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THE EFFECT OF PHOSPHORIC ACID MODIFICATION OF *Manihot esculenta* (CASSAVA) PEELS BIOMASS ON ADSORPTION OF HEAVY METAL FROM AQEUOUS SOLUTION

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ABSTRACT

The equilibrium sorption of the cassava peel modified with phosphoric acid was studied using nickel aqueous solutions. The study revealed that acid modification of the cassava peel adsorbent enhances it capacity for metal uptake even at relatively high concentation compared to the unmodified form. The data so obtained were fitted into Langmuir and Freundlich adsorption isotherms. The R^2 value of Langmuir isotherm model was the highest for both ions. The maximum monolayer coverage (Qm) from Langmuir isotherm model was determined as; Qm 27.778 mg/g, K_L (L/mg) 0.007 and R^2 was 0.978. Also from Freundlich Isotherm model, the sorption intensity (n) which indicates favourable sorption and the correlation value are 1.560 and R^2 was determined as 0.693.

Keywords: Concentation, equilibrium, isotherm, modification, Langmuir

1.0 INTRODUCTION

Heavy metals have come to be one of the main contaminants of water in recent years. They arise from different sources/activities carried out by industries (Sharma, *et al.*, 2014). Unlike organic pollutants, heavy metals are not degradable to form harmless end products and tend to be toxic to aquatic flora and fauna even in relatively low concentrations (Das, *et al.*, 1997; Shanker *et al.*, 2009).

Cadmium (Cd), arsenic (As), chromium (Cr), manganese (Mn), copper (Cu), mercury (Hg), nickel (Ni), iron (Fe), zinc (Zn), and lead (Pb) are some of the metals that are highly hazardous to humans and the ecological environment (Ahalya *et al.*, 2003). Some of these have a potential of being assimilated, stored and concentrated in the human body, inducing chronic pulmonary problems, erythrocyte destruction (Verbost, *et at.*, 1989), nausea, diarrhoea, muscular cramps, renal degradation (Jarup, 2002).

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials (Muhammad *et al*., 2011). Biosorption for example, is a process whereby certain types of inactive dead biomass (such as snail shell, peat, rice husk, fruit peels etc.) may bind and concentrate heavy metals from aqueous solution is considered as an alternative technology for the removal of these heavy metals and other pollutants from wastewater and industrial effluents, (Naja *et al*., 2003; Volesky, 1990). A solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, usually water) containing a dissolved species to be sorbed (sorbate, metal ions) are involved in the biosorption process (Ahalya *et al*., 2003). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms (Ahalya *et al*., 2003). The procedure is repeated until there is a balance between the sum of solid-bound sorbate species and the portion of the solution that remains, and the degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases (Ahalya *et al*., 2003).

These biosorbents have the ability to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. Algae, bacteria and fungi and yeasts have also proved to be potential metal biosorbents (Fourest and Roux, 1992; Volesky, 1986). The major advantages of biosorption over conventional treatment methods include; low cost, high efficiency, minimization of chemical and low biological sludge, no additional nutrient requirement, regeneration of biosorbent, and possibility of metal recovery.

Manihot esculenta, also known as cassava (USDA 2014), is a woody shrub native to South America that belongs to the spurge family, Euphorbiaceae. Cassava is widely grown as an annual crop in tropical and subtropical areas, despite the fact that it is a perennial plant. Cassava is one of West Africa's most important agricultural food crops. According to Mehari *et al*. (2015), Africa produced approximately 57 percent (149.5 mt) of the overall global cassava supply in 2011. Cassava contributes immensely to human nutrition and livelihood of the world (Lebot, 2009) as varieties of products such as starch, garri, cassava flour, and fufuare commonly processed from cassava tubers. Behind rice and maize, cassava is the third-largest source of food carbohydrates in the tropics (Fauquet and Fargette, 1990). Cassava is a major staple food in the developing world, feeding over half a billion people a basic diet (FOA, 1995). Cassava is more widely eaten in its boiled form, although vast amounts are used to extract cassava starch, also known as tapioca, which is used in food, animal feed, and industry.

During the processing of cassava tubers into essential products, an enormous quantity of cassava peels (about 30% of processed cassava tubers) are generated as waste (Adebayo and Sangosina, 2005) and only an insignificant proportion is usually fed to livestock such as goats while the remaining portions are usually thrown along roadsides in places where cultivation and processing of cassava tubers is a common livelihood activity. Since these peels could make up to 10% of the net weight of the roots, they constitute an important potential resource, if properly harnessed (Obadina *et al*., 2006). The use of cassava peel with surface modification to enhance metal removal efficiency will increase its economic benefit, minimize waste disposal costs, and, most significantly, offer a relatively low-cost alternative to currently available commercial adsorbents (Gin et al., 2014).

This study is focused on investigating the effect of acid (phosphoric acid) modification of cassava peel on the adsorption of heavy metal from wastewater.

2.0 MATERIALS AND METHODS

2.1 Samples collection and preparation

The cassava peels were sources from a local cassava processing factory. All chemicals used were analyte grades and all glasswares were thoroughly washed with dilute nitric acid and rinsed properly with distilled water.

2.2 Adsorbent preparation

The cassava peels were thoroughly washed to remove sand and thereafter dried in an oven at 80^{O}C for 2 hours. The dried cassava peels were then pulverized and screened through a set of sieves to obtain particles of size 250µm.
Acid modification of the biomass was done according to Ideriah *et al*. (2012), with slight modification. The finely sieved biomass was treated with 0.1M H_3PO_4 solution for 24 hours, followed by washing with deionized water until pH of 7.2 was achieved and oven dried at 60°C with constant mixing. The prepared biomass was stored in desiccators.

2.3 Synthetic wastewater preparation

Synthetic wastewater was prepared according to Dada *et al*. (2012). The Preparation of adsorbate was carried out by preparing stock solution containing 1000 mg/L of nickel by dissolving 2.6 g of $NiSO_4$ in $1000cm^3$ of distilled water. Working concentrations in the range of 25, 50, 75, 100, and 125 mg/L were prepared by serial dilution from stock solution.

2.4 Adsorption isotherms study

The equilibrium sorption of the nickel ion onto the adsorbent was carried out by contacting 0.5 g of the absorbent with 100 cm^3 of different concentrations of the adsorbate of 20 mg/L – 100mg/L in $250cm^3$ Pyrex conical flasks, shaking intermittently for 60 minutes on the orbital shaker. The mixture was filtered and the residual concentration of the filtrate was analyzed using Atomic Absorption Spectrophotometer (2380 UNICAM AAS). The amount of adsorbed (mg/g) was calculated using the formulae reported by Dada *et al*., (2012). Two different models are considered in this study; Freundlich and Langmuir.

$$q_e = \frac{V\,(C_i - C_e)}{W}$$

Where; q_e = the amount of solute adsorbed from the solution, V = Volume of the adsorbate, C_i = the concentration before adsorption, C_e = the concentration after adsorption and W = the weight in gram of the adsorbent (Senthil and Gayathri, 2009).

The percentsge sorption efficiency was determined by computing the percentage sorption using the formulae (Igwe *et al*., 2005);

$$\% \, Sorption = \frac{(C_i - C_e)}{C_i} \, x \, 100$$

Freundlich isotherm: Freundlich isotherm is one of the empirical formula, it takes into account that the surface is heterogeneous in nature and adsorption is multilayer to the binding sites located on the sorbent surface. The model of freundlich is expressed as:

$$qe = KCe^{1/n}$$

K = mg/g or l/mg; 1/n or n = Freundlich constant related to adsorption capacity; n = Freundlich constant related to adsorption intensity.

Langmuir model: Langmuir model is assumed to be a monolayer adsorption of solutes on to the surface which is comprised of finite number of similar sites with the homogeneity in adsorption energy. The model of Langmuir is expressed as

$$q_e = \frac{q_{max} \, bC_e}{1 + bC_e}$$

q_e = Amount of metal ion removed (mg/g); Ce = Equilibrium concentration (mg/L); *b* = Langmuir constant related to afinity; qmax = maximum metal uptake (mg/g) under the given conditions.

n, K = Freundlich and Langmuir constants (n value greater than 1.0 shows that sorption is favorable physical process) (El-Sikaily *et al*., 2011; Abdi and Kazemi, 2015).

3.0 RESULTS AND DISCUSSION

The results of the use of phosphoric acid modified and unmodified cassava peels biomass as adsorbent for the removal of nickel ion in aqueous solution are presented in Tables 1. Figure 1 shows the percentage sorption for nickel ion onto modified/unmodified cassava peel adsorbent while figures 2 and 3 shows the graph of Langmuir and Freundlich Adsorption Isotherms respectively for nickel ion.

Table 1: Results for the removal Ni^{2+} ions from aqueous solution using phosphoric acid modified/unmodified cassava peels

S/NO	C_o (mg/L)	C_e (mg/L) Modified	% Sorption modified	C_e (mg/L) Unmodified	% Sorption unmodified
1	20	4.92	75.40	8.06	59.70
2	40	10.14	74.65	14.53	63.68
3	60	14.77	75.38	18.34	68.43
4	80	29.46	63.18	34.16	57.30
5	100	39.07	60.93	51.72	48.28

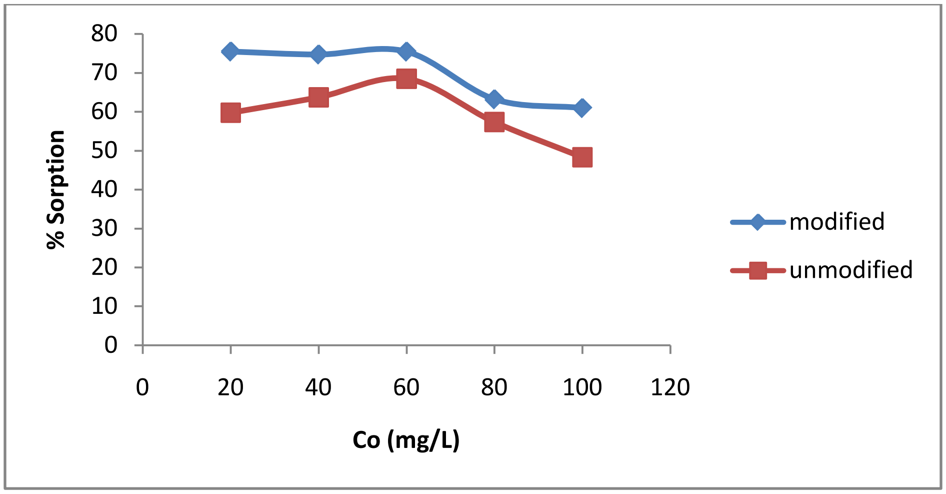

Figure 1: % sorption for Ni^{2+} ion onto modified/unmodified cassava peels

The modified adsorbent showed had better impact compared to the unmodified adsorbent in the removel of nickel ion from aqueous solution. The effect of metal ion concentration showed that the percentage of metal ion removed by the adsorbent decreased with increasing concentration of metal ion solution as shown in Table 1. Phosphoric acid modified cassava peels adsorbent exhibited effectiveness in the removal of nickel ions from aqueous solution up to 75.38 % from an initial concentration of 60 mg/L, while the unmodified recorded 68.43 % and highest from same initial. However, a decrease in the metal uptake by the adsorbent was observed as the initial metal concentration increased above 60 mg/L. This is because at lower concentrations, the biomass adsorbent removed large amount of metal ion from the solution. However, as the concentration of metal ion increased the binding sites gradually became occupied and reduce the amount of metal ion being removed (Ideriah *et al*., 2012). The sorption capacity of the biomass adsorbent decreased with increase in concentration. This observation agrees with the report of Ayawei *et al*. (2005) who studied the effect of concentration on the adsorption of metal ion by *Rhizophora mangle* waste biomass. The observations also indicate that surface saturation is dependent on the metal ion concentration and that the active sites took up the available metal more quickly at low concentrations (Ayawei *et al*., 2005). At higher concentrations, the surface saturation occurred on the biomass surface leading to reduction in biomass concentration as metal ion concentration increases. The differences in the metal ion removal could also be attributed to differences in the size (ionic radii) of the metals (Ideriah *et al*., 2012).

Table 2 shows the parameters for the plotting of Langmuir and Freundlich adsorption isotherms of nickel ion unto modified cassava peel adsorbent. Langmuir and Freundlich Isotherm constants for the adsorption of Ni^{2+} ion onto phosphoric acid modified cassava peels are show in table 3. Langmuir Adsorption Isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place (Fadare *et al*., 2016). Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases (Vermeulan *et al*., 1966). The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites (Dada *et al*., 2013). Nickel ion adsorption on the adsorbent shows that the maximum monolayer coverage capacity (Qm) from Langmuir Isotherm model was determined to be (27.778) mg/g, K_L (Langmuir isotherm constant) is (0.007) L/mg, and the R^2 value (0.978) proving that the sorption data fitted well to Langmuir Isotherm model.

For Fruendlich adsorption isotherm study for the adsorption of Nickel ion on to adsorbent shows that 1/n value (0.641) while n was (1.560) indicating that the sorption of nickel ion unto the biomass is favourable and the R^2 value was (0.918). If n equals one then the partition between the two phases are independent of the concentration. Adsorption of nickel ion on to the modified cassava peels in this research is normal adsorption because the value of 1/n is below one which indicates a normal adsorption (Weber and Chakravarti, 1974). Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where 1/n is a heterogeneity parameter, the smaller 1/n, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when 1/n equals one. If n lies between one and ten, this indicates a favorable sorption process (Goldberg, 2005).

Table 2: Parameters for plotting Langmuir and Freundlich Adsdorption Isotherms of nickel ion unto phosphoric acid modified cassava peel

S/NO	C_o (mg/L)	C_e (mg/L)	$1/C_e$	Log C_e	Q_e (mg/g)	$1/q_e$	Log q_e
1	20	4.92	0.203	0.692	3.016	0.332	0.479
2	40	10.14	0.099	1.006	5.972	0.167	0.776
3	60	14.77	0.068	1.169	9.046	0.111	0.956
4	80	29.46	0.034	1.469	10.108	0.099	1.005
5	100	39.07	0.026	1.592	12.186	0.082	1.086

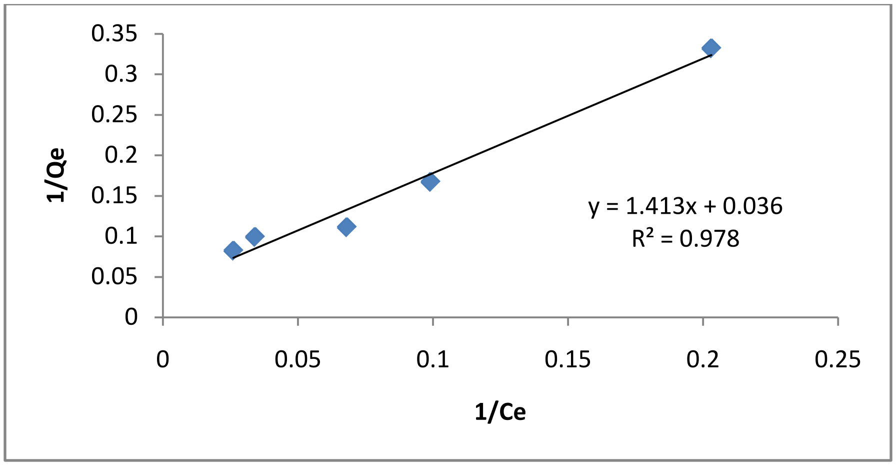

Figure 2: Langmuir Adsorption Isotherm for Ni^{2+} ion

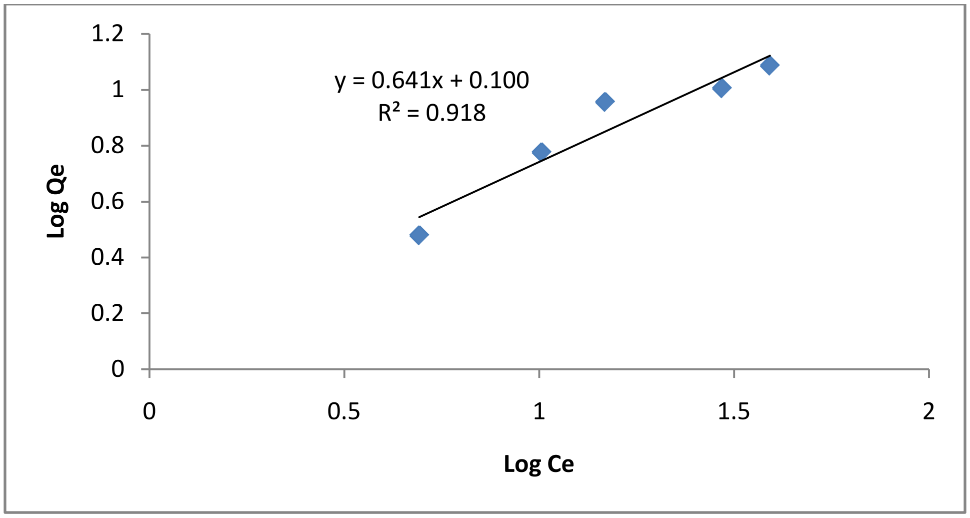

Figure 3: Freundlich Adsorption Isotherm for Ni^{2+} ion

Table 3: Langmuir and Freundlich Isotherm constants for the adsorption of Ni^{2+} ion unto phosphoric acid modified cassava peels.

Metal ion	Langmuir Isotherm			Freundlich Isotherm		
Ni^{2+} ion	Q_m (mg/g)	K_L (L/mg)	R^2	1/n	n	R^2
	27.778	0.007	0.978	0.641	1.560	0.918

4.0 CONCLUSION

This study has shown that acid modification of biomass has the capacity to enhance its metal uptake ability as shown in this work. The adsorption study of heavy metal (nickel ion) onto phosphoric acid modified cassava peels shows that the data fits into Langmuir isotherm more because of it highest regression value when compared with Freundlich isotherms. It could be concluded that this adsorbent has potential as a suitable biosorbent for removal of nickel ions from its aqueous solution.

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