

ENVIRONMENTAL PROTECTION: THE USE OF BIOSORPTION OF NICKEL AND COPPER BY CAMEL FOOT (*PILIOSTIGMA THONNINGII*) POD IN ELIMINATION OF HEAVY METALS FROM SIMULATED WASTEWATERS

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ABSTRACT

Sustainable development stands in three pillars; economic, social and environmental protection. The environment is principal to carry the other pillars. In recent years, the need for safe, efficient and economical methods for the elimination of heavy metals from contaminated waters is topical. This study focused on the use of low-cost alternatives to commercially available activated carbon through camel foot (*Piliostigma thonningi*) pod biomass for the removal of nickel and copper ions from aqueous solution. The study used batch process under various experimental conditions of varying pH, contact time, initial metal ion concentration, particle size, temperature and biomass dose in the analysis. The findings showed that optimum adsorption takes place at pH 4 for both nickel and copper ions with 78% and 72% removal at the optimum time of 4 h and 3 h for nickel and copper ions respectively. The result of the investigation also revealed that the optimum percentage of the ions' removal was obtained at 2.50 g biomass dose, at a particle size of 300 μm , optimum temperature range of 25-30 $^{\circ}\text{C}$, and initial metal concentration of 50 mg/L. Hence, the survey showed that camel foot biomass is an efficient, economical and inexpensive adsorbent for the removal of Ni^{2+} and Cu^{2+} in the treatment of contaminated water and wastewater by chemical and allied industries.

INTRODUCTION

Sustainable development is the hope for the future economies. All efforts to promote the three pillars of sustainable development such as economic, social and educational efforts as well as environmental protection should be embraced. Environment is an essential component of sustainable development. When the environment, especially the water bodies are polluted (e.g. lakes, rivers, oceans, aquifers and groundwater), it results in grave consequences. Water pollution occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. Water pollution affects plants and organisms living in these bodies of water. In almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities.

Water pollution is a major global problem which requires evaluation and revision of water resource policy at all levels (international down to individual aquifers and wells). The sixth Sustainable Development Goal which emphasizes clean water and sanitation for all cannot be achieved if the problem of water pollution lacks proper attention it demands. High heavy metal concentration is a major culprit in the problem of water pollution.

Globally, water pollution is a leading cause of diseases and deaths (Goel, 2006), and about fourteen thousand people die daily from exposure to contaminated water (Mandour, 2012; Chaudhry and Malik, 2017). In addition to the acute problems of water pollution in developing countries, developed countries continue to struggle with pollution problems as well. In the national report on water quality in the United States, 45 percent (45%) of assessed stream miles, 47 percent (47%) of assessed lake acres, and 32 percent (32%) of assessed bays and estuarine square miles were classified as polluted (USEPA, 2007). At the local level here in Nigeria, high mortality in young children in Zamfara state led to confirmation of villages with widespread acute severe lead poisoning in 2010 (Greig *et al.*, 2014; Tirima *et al.*, 2016).

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use such as drinking; and/or undergoes a marked shift in its ability to support its constituent biotic communities as fish. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water (NTP, 2000).

Non-point source pollution (NPS) refers to diffuse contamination that does not originate from a single discrete source. NPS pollution is often the cumulative effect of small amounts of contaminants gathered from a large area. A common example is the leaching out of nitrogen compounds from fertilized agricultural lands. Nutrient runoff in storm water from "sheet flow" over an agricultural field or a forest is also cited as example of NPS pollution (ATSDR, 2005). Contaminated storm water washed-off from parking lots, roads and highways (called urban runoff) is sometimes included under the category of NPS pollution. This runoff is typically channeled into storm drain systems and discharged through pipes to local surface waters, and is a point source (Majumder *et al.*, 2010).

The specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens, and physical or sensory changes such as elevated temperature and discoloration. While many of the chemicals and substances that are implicated may be naturally occurring (calcium, sodium, iron, manganese, etc.) the concentration is often the key in determining what is a natural component of water, and what is a contaminant. This is because high concentrations of naturally occurring substances can have negative impacts on aquatic flora and fauna (Goel, 2006). Oxygen-depleting substances may be natural materials, such as plant matter (e.g., leaves and grasses) as well as man-made chemicals. Other natural and anthropogenic substances may cause turbidity (cloudiness) which blocks light and disrupts plant growth, and clogs the gills of some fish species (USEPA, 2007). Many of the chemical substances are toxic. Pathogens can produce waterborne diseases in either human or animal hosts. Alteration of water's physical chemistry includes acidity (change in pH), electrical conductivity, temperature, and eutrophication.

Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases the primary productivity of the ecosystem. Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur, affecting fish and other animal populations (Selman *et al.*, 2008). Organic water pollutants include detergents, food waste, fats and grease, insecticides and herbicides, a huge range of organohalides and other compounds, petroleum hydrocarbons, lubricants (motor oil), and fuel combustion byproducts, from storm water runoff, tree and bush debris from logging operations, volatile organic compounds (VOCs), such as industrial solvents, from improper storage. Other organic pollutants may also include chlorinated solvents, which are dense non-aqueous phase liquids (DNAPLs) (which may fall to the bottom of reservoirs, since they don't mix well with water and are denser), polychlorinated biphenyl (PCBs), trichloroethylene, perchlorate, various chemical compounds found in personal hygiene and cosmetic products (Wen *et al.*, 2008).

Inorganic water pollutants include: Acidity caused by industrial discharges (especially sulfur dioxide from power plants), Ammonia from food processing waste, chemical as industrial by-products; fertilizers containing nutrients; nitrates and phosphates—which are found in storm water runoff from agriculture, as well as commercial and residential use, heavy metals from motor vehicles (via urban storm water runoff); and acid mine drainage; silt (sediment) in runoff from construction sites, logging, slash and burn practices or land clearing sites (Schueler and Thomas, 2000).

Groundwater pollution is much more difficult to abate than surface pollution because groundwater can move great distances through unseen aquifers. Non-porous aquifers such as clays partially purify water off bacteria by simple filtration (adsorption and absorption), dilution, and, in some cases, chemical reactions and biological activity. However, in some cases, the pollutants merely transform to soil contaminants. Groundwater that moves through cracks and caverns is not filtered

and can be transported as easily as surface water. Groundwater pollution is mainly due to the process of industrialisation and urbanisation that has progressively developed over time without any regard for environmental consequences (Longe and Balogun, 2010).

There are a variety of secondary effects stemming not from the original pollutant, but a derivative condition. An example is silt-bearing surface runoff, which can inhibit the penetration of sunlight through the water column, hampering photosynthesis in aquatic plants. The current trend of increasing industrialization is a major source of pollution as industrial effluents containing organic and toxic inorganic compounds are released into water bodies without proper treatment. These heavy metals (e.g. Hg, Cd Cu, Ni, etc) pose threat to human existence as a result of their toxicity (Kamran *et al.*, 2013).

Effluents from many industries and mining sites contain copper and nickel ions. These effluents when discharged in nearby river without treatment usually cause pollution of the water body which may ultimately cause problem to human health as well as the total environment. Various methods including ion exchange, chemical precipitation, and electrodialysis etc have been employed and studied to remove heavy metals from aqueous system. However, adsorption method is preferred above these methods because it is very cheap, easy to handle, effective and sludge free. Available literatures revealed that many organic and non-organic materials have been used as adsorbents for the removal of heavy metals, but as far as camel foot (*Piliostigma thonningii*) pod is concerned to the best of our knowledge, no work has been published on its ability as a potential adsorbent for copper and nickel ions from contaminated water and industrial waste water. There has been the quest of research experts for economically and effortlessly accessible adsorbents. Since camel foot pod biomass is readily available around us, it is considered a very suitable and cheap option for use as an adsorbent medium for the removal of heavy metal ions like nickel and copper ions.

METHODOLOGY

The study used the adsorbent prepared from the camel's foot (*Piliostigma thonningii*) pods sourced within the premises of Federal University of Technology Akure, Ondo State. The pods were harvested from the top of the *Piliostigma thonningii* trees. The pods were opened, the seeds discarded and the pods were washed with distilled water and oven dried between 95-105 °C for three days. The dried pods were then ground to fine particles and sieved using 300 µm, 850 µm, 1.17 mm and 1.70 mm pore sizes (Adebayo *et al.*, 2012). These were stored in air-tight containers and then used for the subsequent batch sorption studies.

Concerning materials used in the study, 1,000 mg/L stock solution of copper ions (Cu^{2+}) was prepared by dissolving 3.803 g of copper (II) trioxonitrate (v) trihydrate in distilled water of 1,000 cm³ standard volumetric flask and made up with distilled water. 1,000 mg/L stock solution of nickel ions (Ni^{2+}) was also prepared by dissolving 4.475 g of nickel tetraoxosulphate (vi) hexahydrate in distilled water in 1,000 cm³ standard volumetric flask and made up with distilled water. Metal concentrations used for the batch sorption studies were prepared by serial dilution from the stocks as required (Onundi *et al.*, 2010).

Furthermore, adsorption of Ni^{2+} and Cu^{2+} by *Piliostigma thonningii* pod powder was studied using methods reported by Aisien *et al.*, 2013. The pH study investigated the effect of pH, on the sorption of metal ions on the biomass, ten (100 cm³) samples in duplicate of 50 mg/L of each adsorbate were prepared. Their pH was adjusted to pH of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 by using 0.1 M NaOH and 0.1 M HNO₃. About 1.0 g of the adsorbent (850 µm in size) was weighed and added to each of the 100 cm³ of the 50 mg/L simulated water (SW). Each was manually stirred at intervals for 480 mins and then filtered (Anirudhan and Suchithra, 2010). The filtrates were stored in sample bottles already washed and rinsed with distilled water and the residual metal ion concentration in each

filtrate was determined using Perkin Elmer AAnalyst 400 atomic absorption spectrophotometer (AAS).

Contact time study used solution (100 cm³) of 50 mg/L of each metal ion, measured into twenty different beakers to study the effect of contact time on the sorption metal ions. The pH of the SW in each of the beaker was adjusted to pH 4 for both copper and nickel ions obtained as the optimum adsorption pH from the previous study. One gram of the adsorbent was added to each solution and was manually agitated. For each metal ion, the experiment was carried out in duplicate for 5, 15, 30, 60, 90, 120, 180, 240, 300 and 360 minutes. The solutions were filtered after each time interval and the filtrates kept for AAS analysis (Ramya *et al.*, 2011).

Temperature study used one gram of the biomass was added to 100 cm³ of 50 mg/L solution of Ni²⁺ and Cu²⁺ separately having adjusted the pH to the optimum pH. The mixture was equilibrated in a water bath adjusting the temperature to 30 °C, 40 °C, 50 °C and 60 °C in separate studies. The mixture was stirred and allowed to stay for the optimum time, filtered and the filtrate kept for AAS analysis.

Solutions (100 cm³) of 50 mg/L of each metal was measured into eight conical flasks. The pH of the SW was adjusted to the optimum pH and 1.0 g of the following biomass particle sizes (300 µm, 850 µm, 1.17 mm and 1.70 mm) was introduced into it. Each mixture was stirred at intervals for the optimum time at room temperature and was filtered after 3 and 4 hours for Ni and Cu. The residual concentration of Ni²⁺ and Cu²⁺ in each filtrate was determined in each portion

The data obtained from AAS analysis were subjected to graphical analysis, intra-particle diffusion, pseudo first-order and second-order kinetic models.

Effect of pH on the Adsorption of Nickel and Copper Ions

The plot of pH profile study for nickel and copper ions is presented in Figure 4.1. The plot showed an optimum binding at pH 4 for both nickel and copper ions. By increasing the pH from 1.0 to 4.0 the percentage ion adsorbed increased from 30% to 77.59% after which the adsorption decreased with increase in pH. The result (Figure 4.1) showed an optimum binding pH of 4. This is in agreement with what has been earlier reported by other researchers. Enos *et al.*, (2011) described that by increasing the pH from pH 1 to 2, the percentage nickel ion removal increased from 30% to 40.12%, while that of copper ion increased from 25.04% to 29.72%. The pH of the solution has a significant impact on the uptake of heavy metal ions. Adsorption increases as solution pH increases in acidic medium (Kumar *et al.*, 2014).

At pH 3, 55.24% of nickel ion was removed which is a higher percentage and the highest percentage removal of 77.59% was observed at pH 4 whereas for copper ions the increase was gradual, 43.88% of copper ion was adsorbed at pH 3 and at pH 4, the percentage of copper ion adsorbed had risen to 72.85%. At pH 5, there was decrease in adsorption for the two metals. At pH above 5 precipitations occurred for both nickel and copper ions, this is also in agreement with what has been earlier reported by Wang *et al.*, 2005. Lower adsorption recorded at pH below 4 may be as a result of positive charges on the surface of the biomass which led to electrostatic repulsion between the biomass and the adsorbate ions. However, as pH increases, surface H⁺ are replaced by OH⁻, increasing negative surface charge favourable to cationic adsorption and result in increased Ni²⁺ and Cu²⁺ uptake (Enos *et al.*, 2011). The binding of Ni²⁺ and Cu²⁺ to the biomass is evidently dependent on the pH of the reaction medium. This had been confirmed by others (Wang and Qin, 2005). Furthermore, the decrease in the percentage of adsorption after the optimum pH of the ions could also be due to the weakening of electrostatic force of attraction between the oppositely

charged adsorbate and adsorbent which ultimately leads to reduction in the sorption capacity (Baral *et al.*, 2006). This is in addition to the tendency of the ions to precipitate at higher pH.

Contact Time Study

The effect of contact time on the adsorption of Ni^{2+} and Cu^{2+} by camel foot pod powder over a period of eight hours is presented in Figure 4.2. It is observed that the amount of metal ions adsorbed increased initially with time for both nickel and copper ions and at 240 minutes equilibrium was reached for nickel ion while that of copper ion occurred at 180 minutes. There was an initial rapid adsorption of the ions in the first sixty minutes after which there was reduction in the rate of adsorption of the metals` ions from the aqueous solution. The rapidity in adsorption of ions was more pronounced in copper ions in the first 60 minutes than that of nickel ions but later nickel ions uptake had a higher percentage near equilibrium . At equilibrium, nickel ions had a maximum removal of 77%. Equilibrium was reached after 240 minutes after which no ion was further removed but rather there was a decrease in the rate of adsorption as reaction time increased. The adsorption of copper ions also followed the same trend as that of nickel ions but the maximum percentage removal (72.9%) was lower than that of nickel ions at equilibrium. The equilibrium time for copper ions was reached after 180 minutes, after which further increase in contact time did not show any increase in adsorption. The initial rapid removal of Cu^{2+} and Ni^{2+} has been reported in other studies (Mulu, 2013), confirming what was observed in this current study. The importance of rapid adsorption is relevant in a continuous flow system because it enables an optimum metal uptake at a high flow rate. The initial increase in metal ions removal before equilibrium may be due to the fact that active sorption sites in the system have a fixed number and each of them can only adsorb one ion in a monolayer (Aljlil and Alsewailem, 2014). This leads to decrease in adsorption as the competition for decreasing availability of active sites increases by the metal ions remaining in solution.

The result of the analysis of variance for nickel and copper ions shows that there is significant difference in adsorption between the contact time of 5 minutes, 15 minutes and 30 minutes, also there is significant difference between the contact time of 60 minutes, 90 minutes and 120 minutes, and there is significant difference between the contact time of 180 minutes, 240 minutes, 270 minutes, 300 minutes, 330 minutes and 360 minutes. There is significant difference between contact time of nickel and copper ions` adsorption.

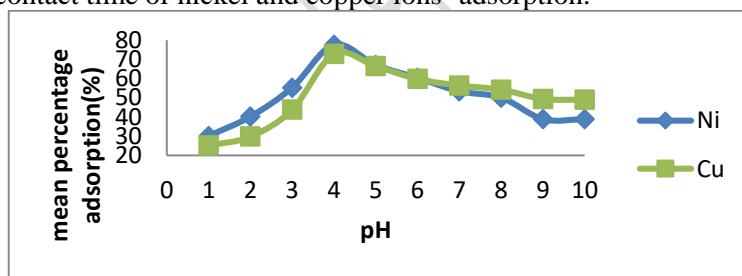


Fig 4.1 Effect of pH on the adsorption of Ni^{2+} and Cu^{2+} by *Piliostigma thonningii* pod powder



Figure 4.2 Effect of contact time on the adsorption of Ni^{2+} and Cu^{2+} by *Piliostigma thonningii* pod powder.

Intra-particle Diffusion Model

The Weber and Morris intra-particle diffusion model expressed as:

$$q_t = K_d \cdot t^{1/2} + I \quad (4.1)$$

was used to establish the rate of diffusion of the metal ions into the biomass (Kadirvelu *et al.*, 2005). Where, I is the intra-particle diffusion constant which is the intercept of the graph, it reflects the boundary layer effect, $t^{1/2}$ is the time in minutes, q_t is the amount of sorbate adsorbed and k_d is the intra-particle diffusion rate constant. Figure 4.3 shows the plot of q_t versus $t^{1/2}$. The plots showed a partial linear distribution of points. The larger the intercept, the greater is the contribution of the surface sorption in the rate controlling step (Aisien *et al.*, 2013). The linear portion indicates the existence of intra-particle diffusion in the process and the curved portions attributed to bulk diffusion. Meanwhile deviation of the curve from origin is interpreted to be that intra-particle transport is not the only rate limiting step (Das *et al.*, 2013) and that other mechanisms are involved in the adsorption process (Jianlong *et al.*, 2000).

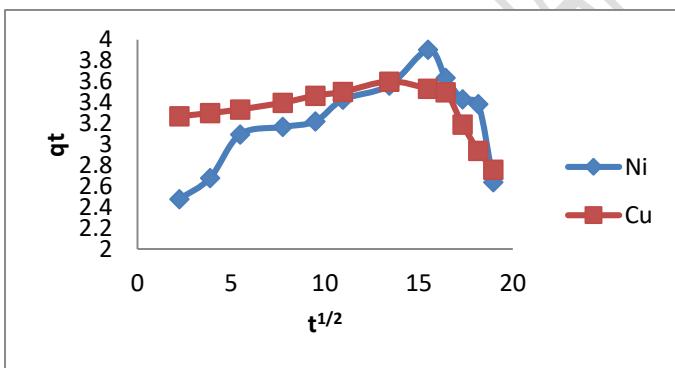


Figure 4.3 Plot of intra-particle diffusion

$$R^2 = 0.190, y = 0.052x + 2.876 \ (\text{Ni}^{2+})$$

$$R^2 = 0.205, y = 0.031x + 3.520 \ (\text{Cu}^{2+})$$

q_t = is the amount of sorbate adsorbed

t = time in minutes

Kinetic Studies of Adsorption of Nickel and Copper Ions

The kinetics studies of nickel and copper ions were undertaken using pseudo-first order Lagergren and pseudo-second order kinetics models. Kinetics is the study of rates of chemical processes and

the factors that influence the rates. In order to analyse the adsorption kinetics of Ni^{2+} and Cu^{2+} on camel foot biomass, the pseudo first order and second order kinetics models were used to analyse the experimental data.

Pseudo First Order Kinetics

A simple kinetic analysis of adsorption is the Lagergren equation. The Lagergren equation, a pseudo first-order equation, describes the kinetics of the adsorption process as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4.2)$$

Where k_1 is the rate constant of pseudo first-order adsorption, and q_e and q_t are the amounts of metals adsorbed per gram of the biomass at equilibrium and at time t (Tshai and Chen, 2010). In many cases, the first-order equation of Lagergren does not fit well for the whole range of contact times and is generally applicable over only the initial stage of the adsorption (Sarin and Pant, 2006). After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$, equation (4.2) becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4.3)$$

A straight line graph of $\ln(q_e - q_t)$ versus t suggests the applicability of this kinetic model to fit the experimental data. The graph (Figure 4.4) obtained in the current study suggests that the pseudo first-order kinetic model is not applicable to this study as can be seen from the non-straight line graph of the kinetics proposing that the rate of adsorption does not depend only on the concentration of a single reactant but on the concentration of both the adsorbent and the adsorbates. Al-Anber and Al-Anber, (2008) also made the same observation while adsorbing iron (III) ions on olive cakes that the adsorption did not obey pseudo-first order reaction perfectly.

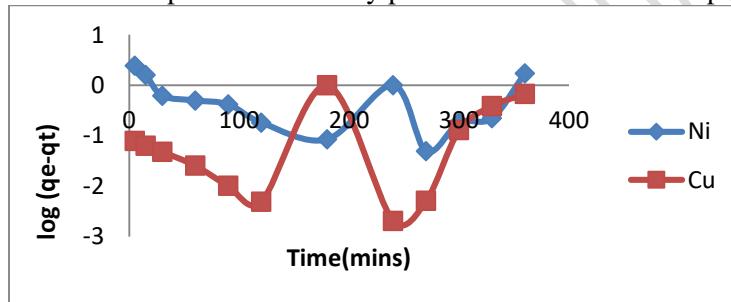


Figure 4.4: Plot of pseudo-first order kinetics

$$R^2 = 0.064, y = 0.001x - 1.617(\text{Ni})$$

$$R^2 = 0.132, y = 0.001x - 0.130(\text{Cu})$$

4.4.2 Second - Order Kinetic Model

The linearized pseudo second-order kinetic model which is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2} \cdot q_e^2 + \frac{1}{q_e} \quad (4.4)$$

$$h_i = K_2 \cdot q_e^2 \quad (h_i = \text{initial metal adsorption rate}) \quad (4.5)$$

This equation (4.4) was used to treat the adsorption data of the metal ions uptake by camel foot pod (Ho and Mckay, 2000) and it fitted well with this model as shown in figures 4.5, 4.6 and 4.7. The slope and intercept of (t/q_t) versus t were used to calculate the pseudo second-order rate constants k_2 and q_e . The best fit values of h_i , q_e , and k_2 along with correlation coefficients for the pseudo-second-order models are shown in Table 4.1. The q_e , experimented and the q_e , calculated values from the pseudo-second-order kinetic model were very close to each other, and, the calculated correlation coefficients, R^2 were also closer to unity for pseudo-second-order kinetics. These suggested that the pseudo second-order adsorption mechanism is predominant in biosorption of Ni^{2+} and Cu^{2+} . Similar processes have been observed in the adsorption of $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$ and Zn

(II) from aqueous solutions with tannin-immobilized calcined hydrotalcite using batch experiment technique by Anirudhan and Suchthra, (2010) and the adsorption of nickel and chromium ions in dye effluents using activated carbon prepared from groundnut shell by Idris *et al.*, (2012).

The experimental data showed a good compliance with the second-order equation and the correlation coefficients for the linear plots were higher than 0.9 for all the experimental data.

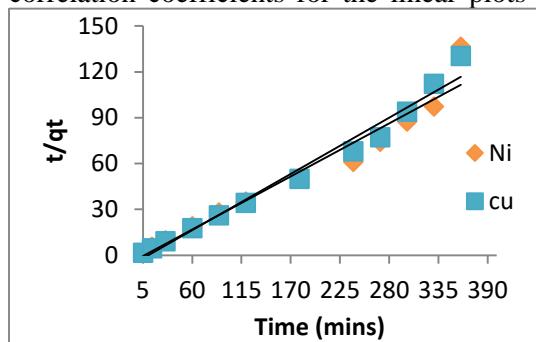


Figure 4.5: Plot of linearized second-order kinetics of Ni^{2+} and Cu^{2+}

$$R^2 = 0.951, y = 0.315x - 2.058 \text{ (Ni)}$$

$$R^2 = 0.978, y = 0.334x - 3.746 \text{ (Cu)}$$

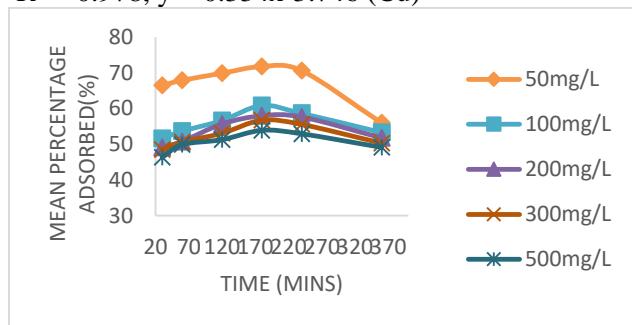


Figure 4.6: Plot of second-order kinetic model of Cu^{2+} at different concentrations.

$$R^2 = 0.970; y = 0.354x - 6.996 \text{ (50 mg/L)}$$

$$R^2 = 0.988; y = 0.188x - 1.398 \text{ (100 mg/L)}$$

$$R^2 = 0.984; y = 0.0998 - 0.814 \text{ (200 mg/L)}$$

$$R^2 = 0.997; y = 0.060x + 0.139 \text{ (300 mg/L)}$$

$$R^2 = 0.997; y = 0.039x - 0.084 \text{ (500 mg/L)}$$

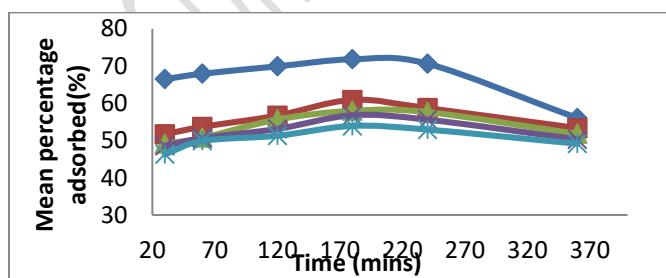


Figure 4.7: Plot of second-order kinetic model of Ni^{2+} at different concentrations.

$$R^{2+} = 0.939; y = 0.360x - 7.485 \text{ (50 mg/L)}$$

$$R^2 = 0.986; y = 0.163x - 1.020 \text{ (100 mg/L)}$$

$$R^2 = 0.992; y = 0.085x - 0.645 \text{ (200 mg/L)}$$

$$R^2 = 0.971; y = 0.057x + 1.123 \text{ (300 mg/L)}$$

$$R^2 = 0.995; y = 0.049x + 0.818 \text{ (500 mg/L)}$$

Table 4.1: Comparison of the Second Order Adsorption Rate Constants and the Calculated and Experimental q_e Values for Initial Adsorbates' Concentrations.

Initial Adsorbate concentration(mg/l)	q_e experimental (mg/g metal)	q_e calculated (mg/g metal)	R^2	K_2	H_i
Ni^{2+}					
50	3.936	3.175	0.951	0.0480	0.4839
100	7.061	6.135	0.986	0.0260	0.9786
200	13.076	11.765	0.992	0.0112	1.5505
300	18.745	17.544	0.971	0.00289	0.8901
500	20.085	20.408	0.995	0.00294	1.2245
Cu^{2+}					
50	3.591	2.994	0.970	0.0298	0.2671
100	6.087	5.319	0.988	0.0253	0.9999
200	11.600	10.204	0.984	0.0118	1.2280
300	17.030	16.667	0.997	0.0259	7.1940
500	26.960	25.641	0.997	0.0181	11.906

Effect of Initial Concentration

Figure 4.8 represents the percentage Ni^{2+} and Cu^{2+} removed by Camel foot biomass after an incubation period of 4h and 3h respectively for the range of study concentrations of Ni^{2+} and Cu^{2+} . The maximum percentage adsorption of Ni^{2+} was 78.7% and that of Cu^{2+} was 71.8% and these were achieved at a starting concentration of 50 mg/L. The percentage metal ions uptake decreased as the starting concentrations of the ions increased from the 50 mg/L to 500 mg/L; however the adsorption capacity increased with increase in concentration of the ions. Ion exchange is thought to be the main mechanism involved in the biosorption process and this involves the competition between metal ions and protons for binding sites on the biomass (Volesky, 2003, Denis, 2000). The lower percentage adsorption of Cu^{2+} and Ni^{2+} by the camel foot biomass at higher concentration of the metals as observed in the study (as shown in the graphs in the next pages) may simply be due to the metals being present in excess, not due to poor adsorption. The higher percentage of adsorption of Ni^{2+} than Cu^{2+} might be an indication that camel foot biomass has a higher affinity for Ni^{2+} than Cu^{2+} (Javaid *et al.*, 2011). Adsorption of lead (II) ions onto activated carbons prepared from the marine green *Ulva fasciata sp.* and commercial activated carbon reported by Jeyakumar and Chandrasekaran, (2014) also followed similar trend of decrease in percentage adsorption as concentration of the metal ions increased. From figure 4.9, as the initial nickel (II) ion concentration increased from 50 to 500 mg/L, the loading capacity of the camel foot pod biomass increased from 3.936 mg/g to 20.085 mg/g. Thus, the adsorption capacity was enhanced with increased initial concentration of the nickel ion. This in agreement with the findings of Ogunleye *et al.*, (2013), while working on the removal of lead (II) ions from aqueous solution using banana (*Musa paradisiaca*) stalk-based activated carbon. From figure 4.10 also, as the initial copper (II) ion concentration increased from 50 to 500 mg/L, the sorption capacity of the camel foot pod biomass increased from 3.591 to 26.960 mg/g. Therefore, it may be concluded that the adsorption capacity was enhanced with increased initial concentration of the copper ion. This agreed with the observation of Teoh *et al.*, (2013), who worked on the adsorption of lead (II) ions from aqueous phase on carbon coated monolith.

The result of the analysis of variance for nickel and copper shows that there is significant difference in adsorption between the concentration of 50 mg/L, 100 mg/L, 200 mg/L, 300 mg/L and 500 mg/L.

There is also significant difference between the concentration study profile of nickel and copper ions.

Adsorbent Dosage Study

The effect of adsorbent dose on the adsorption of heavy metal ions by camel foot biomass is shown in Figure 4.11. Adsorption profile of the metal ions with various dosages of the adsorbent showed that 0.5 g of the adsorbent adsorbed 73.5% of Ni^{2+} and 69.4% of Cu^{2+} , while 2.5 g adsorbed 83.4% of Ni^{2+} and 76.47% of Cu^{2+} of the initial metal ion concentration. The concentration of the metal ions in solution was reduced from 26.5% to 16.7% for Ni^{2+} and 30.64% to 23.5% for Cu^{2+} by increasing the load of the biomass from 0.5 g to 2.5 g. Hala, (2013), recorded the same observation from the removal of heavy metal ions from waste water using agricultural and industrial wastes as adsorbents. This result suggests that the number of sites available for adsorption increases by increasing the adsorbent dose (Mulu 2013, Kanamadi *et al.*, 2006).

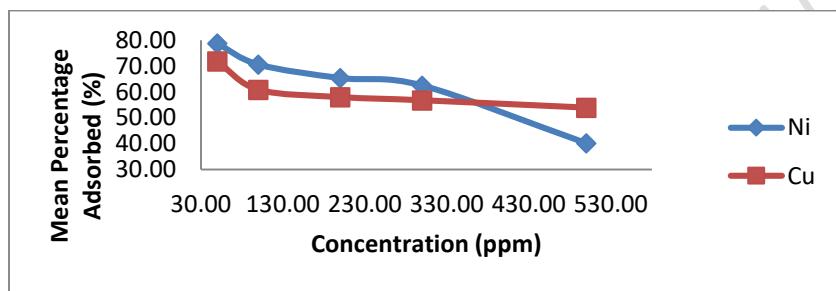


Figure 4.8 Effect of initial concentration on the adsorption of Ni^{2+} and Cu^{2+}

$$R^2 = 0.957; y = -0.678x + 81.59 \quad (\text{Ni}^{2+})$$

$$R^2 = 0.669; y = -0.031x + 67.55 \quad (\text{Cu}^{2+})$$

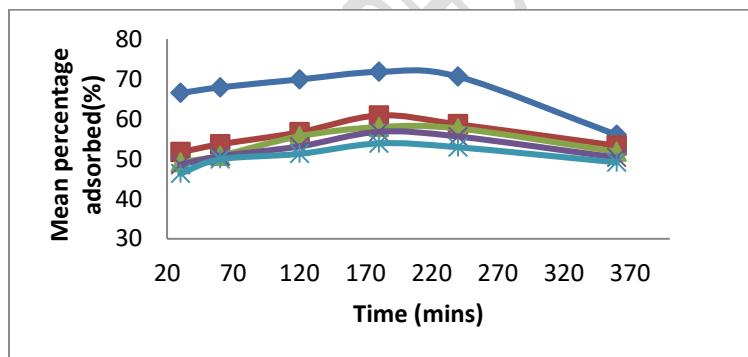


Figure 4.9: Plot of contact time and initial concentration on mean Percentage Adsorption of Ni^{2+}

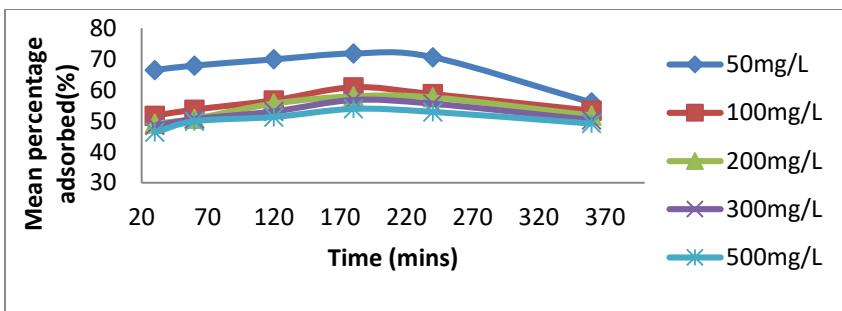


Figure 4.10 Effects of contact time and initial concentration on mean percentage adsorption of Cu²⁺.

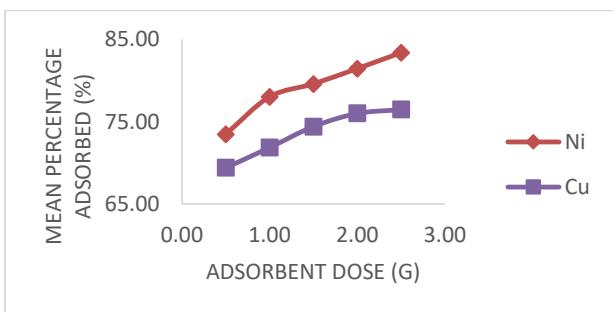


Figure 4.11: Effect of adsorbent dosage on the adsorption of Ni²⁺ and Cu²⁺

Effect of Temperature

The effect of temperature on the equilibrium adsorption of Ni²⁺ and Cu²⁺ as can be inferred from figure 4.12 showed that increase in temperature leads to decrease in percentage of metal ions adsorbed. For Ni²⁺, 69.3% was adsorbed at 30 °C while only 35.9% was adsorbed at temperature of 60 °C. Also, for Cu²⁺, 70.9% was adsorbed at 30 °C while 50.6% was adsorbed at 60 °C.

This indicates that a lower temperature is more favourable for the adsorption of the ions on the biomass. The trend observed is due to the weakening of the attractive force between metal ions and the adsorbent on the one hand and due to enhancement of thermal energies of the adsorbate on the other hand thus making the attractive force between the adsorbates (Ni²⁺ and Cu²⁺) and adsorbent insufficient to retain the adsorbed ions at the binding sites (Jadhav *et al.*, 2007). Babarinde *et al.*, (2012) reported a similar trend for the adsorption of nickel ion, chromium ion and cobalt ion from aqueous solutions using cocoyam (*Colocasia esculenta*) leaves. Mousavi *et al.*, (2010a) and Nor *et al.*, (2013) reported that the adsorption rate could decrease with increasing temperature, a trend which may be indicative of physical adsorption. The increase in the rate of adsorption by decreasing the temperature indicates that the adsorption process is exothermic (Aisien *et al.*, 2013; Jain *et al.*, 2003). An increase in uptake of ions is expected when the adsorption temperature decreases because adsorption is a spontaneous process (Horsfall and Ayebarami, 2005).

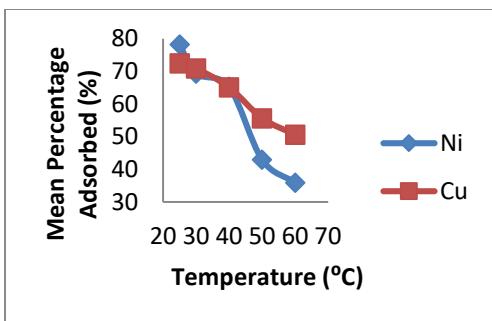


Figure 4.12 Effect of temperature on the mean percentage adsorption of Ni^{2+} and Cu^{2+}

Activation Parameters

In general, the rates of chemical reactions increase with an increase in temperature. In the rate law, temperature dependence appears in the rate constant and the dependence of rate constants on temperature over a limited range can usually be represented by the empirical Van't Hoff and Arrhenius equations (Jiwakar *et al.*, 2010):

$$K_d = A_e^{-Ea/RT} \quad (4.6)$$

where A is the pre-exponential factor and Ea is the activation energy and R is the gas constant. From the alternative logarithmic form of this equation:

$$\ln K_d = \ln A - \frac{Ea}{RT} \quad (4.7)$$

Ea can be obtained by plotting (Arrhenius plot) $\ln K_d$ against the reciprocal of the absolute temperature T. The magnitude of Ea may then give an indication of whether a physical or chemical adsorption process is in operation. In physical adsorption (physisorption) the interaction is easily reversible, equilibrium is rapidly attained and its energy requirements are small so Ea is usually not more than 5-40 kJ/mol (Nollet *et al.*, 2003) because usually weak intermolecular forces are involved. However, with chemical adsorption (chemisorption) much stronger bonding forces are involved and Ea values range from 40-800 kJ/mol (Nollet *et al.*, 2003). In this work, an Ea of 38.31 kJ/mol was determined from the slope of the plot of $\ln K_d$ versus $1/T$ for Ni^{2+} and that of Cu^{2+} was 22.905 kJ/mol. From this it is inferred that the adsorption of Ni^{2+} and Cu^{2+} by camel foot biomass most likely involves a physisorption process. This is a confirmation of what have been earlier reported by Ashjaran and Mehrdad, (2014).

Effect of Particle Size

Figure 4.15 showed the effect of particle size on the adsorption of nickel and copper ions by camel foot pod, and from the graph it was inferred that the amount of Ni^{2+} adsorbed by the biomass increased from 77.9% to 96.5% by decreasing the particle size from 850 μm to 300 μm while the amount of Cu^{2+} increased from 71.9% to 76.9% using the same particle size as in the case of nickel ions. This observation may be due to increase in surface area as the particle size decreases and the number of active sites increases thereby increasing adsorption (Kumar *et al.*, 2009). The smaller the size of the adsorbent particles, the greater the interior surface area and micro pore volume and consequently more active sites are available for adsorption (Annadurai *et al.*, 2000). However, for larger particles, the pore diffusion resistance to mass transfer is higher and most of the internal surfaces of the particle may not be utilized for adsorption and consequently the amount of metal ions adsorbed is small (Annadurai *et al.*, 2000). Similar results were also obtained by Aisien *et al.*, (2013).

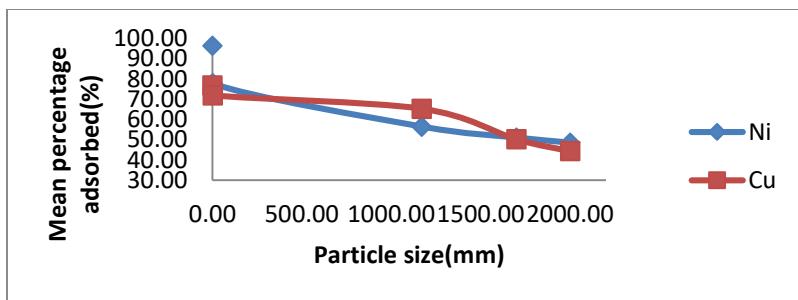


Figure 4.15: Effect of particle size on adsorption of Ni^{2+} and Cu^{2+}

$$R^2 = 0.870; \quad y = -0.020x + 86.33$$

CONCLUSION AND POLICY RECOMMENDATION

Conclusion

Adsorption of nickel and copper ions from aqueous solutions using camel foot (*Piliostigma thoninigii*) biomass was investigated through batch process. The survey showed that camel foot biomass is an efficient, economical and inexpensive adsorbent for Ni^{2+} and Cu^{2+} . The amount of copper and nickel ions uptake increased significantly with increase in pH range from 1 to 4 with the optimum pH being 4. Aqueous solutions of nickel and copper ions with starting concentrations of 50 mg/L gave the best percentage of adsorption by the biomass moreover adsorption capacity increased with increase in concentration of metal ions.

The temperature profile study showed that both the sorption of nickel and copper ions on camel foot biomass is characterized by a rapid initial adsorption step. 60% of the ions adsorbed were bound in the first 1 h of contact with the biomass. The optimum contact time for nickel ion adsorption was 4 h while that of copper ion was 3 h. The equilibrium data for copper ions are best explained by Freundlich adsorption isotherm while that of nickel ions followed Langmuir isotherm.

The effect of adsorbent dosage on the adsorption process showed that the adsorption rate increased with increase in biomass dosage due to availability of more surface area for the adsorption. The study of the effect of particle size on the biomass showed that the rate of adsorption increased with decrease in the size of biomass particles.

The adsorption rates of the ions onto the biomass decreased as temperatures increased and this indicated that the process was exothermic and the optimum temperature for the adsorption using this biomass was 25°C . The activation energy for the sorption process of copper and nickel ions were found to be 38.31 kJ/mol and 22.91 kJ/mol respectively. The values of Gibbs free energy ΔG^0 showed that the reactions were spontaneous. Also, the values of ΔH^0 , ΔG^0 and E_a all suggested that the sorption of copper and nickel ions onto *Piliostigma thoninigii* pod biomass was by physisorption.

Policy Recommendation

The survey showed that camel foot biomass is an efficient, economical and inexpensive adsorbent for Ni^{2+} and Cu^{2+} and can compete effectively with activated carbon.

A policy should be put in place by Nigerian government to implement the use of camel foot pod in the synthesis of composite adsorbent for the treatment of industrial effluents since these materials are cheap and readily available within the country.

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