J. Biol., XXIX, pp. 23-28, (2005).
[10] C.Haluk, Y. Ulki, "Biosorption of Ni(II) and Pb(II) by *Phanerochaete chrysosporium* from a binary metal system kinetics" Water SA, XXVII, pp 15 – 20, (2001).
[11] R. Han, H. Li, Y. Li, J. Zhang, H. Xiao, J. Shi, "Biosorption of copper and lead ion by waste beer yeast" J. Hazard Mater B, CXXXVII, pp. 1569-1576, (2006).
[12] N. J. Abdel-Ghani, M. Hefny, C. El-Chaghaby, "Removal of lead from aqueous solution using low cost abundant available adsorbents. Int. J. Environ. Sci-Tech, IV (1), pp .67-73 (2007).
[13] M. Horsefall, A. I. Spiff, A. A. Abia, "Studies on the influence of mercaptoacetic acid (MMA) modification of cassava (*Manihot sculenta cranz*), Water Res.XXXVII (20), pp. 4913-4923, (2004).
[14] J. C. Igwe, A. A. Abia, "Adsorption isotherm studies of Cd(11), Pb(11) and Zn(11) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob. Eccl. Quim, Sao Paulo, XXXII (1), pp. 33-42, (2007).
[15] J. C. Igwe, A. A. Abia, C. A. Ibeh, "Adsorption kinetics and intraparticulate diffusivities of Hg(II), As(III) and Pb(II) ions on unmodified and thiolated coconut fibre. Int. J. Environ. Sci. Tech. V (1), pp. 83-92, (2008).
[16] C. Agatemor, "A nutritional assessments" Elec. Journ. of Env. Agric and Food Chem., VI (2), pp. 1789 – 1793, (2009).
[17] K. Zuzana, H. Zdenka, F. Anna, "Nutritional and non-nutritional factors of fluted pumpkin seed coat husk" Elec. Journ. of Env. Agric and Food Chem., LXIIV (4), pp. 406-413, (2008)
[18] W. J. Weber, J. C. Morris, "Kinetics of adsorption on carbon from solution" J. Sanit. Egr. Dir Am. Soc. Cir. Eng, XXXLIX, pp. 31-60, (1963).
[19] Y. S. Ho, G. McKay, "A Pseudo-second order model for sorption processes. Process Biochemistry XXXIV, pp. 451-465, (1999).
[20] Y. S. Ho, D. A. J. Wase, C. F. Forster, "Study of the sorption of divalent metal ions onto peat. Adsorp. Sci. Technol. XXVIII, pp. 639-650, (1980)
[21] S. H. Chien, W. R. Clayton, "Application of Elovich equation to the kinetics of phosphate release and

sorption on soils," Soil Sci. Soc. Am. J, XLIV, 265 – 268, (1980).
[22] D. L. Sparks, "Kinetics of reaction in pure and mixed systems in soil," Physical Chemistry, Boca Raton CRC Press, (1986).

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