Communication in Physical Sciences, 2022, 8(4):520-529

Remediation of effluents polluted with toxic heavy metals using *Cola nitida* pod husk.

Felicia Uchechukwu Okwunodulu* and Stevens Azubuike Odoemelam

Received: 01 August 2022/Accepted 21 August 2022/Published online: 29 September 2022

Abstract*: Heavy metal ions such as Cd^{2+}, Ni^{2+} and Pb^{2+} are highly toxic to the entire ecosystem and are mostly produced by several industrial sectors. This study was designed to remove the listed heavy metal ions from an aqueous solution using Cola nitida waste for the batch adsorption process. The waste materials were employed in both raw and modified forms. The results obtained indicated that the adsorption capacity was influenced by initial metal ion concentration and adsorbent dose at a particle size of 250 µm, pH of 7.5, temperature of 25 ^{0}C and period of contact. The extent of adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified waste Cola nitida waste was observed to increase with an increase in concentration and with a decreasing dosage of the adsorbent. At an initial metal ion concentration of 100 mg/l and adsorbent dose of 2g and 3g, maximum adsorptions by the unmodified and modified Cola nitida wastes were recorded for Cd^{2+} and the values obtained were 99.800$\pm$0.418 and 99.999$\pm$0.499; 89.999$\pm$3.439 at 3g and 99.952$\pm$0.166 at 2g. The adsorption behaviour of both the unmodified and modified Cola nitida wastes fitted the tested Freundlich and Temkin adsorption models best and suggested the dominancy of the mechanism of physisorption.*

Keywords: *Adsorption isotherm, heavy metal ion, initial metal ion concentration, adsorbent dose, Cola nitida pod husk.*

Felicia Uchechukwu Okwunodulu*
Department of Chemistry, Michael Okpara University of Agriculture Umudike, Nigeria
Email: okwunodulufelicia@gmail.com
Orcid id: 0000-0001-9880-0046

Stevens Azubuike Odoemelam
Department of Chemistry, Michael Okpara University of Agriculture Umudike, Nigeria.
Email: stevenodoemelam@yahoo.com

1.0 Introduction

Continuing research and literature on the toxicity and detoxification of heavy metals from the environment or sources of generation has been actively stimulated. Environmental pollution with heavy metals can arise through natural and anthropogenic sources (ref) Anthropogenic activities have resulted in elevated concentrations of metals in the environment (Ankley *et al.,* 1994). Heavy metals rank as major environmental pollutants in wastewater both developed and developing countries as a result of rapid industrialization (Asuquo, 1999). The non-biodegradability and persistent nature of some heavy metals, can enhance their accumulation in the environment through the food chain and exert toxic effects on public health (Bakkaloglu *et al.*, 1998; Yetis *et al.*, 1998). For example, acute exposure to cadmium can damage numerous tissues such as the kidney, liver, lung, gastrointestinal tract, central nervous system ovaries and testes (Waalkes and Rehm, 1992; Goering *et al.*, 1994; Alloway and Ayres 1997). Acute levels of nickel exposure through inhalation are a potent precursor for headache, nausea, respiratory disorders and death (Goyer, 1991; Rendall *et al.*, 1994)). Lead concentration in blood at 40 mcg/dl has been reported to be a likely source of damage to the central nervous system (CNS) and is associated reduction in nerve conduction velocities and neuritis (ATSDR, 1993). At blood concentrations above 70 mcg/dl, lead has been shown to cause anaemia, characterized by a reduction in haemoglobin levels, and erythropoiesis i.e. a shortened life span of red blood cells (Goyer, 1998; USEPA, 1986a). In view of their established toxicities and continuous generation in the environment, several conventional methods have been tested and found suitable for the removal of heavy metal

Corresponding *Author*: Felicia Okwunodulu, Email: okwunodulufelicia@gmail.com

ions from solutions including photocatalysis, exchange, filtration, coagulation and others (Eddy *et* al., 2022a-b). However, documented challenges in most of these methods are (i) the toxicity of the adsorbent before and after usage (ii) cost-effectiveness (iii) nonbiodegradability (iv) nonaccessibility (Eddy and Garg, 2021). Consequently, there is a need to develop and implement cost-effective, environmentally friendly and more efficient technologies for the removal of heavy metal ions from solution. Therefore, the present study seeks to process *cola nitida* wastes for the removal of Cd^{2+}, Ni^{2+} and Pb^{2+} from an aqueous solution using batch adsorption technology (Okwunodulu *et al.*, 2016). *Cola nitida* husk pod has high lingo-cellulosic nature Oladayo (2010), hence can be used as an adsorbent. In this work, the effectiveness of using activated unmodified and thioglycolic acid (mercaptoacetic acid) modified *Cola nitida* pod husk for the removal of Cd^{2+}, Ni^{2+} and Pb^{2+} from aqueous solutions was examined, the adsorptive capacities of the unmodified and modified *Cola nitida* pod husk were compared, the effect of variation in the initial metal ion concentration and particle size on the adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+}onto unmodified and modified *Cola nitida* pod husk were investigated and the adsorption process of the metal ions adsorbed by the unmodified and modified *Cola nitida* pod husk via adsorption isotherms was explained. Thus this research aims at finding a more economic ways of removing heavy metals from solutions.

2.0 Materials and Methods

2.1 Sample collection and preparation

The *Cola nitida* was obtained from Gariki Market Okigwe in Imo State Nigeria and dehusked to get the husk. The grounded tiny particle size of the husk was obtained using a manual grinder and sieved through a test-sieve shaker after washing with deionized water and drying in an oven at 50 ^{0}C for 12hrs to get 250µm mesh sizes. Activation of the husk was done by soaking in 2% (v/v) dilute nitric acid solution for 24 hours, filtered, rinsed severally with de-ionized water and allowed to dry in the oven at 105^{0}C for about 6 hours and this was labelled unmodified sample. About 10 g portion of the activated sample was modified using thioglycolic acid by soaking the sample into 1000 cm^3 of 0.3 mol thioglycolic acid for 2hrs at 25^{0}C, filtered, rinsed with de-ionized water and finally dried at 50^{0}C for 12hr and labelled modified sample. Both were used for the sorption batch experiments.

2.2 Effect of adsorbent dose on Cd^{2+}, Ni^{2+} and Pb^{2+} adsorption

To determine the effect of adsorbent dose on Cd^{2+}, Ni^{2+} and Pb^{2+} sorption from their aqueous solutions, various amounts (0.25, 0.50, 1.00, 2.00, 3.00 and 8.00) grams of 250µm particle size of both unmodified and modified samples were put in several flasks to explore the effect of variation in adsorbent dose on uptake levels of the metal ions from their solutions. 50 cm^3 portion (of concentration 100 mg/l) of the metal ion solutions were also introduced to the various flasks. The solution mixtures were shaken intermittently with a rotating shaker for one hour at 30 ^{0}C and a pH of 7.5. After one hour, the solutions were filtered and the filtrate analyzed for residual metals using Flame Atomic Absorption

2.3 Effect of initial metal ion concentration on Cd^{2+}, Ni^{2+} and Pb^{2+} adsorption.

Spectrophotometer (Buck model 200A). For the effect of initial metal ion concentration on Cd^{2+}, Ni^{2+} and Pb^{2+} sorption from their aqueous solutions, equilibrium sorption of Cd^{2+}, Ni^{2+} and Pb^{2+} onto unmodified and modified *Cola nitida* pod husk was carried out using 50 cm^3 of various concentrations (100, 80, 60, 40, 20, and 10 mg/l) at constant metal ion-substrate contact period of 1 hour, the temperature of 25 °C and pH of 7.5. 1gram (250 µm size) of both samples was put into the 50 cm^3 of each of the metal ion solutions of specified (varied) concentrations and the mixture was shaken intermittently with a rotating shaker for 1 hour. The solution mixtures were filtered rapidly into separate sample bottles using Whatman 42 filter paper. The filtrates were analyzed for residual metals using Atomic Absorption Spectrophotometer (Buck model 200A). The equilibrium (final) concentration of each metal ion was determined using Atomic Absorption Spectrophotometer (Buck model 200A). The described procedure for the parameters was triplicated for the sorption of Cd^{2+}, Ni^{2+} and Pb^{2+} onto unmodified and modified *Cola nitida* pod husk. The amounts of Cd^{2+}, Ni^{2+} and Pb^{2+} were sorbed by the unmodified and modified *Cola nitida* pod husk. during the series of the batch, investigations were determined using a simplified mass balance equation as expressed as (Bhatti *et al.*, 2007)

$$Q_e = \frac{C_0 - C^e}{m} \times \frac{V}{1} \qquad (1)$$

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 the solution used.

3.0 Results and discussion.

3.1 Effect of adsorbent dose (mass) on adsorption

Table 1 shows data obtained for the adsorption of different concentrations of cadmium, lead and nickel ions by both modified and unmodified *Cola nitida waste.*

Table 1: Concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+}adsorbed by various adsorbent doses of *Cola nitida* pod husk at 298K.

	Unmodified *Cola nitida* pod husk			Modified *Cola nitida* pod husk		
M (g)	**Cd^{2+} (mg/g)**	**Ni^{2+} (mg/g)**	**Pb^{2+} (mg/g)**	**Cd^{2+} (mg/g)**	**Ni^{2+} (mg/g)**	**Pb^{2+} (mg/g)**
0.25	77.522±1.655	77.640±2.311	89.760 ±0.005	99.016± 0.216	99.157±0.100	90.024±2.141
0.50	78.530±1.243	78.860±1.813	89.800±0.011	99.038± 0.207	99.286±0.047	90.180±2.078
1.00	78.410±1.292	77.970±2.177	89.890 ±0.048	99.664± 0.048	99.462±0.025	96.165±0.366
2.00	89.890±3.395	89.810±2.657	89.780 ±0.003	99.952± 0.166	99.692±0.119	97.227±0.180
3.00	89.999±3.439	89.870±2.682	89.720 ±0.022	99.802±0.105	99.776±0.153	99.021±1.532
8.00	75.100±2.643	85.700±0.971	89.690 ±0.034	99.800± 0.104	99.036±0.149	99.000±1.523

± = error of the mean

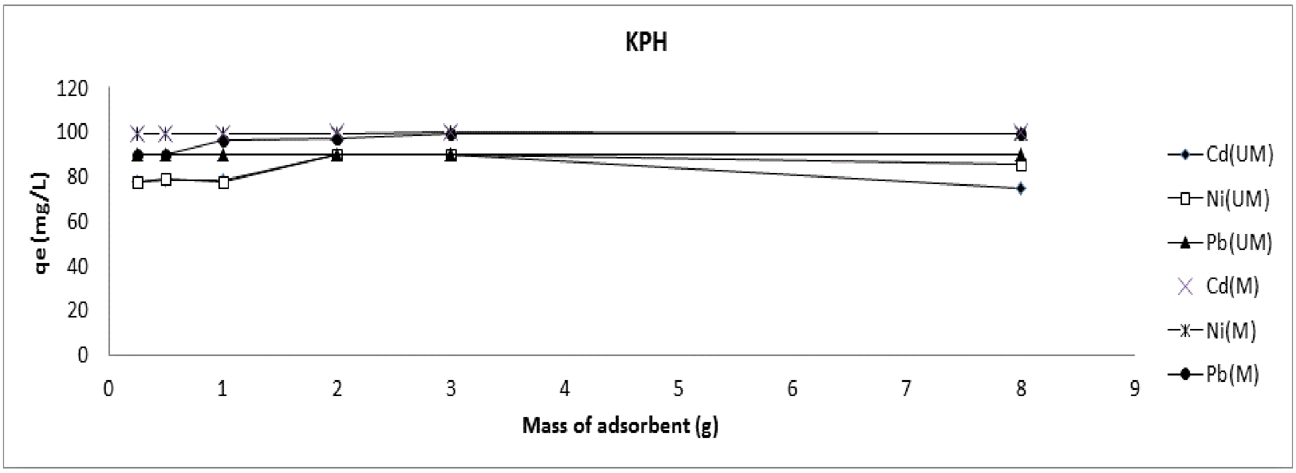

Fig. 1: Plot on the effect of mass of the adsorbent on the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Cola nitida* pod husk

Adsorption capacities of unmodified and modified samples of *Cola nitida* pod husk for Cd^{2+}, Ni^{2+} and Pb^{2+} were found to be influenced by the mass of the adsorbent. Table 1 shows concentrations of heavy metals adsorbed by various grams of the adsorbent at 298 K. From the results obtained, it can be seen that the adsorption capacity of unmodified and modified samples of *Cola nitida* pod husk on Cd^{2+}, Ni^{2+} and Pb^{2+} were all favoured at low doses though there is no significant pattern of variation between the mass of the adsorbent and extent of adsorption by the studied adsorption. Modification slightly improves the adsorption capacities of modified *Cola nitida* pod husk. Fig. 1 shows the variation of the amount of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed with a mass of the adsorbent. The Figure revealed that the adsorption of the studied heavy metal ions by *Cola nitida* pod husk was almost independent of the mass of the adsorbent except for the adsorption of Ni^{2+} by unmodified *Cola nitida* pod husk, which was found to decrease with the mass of the adsorbent. From the results obtained, it is significant to state that the adsorption of Cd^{2+}, $Pb^{2+}$and $Ni^{2+}$by the unmodified and modified *Cola nitida* pod husk does not display a regular pattern of variation with the mass of the respective adsorbent. Several researchers have reported that the increase in the adsorbent dosage is due to the increase in the number of adsorption sites while the decrease in unit adsorption with an increasing dose of the adsorbent is basically due to biosorption sites that remain unsaturated during the adsorption reaction (Garg *et al.*, 2022).

3.2 Effect of initial metal ion concentration on adsorption.

Table 2 presents data for the amount of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by unmodified and modified *Cola nitida* pod husk from aqueous solutions containing various concentrations of the metals at 298K

Table 2: Amount of heavy metal ions adsorbed by unmodified and modified *Cola nitida* pod husk from aqueous solution, containing various concentrations of the metals at 298 K.

	Unmodified *Cola nitida* pod husk			Modified *Cola nitida* pod husk		
C (mg/l)	**Cd^{2+} (mg/g)**	**Ni^{2+} (mg/g)**	**Pb^{2+} (mg/g)**	**Cd^{2+} (mg/g)**	**Ni^{2+} (mg/g)**	**Pb^{2+} (mg/g)**
10	8.527± 0.167	7.444± 0.609	9.307± 0.152	9.201± 0.109	9.307± 0.152	9.824± 0.363
20	13.336±1.705	12.365±2.102	19.747 ±0.912	19.860 ± 0.958	19.889 ±0.970	19.883±0.967
40	39.306±0.088	39.799±0.113	39.444± 0.032	39.739 ± 0.088	39.428± 0.039	39.419±0.042
60	59.401±0.097	59.999±0.147	59.719± 0.033	59.839 ± 0.082	59.768± 0.053	59.104±0.218
80	79.810±0.693	71.231±2.809	78.704± 0.242	79.921 ± 0.738	79.333± 0.498	79.675±0.638
100	99.800±0.418	97.418±0.555	98.671± 0.043	99.999 ± 0.499	98.247± 0.216	98.523±0.103

± = error of the mean

. From Table 2, it can also be seen that maximum concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+}adsorbed by unmodified *Cola nitida* pod husk (i.e 99.800, 97.418 and 98.671 mg/g respectively) and modified *Cola* (i.e 99.999, 98.247 and 98.523 mg/g respectively) were closely related. However, from the results obtained, it can be seen that modification slightly increases the amount of Cd^{2+} and Ni^{2+} adsorbed by *Cola nitida* pod husk but slightly reduces the concentration of Pb^{2+} adsorbed. From the results presented in Table 2, it is evident that the extent of adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *Cola nitida* pod husk increases with an increase in concentration. The relationship between the degree of surface coverage and concentration of adsorbent at constant temperature is often treated in terms of adsorption isotherms. In this study, data obtained from the study were fitted into different adsorption isotherms and from the results obtained, the best isotherms that described the adsorption characteristics of Cd^{2+}, Ni^{2+} and Pb^{2+} onto *Cola nitida* pod husk are Freundlich and Temkin adsorption isotherms.

The expression establishing the Freundlich adsorption isotherm can be written as follows (Foo and Hameed, 2012),

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (2)$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), K_F is the Freundlich adsorption constant (mg/g) (dm^3/g) related to the adsorption capacity and C_e is the equilibrium concentration of the adsorbate (mg/l). Simplification and linearizing equation 2 yielded equation 3,

$$log q_e = log K_F + \frac{1}{n} log C_e \qquad (3)$$

From equation 3, the Freundlich isotherm plot is fitted by plotting values of logq_e against logC_e and the slope of the plot should be equal to the reciprocal of n while the intercept should be equal to K_F. Figs. 2 and 3 show the Freundlich adsorption isotherms for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by *nitida* pod husk before and after modification respectively. Values of Freundlich adsorption parameters deduced from the plots are presented in Table 3. From the results obtained, it can be seen that values of R^2 approached unity in all cases indicating the application of the Freundlich adsorption model for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified *nitida* pod husk. The suitability of the Freundlich isotherm to the adsorption of the studied ions also implies that there is multilayer adsorption with non-uniform distribution over the heterogeneous surface (Adamson and Gast, 1997). According to Haghseresht and Lu (1998), the value of 1/n is an index for measuring the adsorption intensity. Generally, when the values of 1/n are in the range, 0 to 1, is a measure of the adsorption intensity or surface heterogeneity. The surface becomes more heterogeneous as the value of n tends toward 0 (Foo and Hameed, 2010). On the other hand, 1/n value less than unity suggests a chemisorption mechanism whereas 1/n value above unity point toward cooperative adsorption. Therefore, the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} supports the mechanism of physical adsorption since values of 1/n are above unity.

It has been found that the Freundlich adsorption constant (K_F) is related to the free energy of adsorption according to the following equation (Mittal *et al.*, 2007);

$$\Delta G^0_{ads} = -2.303RTlogK_F \qquad 4$$

where R is the universal gas constant and T is the temperature. Values of ΔG^0_{ads} calculated from equation 4 are also presented in Table 3. From the results obtained, it can be seen that the free energies are negatively less than the threshold value needed for the mechanism of chemisorption. Therefore the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} unto unmodified and modified Cola *nitida* pod husk is spontaneous and is consistent with the mechanism of physical adsorption.

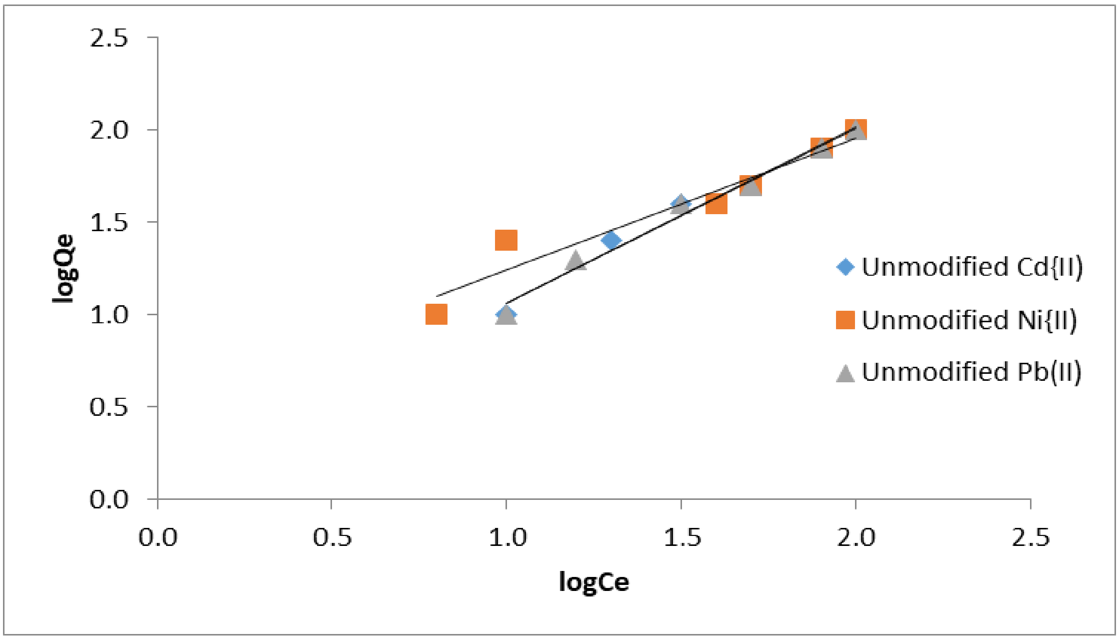

Fig. 2: Variation of logq_e with logC_e (Freundlich isotherm plot) for the adsorption of Cd^{2+}, Ni^{2+} and $Pb^{2+}$by unmodified Cola *nitida* pod husk.

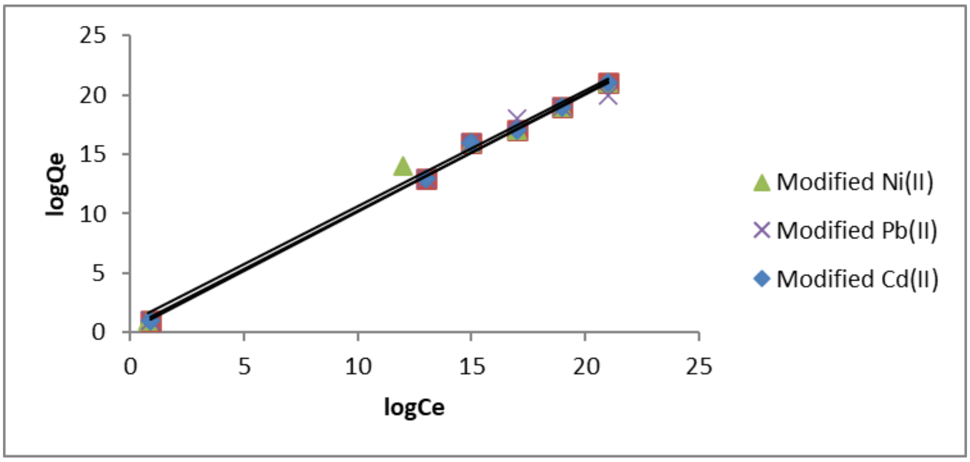

Fig. 3: Variation of $\log q_e$ with $\log C_e$ (Freundlich Isotherm plot) for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by modified Cola *nitida* pod husk.

Table 3: Freundlich parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified Cola *nitida* pod husk (CnPH).

System	Ions	Slope	Intercept	1/n	ΔG^0 (J/mol)	R^2
	Cd(UM)	1.0000	0.0000	1.00	0.00	1.000
CnPH	Ni(UM)	1.1616	-0.3250	0.86	-1885.51	0.983
	Pb(UM)	1.0003	0.0058	1.00	33.65	1.000
	Cd(M)	1.0302	-0.0556	0.97	-322.57	0.996
CnPH	Ni(M)	1.0202	-0.0411	0.98	-238.45	0.987
	Pb(M)	1.0202	-0.0411	0.98	-238.45	0.989

The adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} unto modified and unmodified Cola *nitida* pod husk was also found to obey the Temkin adsorption model, which can be written as follows (Foo and Hameed, 2012);

$$q_e = \frac{RT}{b_T} lnA_r C_e \qquad 5$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium, R is the gas constant, T is the temperature, b_T is the Temkin isotherm constant, A_r is the Temkin isotherm equilibrium binding constant and C_e is the equilibrium concentration. Equation 5 can be simplified to a linear form as follows,

$$q_e = \frac{RT}{b_T} lnA_r + \frac{RT}{b_T} lnC_e \qquad 6F$$

rom equation 5, a plot of q_e versus $\ln C_e$ should be linear with slope and intercept equal to $\frac{RT}{b_T}$ and $\frac{RT}{b_T}\ln A_r$ respectively. Fig. 4 shows the Temkin isotherm for the adsorption of Cd^{2+}, Ni^{2+} and $Pb^{2+}$by modified and unmodified Cola *nitida* pod husk respectively. R^2 values calculated from the plots were very close to unity indicating the application of the Temkin isotherm for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by modified and unmodified Cola *nitida* pod husk. B_T values were positive and relatively low indicating the attractive behavior of the adsorbent. Generally, the higher the value of b_T, the higher the degree of interaction between the adsorbate and the adsorbent. The present data strongly point toward a relatively weak interaction, which also supports the mechanism of physical adsorption. The Temkin equilibrium constant can be used to estimate the free energy of adsorption of the heavy metal ions using the following equation,

$$\Delta G^0_{ads} = -2.303RTlogA_r \qquad 7$$

Values of ΔG^0_{ads} calculated from equation 7 are also recorded in Table 4

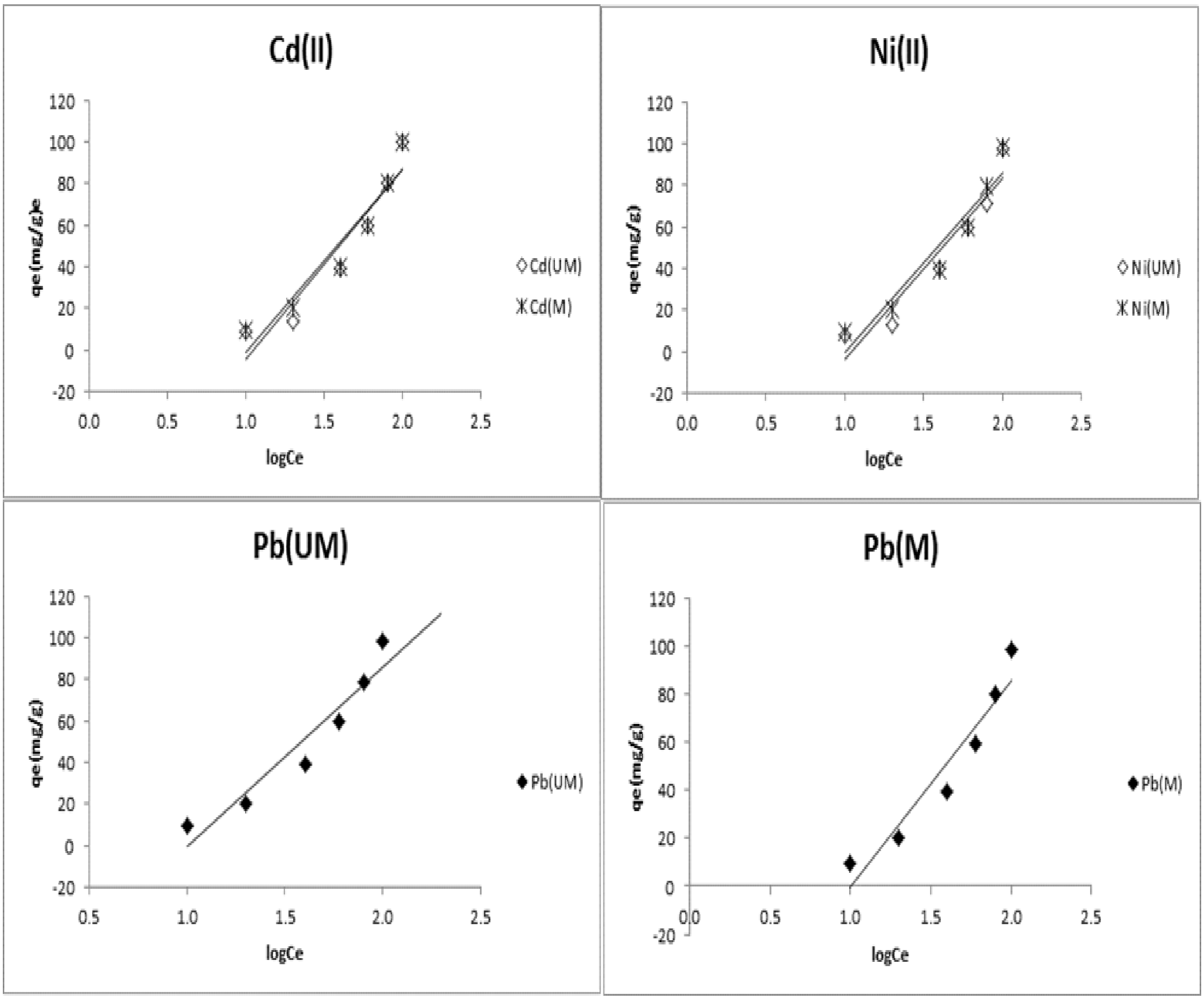

Fig. 4: Variation of q_e with $\log C_e$ (Temkin isotherm plot) for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified Cola *nitida* pod husk.

Table 4: Temkin parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and unmodified Cola *nitida* pod husk (CnPH).

System	Ions	Slope	Intercept	$\ln A_r$	A_r	b_T	ΔG^0 (J/mol)	R^2
CnPH	Cd(UM)	90.666	-94.799	-1.046	0.351	27.7849	-2633.98	0.9080
	Ni(UM)	87.206	-91.258	-1.046	0.351	28.8873	-2636.19	0.9126
	Pb(UM)	86.436	-87.140	-1.008	0.365	29.1446	-2539.66	0.9181
CnPH	Cd(UM)	87.745	-88.737	-1.011	0.364	28.7098	-2547.62	0.9164
	Ni(UM)	86.420	-87.051	-1.007	0.365	29.1500	-2537.54	0.9197
	Pb(UM)	86.132	-86.514	-1.004	0.366	29.2475	-2530.31	0.9148

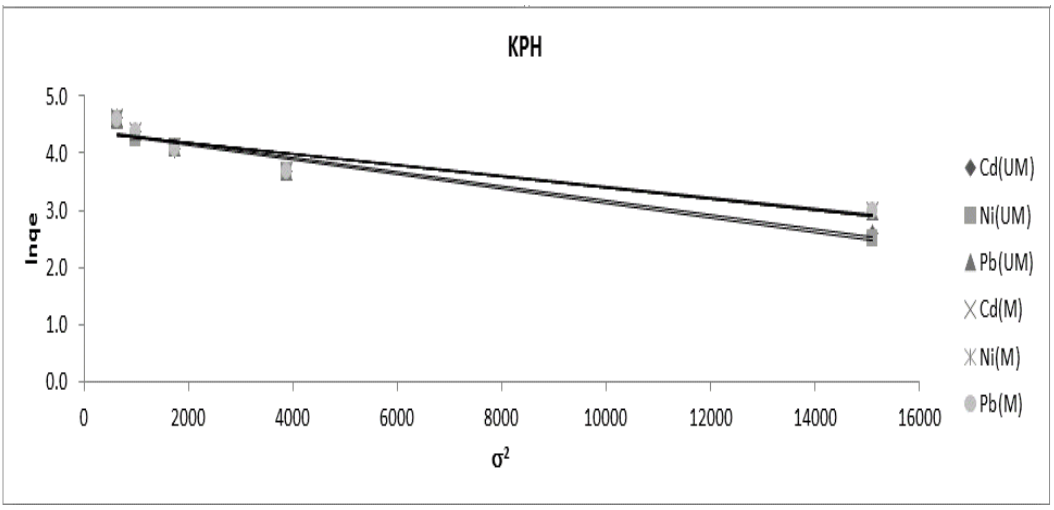

Fig 5: Dubinin-Radushkevich isotherm for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified Cola *nitida* pod husk

.

From the results obtained, the free energies are negatively less than the threshold value expected for the mechanism of chemical adsorption, which also confirms that, the adsorption of Cd^{2+}, Pb^{2+} and Ni^{2+} unto Cola *nitida* pod husk is consistent with a mechanism of physical adsorption

Distinction between physical and chemical adsorption can be confirmed through the Dubinin-Radushkevich (D-RIM) adsorption isotherm, which can be expressed according to equation (Noor, 2009);

$$\ln q_e = \ln Q_{max} - a\sigma^2 \quad (8)$$

where Q_{max} is the maximum surface coverage and σ is the Polanyi potential and can be estimated from the following equation,

$$\sigma = RT\ln\left(1 + \frac{1}{Ce}\right) \quad (9)$$

where R is the gas constant (8.31 $Jmol^{-1}K^{-1}$) and T is the temperature (K). From equation 8, a plot of $\ln q_e$ versus σ^2 should give a straight line with a slope equal to a constant, 'a'. This constant, 'a' can be defined as half the square of the reciprocal of the mean adsorption energy (i.e. a = ½ $(1/E)^2$. It has been found that E value of less than 8 kJ/mol supports the mechanism of physical adsorption but E values greater than 8 kJ/mol are consistent with the mechanism of chemisorption. Fig. 5 shows D-RIM isotherm for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified Cola *nitida* pod husk. R^2 values for the plots (Table 5) were very close to unity while the value of E (707 J/mol) was constant (Table 5) for all the systems indicating that the mechanism of physical adsorption is most likely. .

Table 5: Dubinin-Radushkevich parameters for the adsorption of Cd^{2+}, $Ni^{2+}$and $Pb^{2+}$by unmodified and modified Cola Fig *nitida* pod husk (CnPH).

System	Ions	Slope	Intercept	E (J/mol)	R^2
CnPH	Cd(UM)	0.0001	4.404	7.07E+01	0.9261
	Ni(UM)	0.0001	4.3881	7.07E+01	0.8693
	Pb(UM)	0.0001	4.1387	7.07E+01	0.7833
CnPH	Cd(M)	0.0001	4.385	7.07E+01	0.8705
	Ni(M)	0.0001	4.3782	7.07E+01	0.8672
	Pb(M)	0.0001	4.3679	7.07E+01	0.8939

4. Conclusion

Detoxification of toxic heavy metals from industrial wastewater using Cola *nitida* pod husk was investigated. The adsorption capacity of unmodified and modified Cola *nitida* pod husk on Cd^{2+}, Ni^{2+} and Pb^{2+} were all favoured at low doses and modification tends to enhance its sorption capacity. The adsorption behaviour of the Cola *nitida* pod husk was better described by Freundlich and Temkin adsorption models. However, the adsorption potential of the modified Cola *nitida* pod husk was better than the unmodified Cola *nitida* pod husk.

5.0 References

Adamson, A. W. & Gast, A. P. (1997), Physical chemistry of surface (6th Ed.) Wiley-Interscience, New York.

Alloway, B. J. & Ayres, D. C. (1997). Chemical Principles of Environmental Pollution, (2nd Edition) Blackie Academic and Professional Publication, Chapman and Hall, London.

Ankley, G. T., Mattson, V. R. & Leonard, E. N. (1994). Prediction of bioaccumulation of metals from contaminated sediments by the Oligochaate L. variegatus. *Journal of Water Research*, 28, pp. 1071-1076.

Asuquo, F. E. (1999). Sorption kinetics and intraparticulate diffusivity of As (III) ions. *Global Journal of Pure and Applied Sciences*, 5, pp. 595 – 600.

ATSDR (1993). Agency for toxic substances and disease registry toxicological profile for chromium, U.S. Department of Health and Human Services: Public Health Service Report HTP-92108.

Bakkaloglu, I., Butter, T. J., Evison, I. M., Holland, F. S. & Hancock, I. C. (1998). Screening of various types of biomass for removal and recovery of heavy metals (Zn, Cu, Ni) by biosprtion, sedimentation and desorption. *Water sci. Technol.*, 38, pp. 269-277.

Bhatti, H. N., Muntaz, B., Hanif, M. A., & Nadeem, R. (2007). Removal of Zn(II) ions from aqueous solution using *Moringa oleifera. Process Biochem*., 42, pp. 547 – 553.

Bossrez, S., Remade, J. & Goyette, J. (1997). Adsorption of nickel by *Enterococcus hirae* cell walls. *Journal of chemical technol. and biotechnol.*, 90, pp. 45 – 50.

Eddy, N. O., Garg, R., Garg, R., Aikoye, A. and Ita, B. I. (2022). Waste to resource recovery: mesoporous adsorbent from orange peel for the removal of trypan blue dye from aqueous solution. *Biomass Conversion and Biorefinery*, doi: 10.1007/s13399-022-02571-5.

Eddy, N. O., Ukpe, R. A., Ameh, P., Ogbodo, R., Garg, R. and Garg, R. (2022). Theoretical and experimental studies on photocatalytic removal of methylene blue (MetB) from aqueous solution using oyster shell synthesized CaO nanoparticles (CaONP-O). Environmental Science and Pollution Research, https://doi.org/10.1007/s11356-022-22747-w.

Foo, K. Y. & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156, pp. 2 -10.

Foo, K. Y. & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156, pp. 2 -10.

Foo, K. Y. & Hameed, B. H. (2012). A rapid regeneration of methylene blue dye loaded activated carbons with microwave heating. *Journal of Analytical and Applied Pyrolysis*, 98, pp. 123 – 128.

Garg, R., Garg, R., Eddy, N. O., Almohana, A. I., Fahad, S., Khan, M. A. and Hong, S. H. (2022). Biosynthesized silica-based zinc oxide nanocomposites for the sequestration of heavy metal ions from aqueous solutions. *Journal of King Saud University*-Science https://doi.org/10.1016/j.jksus.2022.101996

Goering, P. L., Waalkes, M. P. & Klaassen, C. D. (1994). Cadmium toxicity: In handbook of experimental pharmacology, toxicology of metals and biochemical effects, (R.A. Goyer and M.G. Cherian, Eds.) Springer-verlag, New York.

Goyer, R. (1991). Toxic effects of metals, In: Casarett and Doull's Toxicology, (4th ed.) Amidur, M. O., Doull, J. D and Klaassen, C. D. eds., Pergamon Press, New York.

Goyer, R. A. (1988). Lead In: Handbook on Toxicity of Inorganic Compounds, (H. G. Seiler and H. Sigel, eds.) Marcel Deckker Inc., New York.

Haghseresht, F. & Lu, G. (1998). Adsorption characteristics of phenolic compounds onto coal-rejec-derived adsorbents. *Energy fuel*, 12, pp. 1100 – 1107.

Holan, Z. R. & Volesky, B. (1994). Biosorption of lead and nickel by biomass of marine algae. *Biotechnol. Bioeng.*, 43, pp. 1001-1009

Mittal, A., Kurup, L. & Mittal, J. (2007). Freundlich and Langmuir adsorption isotherms and kinetics for the removal of tartrazine from aqueous solutions using hen feathers. *Journal of Hazardous Materials*, 146, pp. 243–248.

Nilanjana, D., Lakshmi, V., Greetanjali, B. & Devlina, D. (2012). Kinetics and equilibrium studies on removal of Zn(II) by untreated and anionic surfactant treated dead biomass of yeast, batch and column mode. *Biochemical Engineering Journal*, 64, pp. 30 – 47.

Noor, E. A. (2009). Potential of aqueous extract of *Hibiscus sabdariffa* leaves for inhibiting the corrosion of aluminum in alkaline solutions. *J. Appl. Electrochem.*, 39, pp. 1465–1475.

Okwunodulu, F. U., Odoemelam, S. A. & Okon, E. N. (2016). Effect of adsorbent dose and initial metal ion concentrations on the sorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by *Telfairia occidentalis* seed coat from industrial effluent. Chemical Society of Nigeria, ANACHEM Journal, 6, pp. 1178 – 1188.

Oladayo, A. (2010). Proximate composition of some agricultural wastes in Nigeria and their potential use in activated carbon production. *J. Appl. Sc. Environs. Manage.*, 14, pp. 55-58.

Rendall, R. E. G., Philips, J. I. & Renton, K. A. (1994). Death following exposure to fine particulate nickel from a mental arc. *Process, Ann. Occup. Hyg.,* 38, pp. 921-930.

Singh, S., Rail, B. N. & Rai, L. C. (2001). Ni(II) and Cr(VI) Sorption kinetics by microcystis in single and multimetallic system. *Process Biochem,* 36, pp. 1205-1213.

U.S.EPA (1986a). Lead effects on cardiovascular function, early development and stature: an addendum to EPA Air Quality Criteria for Lead. Volume 1.

Volesky, B., Holan, Z. R. & Leusch, A. (1995). Biosorption of heavy metals (Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) by chemically reinforced biomass of marine algae. *Journal of chemical Technology and Biotechnology*. 1995, 62, pp. 279 – 288.

Waalkes, M. P. & Rehm, S. (1992). Carcinogenicity of oral cadmium in the male Wistar (WF/NCr) rat: effect of chronic dietary zinc deficiency. *Fundam. Appl. Toxicol***.,** 19, pp. 512-520.

Yetis, U., Ozcengiz, G., Filiz, B., Ergen, N., Erbay, A. & Dolek, A. (1998). Heavy metal biosorption by white-rot fungi. *Wat. Sci. Tech.*, 38, pp. 323 – 330.

Yu, Q. & Kaewsarn, P. (1999). Binary adsorption of copper(II) and cadmium(II) from aqueous solutions by biomass of marine algae Durvillaea potatorum. *Separation science and technology,* 34, pp. 1595-1605.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data public

Competing interest

The authors declared no conflict of interest.

There is no source of external funding

Authors Contributions

All the authors contributed to the research that produced this article. The work was designed by Felicia and the write-up was supervised by the other authors

.