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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 thonningii*) 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.

Keywords: environment, protection, biosorption, nickel, copper, camel foot

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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 electro dialysis 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 Ni²⁺ and Cu²⁺ 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.

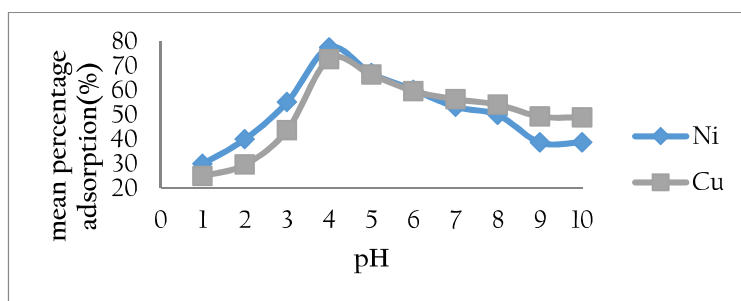


Fig 4.1 Effect of pH on the adsorption of Ni^{2+} and Cu^{2+} by *Piliostigma thonningii* pod powder

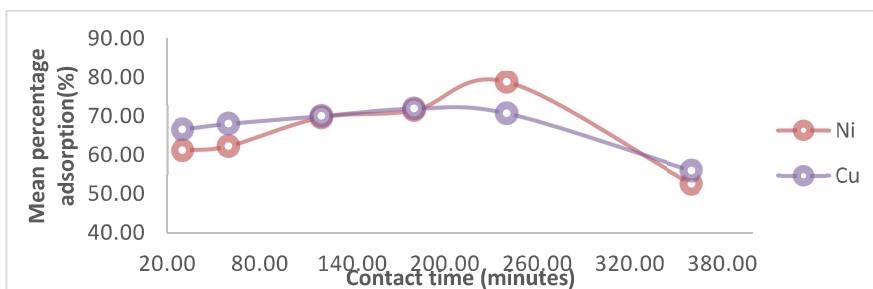


Figure 4.2 Effect of contact time on the adsorption of Ni^{2+} and Cu^{2+} by *Piliostigma thonningii* pod powder.

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).

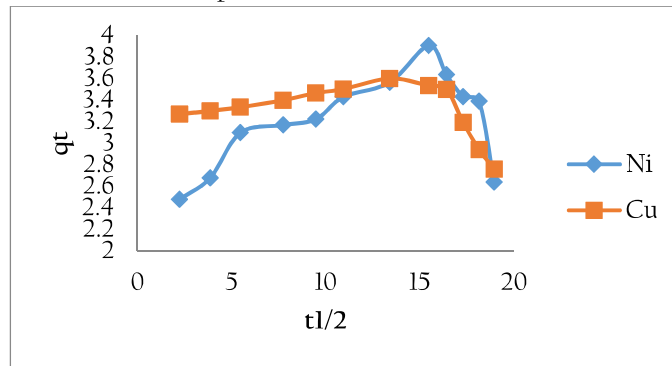


Figure 4.3 Plot of intra-particle diffusion

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

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

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.

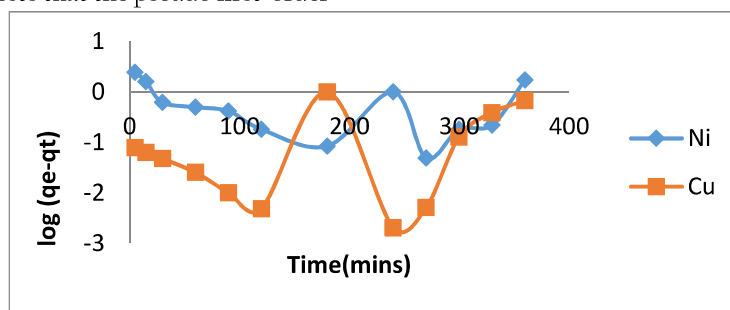


Figure 4.4: Plot of pseudo-first order kinetics

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

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

Second - Order Kinetic Model

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

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

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

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 Cu (II), Cd (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.

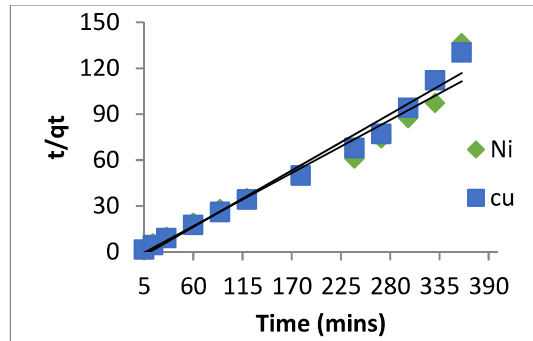


Figure 4.5: Plot of linearized second-order kinetics

of Ni^{2+} and Cu^{2+}

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

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

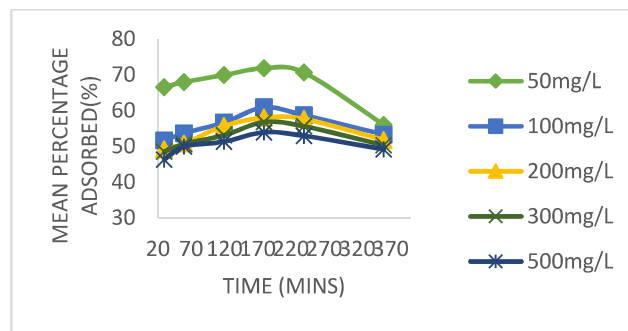


Figure 4.6: Plot of second-order kinetic model of Cu^{2+} at different concentrations.

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

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

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

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

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

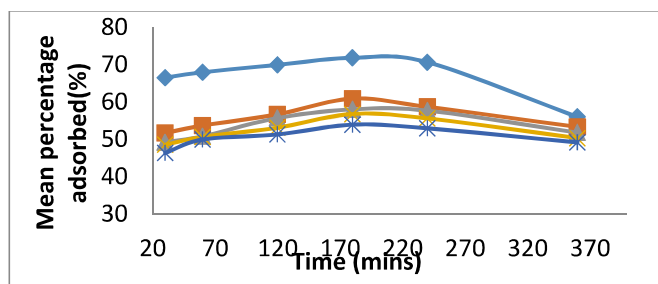


Figure 4.7: Plot of second-order kinetic model of Ni²⁺ at different concentrations.

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

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

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

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

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

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 Ni²⁺ and Cu²⁺ removed by Camel foot biomass after an incubation period of 4h and 3h respectively for the range of study concentrations of Ni²⁺ and Cu²⁺.

The maximum percentage adsorption of Ni²⁺ was 78.7% and that of Cu²⁺ 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).

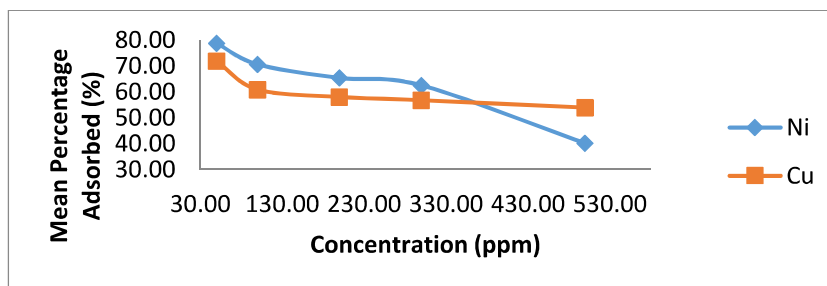


Figure 4.8 Effect of initial concentration on the adsorption of Ni^{2+} and Cu^{2+}



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

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

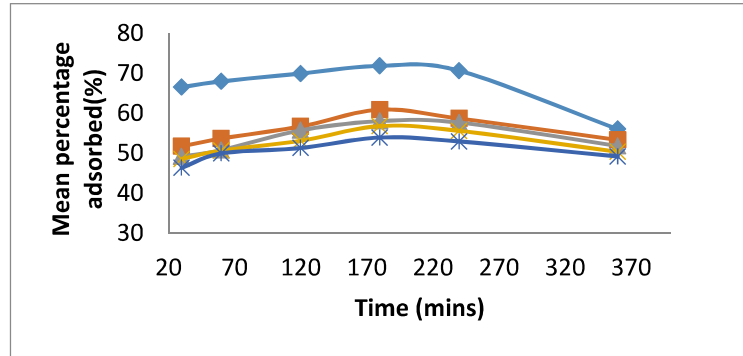


Figure 4.9: Plot of contact time and initial concentration on mean Percentage Adsorption of Ni²⁺

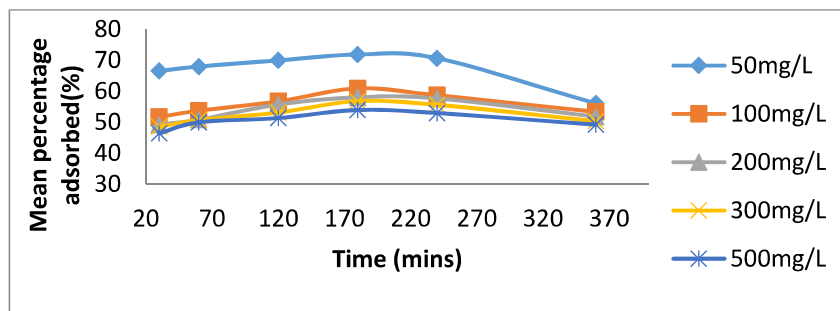


Figure 4.10 Effects of contact time and initial concentration on mean percentage adsorption of Cu²⁺.

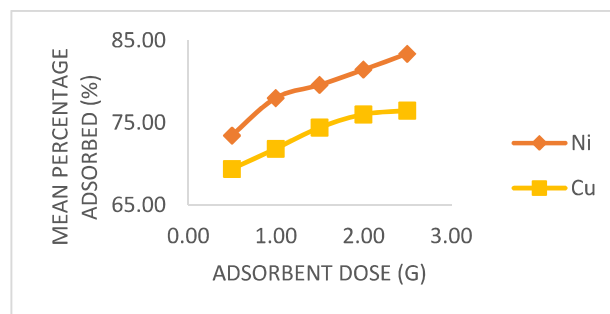


Figure 4.11: Effect of adsorbent dosage on the adsorption of Ni²⁺ and Cu²⁺

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 Ayebaemi, 2005).

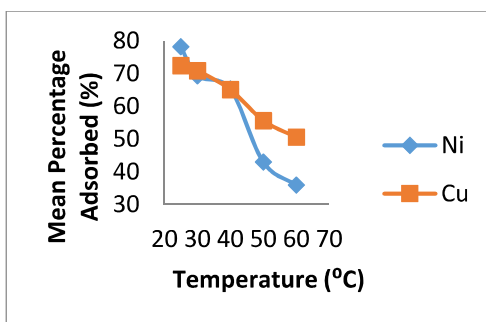


Figure 4.12 Effect of temperature on the mean percentage adsorption of Ni²⁺ and Cu²⁺

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 (Jiwalak *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 Ni²⁺ and that of Cu²⁺ 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 Ashjara 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).

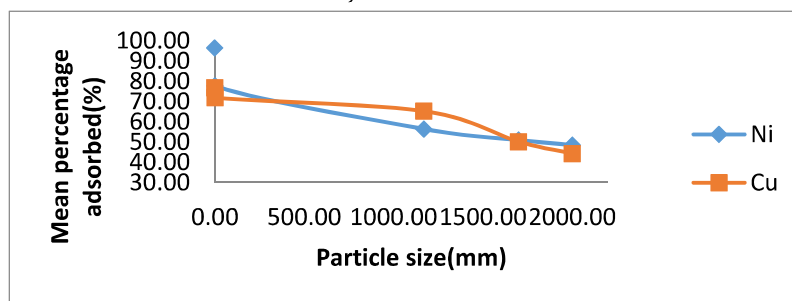


Figure 4.15: Effect of particle size on adsorption of Ni^{2+} and Cu^{2+}
 $R^2 = 0.870$; $y = -0.020x + 86.33$

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 thoninigi* 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.

REFERENCES

- Aderhold D., Williams C.J., and Edyvean R.G.J. (1996). The removal of heavy-metal ions by seaweeds and their derivatives. *Bioresource Technology*, 58 (1): 1–6.
- Adebayo J.O., Santana A.E.G. and Krettli A.U. (2012). Evaluation of the antiplasmodial and cytotoxicity potentials of husk fibre extracts from *Cocos nucifera*, a medicinal plant used in Nigeria to treat human malaria. *Human and Experimental Toxicology*, 31 (3) : 244-249.
- Agency for Toxic Substances and Disease Registry – ATSDR (2000). Toxicological profile for arsenic. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Humans Services, Centers for Diseases Control. Atlanta.
- Agency for Toxic Substance and Disease Registry (ATSDR). (2003a). Toxicological Profile for Arsenic U.S. Department of Health and Humans Services, Public Health Humans Services, Centers for Diseases Control. Atlanta.
- Agency for Toxic Substance and Disease Registry (ATSDR). (2003b). Toxicological Profile for Mercury U.S. Department of Health and Humans Services, Public Health Human Services, Centers for Diseases Control. Atlanta.
- Agency for Toxic Substances and Disease Registry (ATSDR). (2004). Toxicological Profile for Copper. U.S. Department of Health and Humans Services, Public Health Service, Centers for Diseases Control. Atlanta.
- Agency for Toxic Substance and Disease Registry (ATSDR), (2005). Toxicological Profile for Nickel. U.S. Department of Public Health Service, Centers for Diseases Control. Atlanta.
- Agency for Toxic Substance and Disease Registry (ATSDR). (2007). Toxicological Profile for Lead U.S. Department of Health and



- Humans Services, Public Health Humans Services, Centers for Diseases Control. Atlanta.
- Agency for Toxic Substance and Disease Registry (ATSDR). (2008). Draft Toxicological Profile for Cadmium U.S. Department of Health and Humans Services, Public Health Humans Services, Centers for Diseases Control. Atlanta.
- Ahalya N., Ramachandra T.V. and Kanamadi R.D. (2003). Biosorption of Heavy metals. *Research Journal of Chemistry and Environment*; 7 (4):71-78.
- Ahamed A.J. and Balakrishnan V. (2010). Studies on the adsorption of ferrous ions from aqueous solution by low cost carbon. *Journal of Chemical and Pharmaceutical Research*, 2 (3): 733-745.
- Aisien F.A., Amenaghawon A.N., and Adeboyejo A.R. (2013). "Application of Recycled Rubber from Scrap Tire in the Removal of Phenol from Aqueous Solution". *Pacific Journal of Science and Technology*, 14 (2):330-341.
- Akpor O. B. and Muchie M. (2010). Remediation of heavy metals in drinking water and wastewater treatment systems: Processes and applications. *International Journal of Physical Sciences*, 5 (12): 1807-1817.
- Al-Anber, Z.M. and Al-Anber M. A. S. (2008). Thermodynamics and Kinetic Studies of Iron (III) Adsorption by Olive Cake in a Batch System. *Journal of the Mexican Chemical Society*, 52: 108-115.
- Aljlil A.S. and Alsewailem F.D. (2014). Adsorption of Cu and Ni ions on Bentonite Clay from waste water. *Athens Journal of Natural and Formal Sciences*, I(1): 21-30.
- Allen S.J., Mckey G. and Porter J.F. (2004). Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *Journal of Colloid and Interface Science*, 280 (2): 322-333.
- Alva A.K., Graham J.H. and Anderson C.A. (1995). Soil pH and copper effects on young 'Hamlin' orange trees. *Soil Science Society of America Journal*, 59: 481-487.
- Andersen A., Berge S.R., Engeland A. and Norseth T. (1996). Exposure to nickel compounds and smoking in relation to incidence of lung and nasal cancer among nickel refinery workers. *Occupational and Environmental Medicine*, 53: 708-713.
- Anirudhan T.S. and Radhakrishnan P.G. (2008). Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell. *Journal of Chemical Thermodynamics*, 40(4): 702-709.
- Anirudhan T.S. and Suchithra P.S. (2010). Equilibrium, kinetics and thermodynamics modeling for the adsorption of heavy metals onto chemically modified hydrotalcite. *Indian Journal of Chemical Technology*; 17: 247-249.
- Annadurai G., Rajesh B.S., Mahesh K.P.O. and Murugesan T. (2000). "Adsorption and Biodegradation of Phenol by Chitosan-Immobilised *Pseudomonas putida*". *Bioprocess Engineering*, 22:493-501.
- Anonymous (2005). "China says water pollution so severe that cities could lack safe Supplies". Chinadaily.com.cn.
- Anttila A., Pukkala E. and Aitio A. (1998). Update of cancer incidence among workers at a copper/nickel smelter and nickel refinery. *International Arch Occupational Environmental Health*, 71:245-250.
- Ashjaran A. and Mehrdad H. (2014). Adsorptions of anionic dye on direct blue 71 dye with bacterial and plant cellulose: thermodynamic and kinetic study. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 4 (3): 985-994.
- Athar R. and Ahmad M. (2002). Heavy metal toxicity: effect on plant growth and metal uptake by



- wheat, and on free living *Azotobacter*. *Water, Air and Soil Pollution*, 138: 165-180.
- Aydln H., Bulut Y. and Yerlikaya C. (2008). Removal of Cu^{2+} from aqueous solution by adsorption onto low cost adsorbents. *Journal of Environmental Management*, 87: 37-45.
- Babarinde A., Babalola J.O., Adegoke J., Osundeko A.O., Ibadapo T.J., Nwabugwu C.A. and Ogundimu O.F. (2012). "Biosorption of Ni (II), Cr (III), and Co (II) from Aqueous Solutions using Cocoyam (*Colocasia esculenta*) Leaf: Kinetic, Equilibrium, and Thermodynamic Studies". *Pacific Journal of Science and Technology*. 13(2):272-282.
- Bansal M., Singh D., Garg V.K. and Rose P. (2009). Use of agricultural waste for the removal of nickel ions from aqueous solutions: Equilibrium and kinetic studies. *World Academic Science Engineering Technology*; 51:431-437.
- Baral S.S., Das S.N. and Rath P. (2006). "Hexavalent Chromium removal from aqueous solution by adsorption on treated sawdust." *Biochemical Engineering Journal*, 31(3):216-222.
- Barbante C., Boutron C. and Moreau A.L. (2002). Seasonal variations in nickel and vanadium in Mont Blanc snow and ice dated from the 1960s and 1990s. *Journal of Environmental Monitoring*, 4: 960-966.
- Barceloux D.G. (1999). Copper and nickel toxicology. *Journal of Toxicology - Clinical Toxicology*, 37: 217-23.
- Benson J. M., Cheng Y.S., Eidson E.F., Hahn F. H., Henderson R. H. and Pickrell J. A. (1995). Pulmonary toxicity of nickel subsulfide in F344/N rats exposed for 1-22 days. *Toxicology*, 103:9-22.
- Beyersmann D. and Hartwig A. (2008). Carcinogenic metal compounds: recent insight into molecular and cellular mechanisms. *Arch Toxicology*, 82: 493-512.
- Błasiak J., Arabski M. and Pertyński T. (2002). DNA damage in human colonic mucosa cells evoked by nickel and protective action of quercetin – involvement of free radicals. *Cell Biology and Toxicology journal*, 18: 279-288.
- Brower J.B., Ryan R.L. and Pazirandeh M. (1997). Comparison of ion-exchange resins and biosorbents for the removal of heavy metals from plating factory, *Environmental Science and Technology*, 31: 2910-2914.
- Caicedo M., Jacobs J.J. and Reddy A. (2007). Analysis of metal ion-induced DNA damage, apoptosis, and necrosis in human (Jurkat) T-cells demonstrates Ni(2+) and V(3+) are more toxic than other metals: Al(3+), Be(2+), Co(2+), Cr(3+), Cu(2+), Fe(3+), Mo(5+), Nb(5+), Zr(2+). *Journal of Biomedicine Materials Resources*, 86: 905-913.
- Candelaria M., Garcia-Arias A., Cetina L. and Dueñas-Gonzalez A. (2006). Radio sensitizers in cervical cancer: Cisplatin and beyond. *Radiation Oncology*, 1: 15-32.
- CAREX Canada (2011). Available at: http://www.carexcanada.ca/en/nickel/occupational_exposure_estimates/phase_2/
- Carol P. (2004). Copper in drinking water; using symptoms of exposure to define safety. *Journal of Environmental Health Perspectives*, 112: 10.
- Castro-González M.I. and Méndez-Armenta M. (2008). Heavy metals: Implications associated to fish consumption. *Environmental Toxicology & Pharmacology*, 26: 263-271.
- Chakrabarti S.K., Bai C. and Subramanian K.S. (2001). DNA-protein crosslinks induced by nickel compounds in isolated rat lymphocytes: role of reactive oxygen species and specific amino acids. *Toxicology and Applied Pharmacology*, 170: 153-165.
- Chaudhry FN, Malik MF (2017) Factors Affecting Water Pollution: A Review. *Journal of*



- Ecosystem Ecology 7: 225. doi: 10.4172/2157-7625.1000225
- Chen C.Y., Wang Y.F., Huang W.R. and Huang Y.T. (2003). Nickel induces oxidative stress and genotoxicity in human lymphocyte. *Toxicology and Applied Pharmacology*, 189:153-159.
- Chiarelli R. and Roccheri M.C. (2012). Heavy metals and metalloids as autophagy inducing agents, focus on cadmium and arsenic. *Cells*, 1(3): 597-616.
- Chiou M.S., Ho P.Y. and Li H.Y. (2004). Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. *Dyes Pigments*, 60 (1): 69-84.
- Chowdhury Z.Z., Zain S.M., Khan R.A. and Ashraf M.A. (2011). Preparation, characterization and adsorption performance of the KOH-activated carbons derived from kenaf fiber for lead (II) removal from waste water. *Scientific Research and Essays*, 6 (29): 6185-6196.
- Conrad K., Bruun and Hansen H.C. (2007). Sorption of zinc and lead on coir. *Bioresource. Technology*, 98: 89-97.
- Costa M., Yan Y., Zhao D. and Salnikow K. (2003). Molecular mechanisms of nickel carcinogenesis: gene silencing by nickel delivery to the nucleus and gene activation/inactivation by nickel-induced cell signaling. *Journal of Environmental Monitoring*, 5: 222-223.
- Costa M., Davidson T.L. and Chen H. (2005). Nickel carcinogenesis: epigenetics and hypoxia signalling. *Mutation Resources*, 592: 79-88.
- Cuhiou M.S. and Li H.Y. (2003). Adsorption behavior of reactive dye in aqueous solution on chemical crosslinked chitosan beads. *Chemosphere*, 50(8): 1095-1105.
- Dada A.O., Olalekan A.P., Olatunya A.M. and Dada O. (2012). Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. *Journal of Applied Chemistry*, 3 (1): 38-45.
- Dada A.O., Ojedokun J.O. and Abiodun P.O. (2013). Sorption of Pb^{2+} from aqueous solution unto modified rice husk: Isotherms studies. *Advances in Physical Chemistry*, 13:1-6.
- Das B., Mondal N.K., Roy P. and Chatterji S. (2013). Equilibrium, kinetic and thermodynamic Study on chromium (VI) removal from aqueous solutions using *Pistia stratiotes* biomass. *Chemical Science Trans*, 2(1):85-104.
- Denis A.T. (2000). Removal of copper and nickel from solution by the non-viable biomass of the water fern *Azolla filiculoides* in an upscaled fixed-bed column system. A M.Sc. Thesis submitted to the University of Rhodes, South Africa, 43-49.
- Deokar R. and Sabale A. (2014). Biosorption of methylene blue and malachite green from binary solution onto *Ulva lactuca*. *International Journal of Current Microbiology and Applied Sciences*, 3(5): 295-304.
- Duffus J. (2002). Heavy metals: a meaningless term. *Pure and Applied Chemistry*, 74 (5):793-807.
- Durham T.R. and Snow E.T. (2006). Metal ions and carcinogenesis. *Search for Excellence*, 96: 97-130.
- Elst P., Ahankour F. and Tjalma W. (2007). Management of recurrent cervical cancer. *European Journal of Gynaecology and Oncology*; 28: 435-41.
- Eman M .A. and Gordon A.F. (2011). Heavy metal poisoning and cardiovascular Disease. *Journal of Toxicology*; 11 (8): 1-21.
- Enos W.W., Gerald K. M., Joseph W.K. and Paul M.S. (2011). Kinetics and thermodynamics of aqueous Cu (II) adsorption on heat regenerated spent bleaching earth. *Chemical Society of Ethiopia*; 25(2): 181-190.
- European Commission. (2006). Regulation (EC) No 1881. pp. 5-24.



- EVM (2002). Expert Group on Vitamins and Minerals: Revised Review of Nickel. *EVM*, 99:24.
- Feng D., Aldrich C. and Tan H. (2000). Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Mineral Engineering*, 13(6):623-642.
- Figueira M.M. (2000). Biosorption of Metals in brown seed biomass. *Water Resources*, 34: 196-204.
- Figuroa E. (2008). Are more restrictive food cadmium standards justifiable health safety measures or opportunistic barriers to trade? An answer from economics and public health. *Science of the Total Environment*; 389: 1-9.
- Fu F. and Wang Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, 92: 407- 418.
- Galletti C., Nunzio R. and Fino D. (2015). Zn²⁺ removal from waste water using rice huskas an adsorbent. *Chemical Engineering Research Studies*, 2(1): 55-60.
- Gardea-Torresdey J.L., Peralta-Videa J.R., Rosa G.D. and Parsons J.G. (2005). Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy. *Coordination Chemistry Review*; 249(17-18): 1797-1810.
- Garelick H., Jones H., Dybowska A. and Valsami-Jones E. (2008). Arsenic pollution sources. *Review of Environmental Contamination and Toxicology*; 197: 17-60.
- Goel P.K. (2006). *Water Pollution - Causes, Effects and Control*. New Age International. New Delhi, Pp.179.
- González-Cortijo L., Carballo N. and González-Martín A. (2008). Novel chemotherapy approaches in chemoradiation protocols. *Gynecology Oncology*; 110: 45-8.
- Graeme K.A. and Pollack C.V. Jr. (1998). Heavy metal toxicity, Part I: Arsenic and mercury. *Journal of Emergency Medicine*, 16: 45-56.
- Greig J., Thurtle N., Cooney L., Ariti C., Ahmed A.O., Ashagre T., Ayela A., Chukwumalu K., Criado-Perez A., Gomez- Restrepo C., Meredith C., Neri A., Sfellmach D., Sani-Gwarzo N., Nasidi A., Shanks L. and Darga P.I. (2014). Association of blood lead level with neurological features in 972 children affected by an acute severe lead poisoning outbreak in Zamfara state, Northern Nigeria. *PLoS ONE* 9(4): e93716.
- Grimsrud T.K., Berge S.R., Haldorsen T. and Andersen A. (2002). Exposure to different forms of nickel and risk of lung cancer. *American Journal of Epidemiology*, 156: 1123-1132.
- Grimsrud T.K., Berge S.R. and Resmann S.R. (2000). Assessment of historical exposures in a nickel refinery in Norway. *Scandinavian Journal of Work, Environment and Health*, 26: 338-345.
- Grimsrud T.K., Berge S.R., Martinsen J.I. and Andersen A. (2003). Lung cancer incidence among Norwegian nickel-refinery workers 1953-2000. *Journal of Environmental Monitoring*, 5:190-197.
- Grimsrud T.K., Berge S.R., Haldorsen T. and Andersen A. (2005). Can lung cancer risk among nickel refinery workers be explained by occupational exposures other than nickel? *Epidemiology*, 16: 146-154.
- Grimsrud T.K. and Peto J. (2006). Persisting risk of nickel related lung cancer and nasal cancer among Clydach refiners. *Occupational and Environmental Medicine*, 63: 365-366.
- Guibal E. (2004). Interactions of metal ions with chitosan-based sorbents: a review. *Separation and Purification Technology*, 38: 43-74.
- Guixia Z., Xilin W., Xiaoli T. and Xiangke W. (2011). Sorption of heavy metal ions from aqueous Solutions: A Review. *The open Colloid Science Journal*, 4: 19-31.



- Guo X.Y., Zhang A.Z. and Shan X.Q. (2008). Adsorption of metal ions on lignin. *Journal of Hazardous Material*, 151: 134-142.
- Hala A.H. (2013). Removal of heavy metals from waste water using agricultural and industrial wastes as adsorbents. *House and Building National Research Centre Journal*, 9 (3): 276-282.
- Hameed B. H., Din A. T. M. and Ahmad A. L. (2007). Adsorption of methylene blue onto bamboo based activated carbon: Kinetic and equilibrium studies. *Journal of Hazardous Materials*, 141: 819-825.
- Hanawa T. (2004). Metal ion release from metal implants. *Material Science Engineering*, 24(68): 745-52.
- Harris G.K. and Shi X. (2003). Signaling by carcinogenic metals and metal-induced reactive oxygen species. *Mutation Resources*, 533: 183-200.
- Hartwig A., Asmuss M., and Ehleben I. (2002). Interference by toxic metal ions with DNA repair processes and cell cycle control: molecular mechanisms. *Environmental Health Perspective*, 110: 5797-799.
- Higgins S. J. (1995). Nickel. *Coordination Chemistry Reviews*, 146:115-201.
- Holtzman A. (1994). Cyanide and heavy metal removal: comparison of different chemistries with emphasis on an innovative new treatment method. *Advanced Chemical Technology, Inc.* Available from http://www.actglobal.net/products_wastewater_heavy_metals.htm. Accessed 07/07/2010.
- Horsfall M.J. and Ayebaemi I.S. (2005). Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by *Caladium bicolor* (wild cocoyam) biomass. *Electronic Journal of Biotechnology*, 8 (2): 612-169.
- Ho Y.S. and McKay G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Resources*, 34(3):735-742.
- Hussein H., Ibrahim S.F., Kandeel K. and Moawad H. (2004). Biosorption of heavy metals from waste water using *Pseudomonas sp.* *Electronic Journal of Biotechnology*, 7(1): 1-6.
- Hussein H., Farag S., Kandil K. and Moawad H. (2005). Resistance and uptake of heavy metals by *Pseudomonas*. *Process Biochemistry*, 40:955-961.
- Hussain I., Ullah R., Khurram M., Ullah N., Baseer A., Khan F.A., Khan N., Khattak M.R., Zahoor M. and Khan J. (2011). Heavy metals and inorganic constituents in medicinal plants selected Districts of Khyber Pakhtoonkhwa, Pakistan. *African Journal of Biotechnology*, 10(42): 517-8522.
- Idris S., Iyaka Y. A., Dauda B. E. N., Ndamitso M. M. and Umar M. T. (2012). Kinetic study of utilizing groundnut shell as an adsorbent in removing chromium and nickel from dye effluent. *American Chemical Science Journal*, 2(1): 12-24.
- Inove K.I. (2013). Heavy metal toxicity. *Journal of Clinical Toxicology*, 8(3):1-2.
- Jadhav D.N. and Vangara A.K. (2004). "Removal of phenol from wastewater using sawdust and sawdust carbon". *Indian Journal of Chemical Technology*, 11:35-45.
- Jadhav J.P., Parshetti G. K., Kalme S. D. and Govindwar S.P. (2007). Decolourization of azo dye methylred by *Saccharomyces cerevisiae*. *Chemosphere*, 68(2):494-500.
- Jain A.K., Gupta V.K., Bhatnagar A. and Suhas A. (2003). "Utilization of Industrial Waste Products as Adsorbents for the Removal of Dyes". *Journal of Hazardous Materials*. 101(1):31-42.
- Jarup L. (2003). Hazards of heavy metal contamination. *British Medical Journal*, 68: 167-182)
- Javaid A., Bajwa R., Shafique U. and Anwar J. (2011). Removal of heavy metals by adsorption on



- Pleurotus ostreatus*. *Biomass and Bioenergy*, 35:1675-1682.
- Jeyakumar R. P. and Chandrasekaran V. (2014). Adsorption of lead (II) ions by activated carbons prepared from marine green algae: equilibrium and kinetics studies. *International Journal of Industrial Chemistry*, 5 (2): 5547-5552.
- Jianlong W., Xinmin Z. and Yi Q. (2000). "Removal of Cr (vi) from aqueous solution by macroporous resin adsorption". *Journal of Environmental Science Health*, 5(7):1211- 1230.
- Jiwalak N., Rattanaphani S., Bremner J. B. and Rattanaphani V. (2010). Equilibrium and kinetic modeling of the adsorption of indigo carmine onto silk. *Fibers and Polymers*, 11 (4): 572-579.
- Kadirvelu K., Karthika C., Venilamani N. and Pattabhi S. (2005). Activated carbon prepared from industrial solid waste as an adsorbent for the removal of Rhodamine-B from aqueous solution: Kinetic and equilibrium studies. *Chemosphere* ,60:1009-1017.
- Kamran S., Shafaqat A., Samra H., Sana A., Samar F., Muhammad B. S., Saima A. B. and Hafiz M. T. (2013). Heavy Metals Contamination and what are the Impacts on Living Organisms. *Greener Journal of Environmental Management and Public Safety*, 2 (4): 172-179.
- Kanamadi R.D., Ahalya N. and Ramachandra T.V. (2006). Biosorption of Heavy metals by low cost Adsorbents. *Ces technical report*; 110 - 112.
- Kasprzak K.S., Sunderman F.W. Jr, and Salnikow K. (2003). Nickel carcinogenesis. *Mutation Resources*, 533: 67-97.
- Kaur R., Singh. J., Khare. R. and Ali. A. (2012). Biosorption the possible alternative to existing convectional technologies for sequestering heavy metal ions from aqueous streams: A review. *Universal Journal of Environmental Research Technology*, 2 (4): 325-335.
- Kawanishi S., Inoue S. and Oikawa S. (2001). Oxidative DNA damage in cultured cells and rat lungs by carcinogenic nickel compounds. *Free Radical and Biological Medicine*, 31: 108-116.
- Kawanishi S., Oikawa S., Inoue S. and Nishino K. (2002). Distinct mechanisms of oxidative DNA damage induced by carcinogenic nickel subsulfide and nickel oxides. *Environmental Health Perspective*, 110: 5789-5791.
- Kerfoot D.G.E. (2002). Nickel. In: Ullmann's *Encyclopedia of Industrial Chemistry*. Wiley VCH Verlag GmbH & Co.
- Keskinkan O., Goksu M.Z.L., Yusser A., Basibuyuk M. and Forstre C.F. (2003). Heavy metal adsorption characteristics of a submerged aquatic plant (*Myriophyllum spicatum*). *Process Biochemistry*, 39:179-183.
- Khelifi R. and Hamza-Chaffai A. (2010). Head and neck cancer due to heavy metal exposure via tobacco smoking and professional exposure: A review. *Toxicology and Applied Pharmacology*, 248: 71-88.
- Kratochvil D., Pimentel P., Volesky B. (1998). Removal of trivalent and hexavalent chromium by seaweed biosorbent. *Environmental Science Technology*, 32: 2693-2698.
- Kuck P.H. (2008). Nickel. In: Mineral commodity summaries. Reston, VA, US Geological Survey. Ref Type: Report.
- Kumar U. and Bandyopadhyay Y. (2006). Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology*, 97(1): 104-109.
- Kumar K.V. and Porkodi K. (2007). "Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum. notatum*" *Journal of Hazardous Material*, 146: 214-226.
- Kumar S.N., Venkata S.M., Subba R.A. and Krishnaiah A. (2009). Biosorption of phenolic



- compounds from aqueous solutions onto Chitosan abraspicatorius blended beads. *Journal of Chemical Technology and Biotechnology*, 84: 972-981.
- Kumar A., Bisht B. S. and Joshi V.D. (2012). Biosorption of Heavy Metals: A Review. *Journal of Biotechnology*, 5 (3): 7-21.
- Kumar S., Mishra A.K., Upadhyay M., Singh D., Mishra M. and Kumar S. (2014). Kinetic, thermodynamic and equilibrium study on removal of lead (II) from aqueous solution using fly ash. *International Resource Journal of Environmental Science*, 3(2): 83-92.
- Larry W. (2006). "World Water Day: A Billion People Worldwide Lack Safe Drinking Water". "A special report on India: Creaking, groaning: Infrastructure is India's biggest handicap"
- Lee Y.W., Klein C.B. and Kargacin B. (1995). Carcinogenic nickel silences gene expression by chromatin condensation and DNA methylation: a new model for epigenetic carcinogens. *Molecular Cell Biology*, 15: 2547-2557.
- Lee H.S. and Volesky B. (1997). Interaction of light metals and protons with seaweed biosorbent. *Water Resources*, 31: 3082-3088.
- Lee M., Paik I.S., Kim I., Kang H. and Lee S. (2007). Remediation of heavy metal contaminated groundwater originated from abandoned mine using lime and calcium carbonate. *Journal of Hazardous Materials*, 144(1-2): 208-214.
- Leikauf G.D. (2002). Hazardous air pollutants and asthma. *Environmental Health Perspective*, 110: 4505-526.
- Limousine G., Gaudet J.P., Charlet L., Szenlenect S., Barthes V. and Krimissa M. (2007). Sorption Isotherms: Physical Bases, Modeling and Management. *Applied Geochemistry*, 22: 249-275.
- Lin K. C. and Chou I. N. (1990). Studies on the mechanisms of Ni²⁺-induced cell injury: In Effects of Ni²⁺ on Microtubules. *Toxicology and Applied Pharmacology*, 106:209-221.
- Lone M.I., HE Z., Stoffella P.J. and Yang X. (2008). Phytoremediation of heavy metals polluted soils and water: progress and perspectives. *Universal Science*, 9(3): 210-220.
- Longe E.O. and Balogun M.R. (2010): Groundwater quality assessment near a municipal landfill, Lagos, Nigeria. *Research Journal of Applied Sciences, Engineering and Technology*, 2: 39-44.
- Lu H., Shi X., Costa M. and Huang C. (2005). Carcinogenic effect of nickel compounds. *Molecular Cell Biochemistry*, 279:45-67.
- Madaan N. and Mudgal V. (2009). Differential tolerance behaviour of safflower accessions to some heavy metals. *International Journal of Applied Environmental Science*, 4(4):413-420.
- Majumder M., Roy P., Barman R.N. and Mazumder A. (2010). *Impact of Climate Change on Natural Resource Management*. Springer Science, Pp 203-205.
- Mandour R. A. (2012). Human health impacts of drinking water (surface and ground) pollution Dakahlyia Governorate, Egypt. *Applied Water Science* (2012) 2:157-163. DOI 10.1007/s13201-012-0041-6
- Martin-Gonzalez A., Diaz S., Borniquel S., Gallego A. and Gutierrez J.C. (2006). Cytotoxicity and bioaccumulation of heavy metals by ciliated protozoa isolated from urban wastewater treatment plants. *Resource Microbiology*, 157: 108-118.
- Matlock M.M., Howerton B.S. and Atwood D.A. (2002). Chemical precipitation of heavy metals from acid mine drainage. *Water Resources*, 36(19): 4757-4764.
- Mbadcam J.K., Anagho S.G., Nsami J.N. and Kammegne A.M. (2011). Kinetic and equilibrium studies of the adsorption of lead (II) ions from aqueous solution onto two Cameroon clays: kaolinite and smectite.



- Journal of Environmental Chemistry and Ecotoxicology*, 3(11): 290-297.
- Mehdizadeh S., Sadjadi S., Ahmadi S.J. and Outokesh. (2014). Removal of heavy metals from aqueous solution using platinum nanoparticles/Zeolite-4A. *Journal of Environmental Health Science and Engineering*, 12 (7):1-7.
- Miretzky P. and Cirelli A.F. (2009). Hg (II) removal from water by chitosan and chitosan derivatives: A review. *Journal of Hazardous Matter*, 167: 10-23.
- Moor M.R. (2004). A commentary on the impacts of metals and metalloids in the environment upon the metabolism of drugs and chemicals. *Toxicology Letter*. 148:153-158.
- Mousavi H.Z., Hosseynifar A., Jaheed V. and Dehghani S.A. (2010a). "Removal of Lead from Aqueous Solution using Waste Tire Rubber Ash as Adsorbent". *Brazilian Journal of Chemical Engineering*, 27(1):79-87.
- Mudgal V., Madaan N. and Mudgal A. (2010). Heavy metals in plants: phytoremediation: plants used to remediate heavy metal pollution. *Agricultural and Biological Journal*, 1(1): 40-46.
- Mulu B.D. (2013). Batch Sorption Experiments: Langmuir and Freundlich Isotherm studies for the Adsorption of textile metal ions onto Teff straw (*Eragrostis tef*) Agricultural waste. *Journal of Thermodynamics*, 13: 1-6.
- NEESA. (1993). Precipitation of metals from ground water. NEESA Document Number 20.2051.6, Novel Energy and Environmental Support Activity, Port Hueneme, CA.
- Neto V.O.S., Oliveira A.G., Teixeira R.N.P., Silva M.A., Freire P.T.C., Keukeire D.D. and Nascimento R.F. (2011). Evaluation of two biosorbents in removal of metal ions in aqueous solution using a pilot scale fixed -bed system. *Bio Resources*, 6: 3376-3395.
- Neto V.D.S., Rauilino G.S.C., Freire P.T.C., Silva M.A. and Nascimento R.F. (2013). "Equilibrium and kinetic ions for waste water treatment In: Surface Modification of Biopolymers. John Willy and Sons. pp 163.
- Ngah W.S. and Hanafiah M.A.K. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology*, 99: 3935-3948.
- Nollet H., Roels M., Lutgen P., Meeren P. V. and Verstraete W. (2003). *Chemosphere*, 53: 655.
- Nomanbhay S.M. and Palanisamy K. (2005). Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology*, 8(1): 15.
- Nor A.R., Suzana Y. and Lam H.L. (2013). Kinetic Studies on Carbon Dioxide Capturing using Activated Carbon. *Chemical Engineering Transactions*, 35:361-367.
- Norton L., Baskaran K. and McKenzie T. (2003). Biosorption of zinc from aqueous solutions using biosolids, *Advanced Environmental Resources*, 8: 629-635.
- NTP. (2000). Final Report on Carcinogens Background Document for Metallic Nickel and Certain Nickel Alloys. Research Triangle Park, NC.
- Ogunleye O. O., Adio O. and Salawudeen T. O. (2014). Removal of lead (II) from aqueous solution using banana (*Musa paradisiaca*) stalk-based activated carbon. *Chemical and Process Engineering Research*, 28: 45-60.
- Ohshima S. (2003). Induction of genetic instability and chromosomal instability by nickel sulfate in V79 Chinese hamster cells. *Mutagenesis*; 18: 133-137.
- Ojarjarvi I.A., Partanen T.J. and Ahlbom A. (2000). Occupational exposures and pancreatic cancer: a metal analysis. *Occupational and Environmental Medicine*; 57: 316-324.



- Oliveira J.P., de Siqueira M.E. and da Silva C.S. (2000). Urinary nickel as bio indicator of workers' Ni exposure in a galvanizing plant in Brazil. *International Arch Occupational and Environmental Health*, 73: 65–68.
- Oller A.R. and Erexson G. (2007). Lack of micronuclei formation in bone marrow of rats after repeated oral exposure to nickel sulfate hexahydrate. *Mutation Resources*, 626: 102–110.
- Okuda J. and Iida K. (2005). Preparation of a “chronological table of main diseases in Japanese history” for pharmacy students of the 6-year program. *Yakushigaku Zasshi*, 40: 137–146.
- Onundi Y. B., Mamun A. A., Al Khatib M. F. and Ahmed Y. M. (2010). Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon. *International Journal of Environmental Science and Technology*, 7 (4): 751–758.
- Osredkar J., Bernard Z., Darja K.G., Mladen K., Saso D., Milena H. and Alfred B.K. (2005). Analysis of the Relationship between Pineal Hormone Melatonin Level and Occupational Mercury Exposure in Ex-miners with machine learning methods. *Metodoloski Zvezki*; 2(1):161–172.
- Pagnanelli F., Mainelli S., Vegli F. and Toro L. (2003). Heavy metal removal by olive pomace: biosorbent characterisation and equilibrium modeling. *Chemical Engineering Science*, 58: 4709–4717.
- Pawlak Z., Zak S. and Zablocki L. (2005). Removal of hazardous metals from groundwater by reverse osmosis. *Journal of Pollution and Environmental Studies*; 15(4): 579–583.
- Pivetz B.E. (2001). Phytoremediation of contaminated soil and groundwater at hazardous waste sites. *EPA Ground Water*; EPA/540/S-01/500.
- Quick S.Y., Wase D.A. and Forster C.F. (1998). The use of sago waste for the sorption of lead and copper, *Water SA* 24, Pp 251–256.
- Ramya R., Sankar P., Anbalagan S. and Sudha P.N. (2011). Adsorption of Cu (II) and Ni (II) ions from metal solution using cross linked chitosan acrylonitrile copolymer. *International Journal of environmental Science*, 1 (6):1323–1338.
- Reddy Y.S., Pullakhandam R. and Radhakrishna K.V. (2011). Lead and essential trace element levels in school children: A cross-sectional study. *Annals of Human Biology*; 38:372–377.
- Rydh C.J. and Svard B. (2003). Impact on global metal flows arising from the use of portable chargeable batteries. *Science of Total Environment*, 302: 167–184.
- Sag Y. and Kutsal T. (2000). “Determination of the biosorption heats of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus*”. *Biochemical Engineering Journal*, 6: 145–151.
- Salnikow K., Su W., Blagosklonny M.V. and Costa M. (2000). Carcinogenic metals induce hypoxia-inducible factor stimulated transcription by reactive oxygen species independent mechanism. *Cancer Resources*, 60: 3375–3378.
- Salnikow K. and Zhitkovich A. (2008). Genetic and epigenetic mechanisms in metal carcinogenesis and cocarcinogenesis: nickel, arsenic, and chromium. *Chemical Resources Toxicology*, 21: 28–44.
- Santos E.E., Lauria D.C. and Porto da Silveira C.L. (2004). Assessment of daily intake of trace elements due to consumption of foodstuffs by adult inhabitants of Rio de Janeiro city. *Science of Total Environment*, 327: 69–79.
- Sarin V. and Pant K.K. (2006). Removal of chromium from industrial waste by using eucalyptus bark. *Bioresource Technology*, 97(1):15–20.



- Schmidt E., Lolter M. and McClelland W. (2002). Trees and Shrubs of Mpumalaga and Kruger National Park, Pp 702.
- Schoof R. A. (2003a). Guide for incorporating bioavailability adjustments into human health and ecological risk assessments at U.S. Department of Defense facilities. Part 1: Overview of metals bioavailability Washington DC: Naval Facilities Engineering Service Center, Air Force Center for Environmental Excellence, and Army Environmental Center.
- Schoof R. A. (2003b). Guide for incorporating bioavailability adjustments into human health and ecological risk assessments at U.S. Department of Defense facilities. Part 2: Technical background document for assessing metals bioavailability Washington DC: Naval Facilities Engineering Service Center, Air Force Center for Environmental Excellence, and Army Environmental Center.
- Schueler O. and Thomas R. (2000). "Microbes and Urban Watersheds: Concentrations, Sources, and Pathways." Reprinted in *The Practice of Watershed Protection*. Center for Watershed Protection. Ellicott City, MD.
- Schwerdtle T. and Hartwig A. (2006). Bioavailability and genotoxicity of soluble and particulate nickel compounds in cultured human lung cells. *Materialwiss Werkstofftech*, 37: 521-525.
- Seilkop S. (2002). Occupational exposures and pancreatic cancer. *Occupation and Environmental Medicine*, 58: 63-64.
- Selman M.S., Greenhalgh R.D. and Suggy Z. (2008). Eutrophication and hypoxia in coastal area: A Global Assessment of the State of knowledge. Water quality: Eutrophication and Hypoxia Policy Note Series No.1. Washington, DC: World Resource Institute.
- Senarathne P. and Pathiratne K.A.S. (2007). Accumulation of heavy metals in a food fish *Mystus gulio* inhabiting Bolgoda lake, Srialanka. *Srialankan Journal of aquatic Science*, 12:61-75
- Seoane A.I. and Dulout F.N. (2001). Genotoxic ability of cadmium, chromium and nickel salts studied by kinetochore staining in the cytokinesis-blocked micronucleus assay. *Mutation Resources*, 490: 99-106.
- Serin I.S., Ozcelik B., Basbug M., Aygen E., Kula M., and Erez R. (2011). Long term effects of continuous oral and transdermal estrogen replacement therapy on sex hormone binding globulin and free testosterone levels. *European Journal of Obstetrics, Gynaecology and reproductive biology*, 99 (2): 222-225.
- Shah M., Chandalia M., Adam-Huet B., Brinkley L.J., Sakhaee K., Grundy S.M. and Garg A. (2009). Effect of a high-fibre diet compared with a moderate-fibre diet on calcium and other mineral balances in subjects with type 2 diabetes. *Diabetes care*, 32 (6): 990-995.
- Shalini S. and Pritee G. (2010). Metal decontamination: techniques used so far. *Environmental Science and Engineering*, 10:21-29.
- Silva A.O., Paulo R.G.B., Silvana C.T. and Josino C.M. (2005). Exposure to heavy metals. *Brazilian Journal of Plant Physiology*, 17 (1):93-97.
- Sivulka D.J. (2005). Assessment of respiratory carcinogenicity associated with exposure to metallic nickel: a review. *Regulatory Toxicology Pharmacology*, 43: 117-133.
- Stern B.R. (2007). "Copper and Human Health, Biochemistry, genetics, and strategies for modeling dose response relationships". *Journal of Toxicology and environmental Health*, 10 (3): 157 - 222.
- Stern B.R. (2010). "Essentiality and toxicity in copper health risk assessment overview, update and regulatory consideration". *Journal of Toxicology and environmental Health*, 73 (2-3): 114-127.



- Steve K., Erika T., Reynolds T. and Paul M. (1998). "Activated Carbon; A unit operations and processes of activated carbon. *Environmental Engineering*, 25: 350-749.
- Sunderman F. W., Jr., Varghese A. H., Kroftova O. S., Grbac-Ivankovic S., Kotyza A. K., Sunilson J.A.J, Rejitha G. and Anandarajagopal K. (2009). Cytotoxic effect of cayratia carnosa leaves on human breast cancer cell lines. *International Journal of Cancer Resources*, 5: 1-7.
- Teoh Y. P., Khan M.A. and Choong T.S.Y. (2013). Kinetic and isotherm studies for lead adsorption from aqueous phase on carbon coated monolith. *Chemical Engineering Journal*, 217:248 – 255.
- Thompson M. (2010). *Piliostigma thonninSgii*. Walter Sisulu National Botanical Garden, South Africa. <http://www.plantzafrica.com/> Accessed on 12/2/2015.
- Tichaona N. and Jacob N.T. (2013). Single and binary sorption of lead (II) and zinc (II) ions onto *Eichhornia crassipes* (water hyacinth) ash. *International Journal of Engineering Science and Innovative Technology*, 2(4): 419-426.
- Tirima S, Bartrem C, von Lindern I, von Braun M, Lind D, Anka SM, Abdullahi A. 2016. Environmental remediation to address childhood lead poisoning epidemic due to artisanal gold mining in Zamfara, Nigeria. *Environ Health Perspective* 124:1471-1478; <http://dx.doi.org/10.1289/ehp.1510145>
- Tshai W.T. and Chen H.R. (2010). Removal of malachite green from aqueous solution using low cost chlorellabased biomass. *Journal of Hazardous Material*, 175 (1-3): 844-849.
- Tundermann J.H., Tien J.K. and Howson T.E. (2005). Nickel and nickel alloys. In: Kirk-Othmer Encyclopedia of Chemical Technology. Volume 17. (online edition)
- Umanzor J., Aguiluz M. and Pineda C. (2006). Concurrent cisplatin/gemcitabine chemotherapy along with radiotherapy in locally advanced cervical carcinoma: A phase II trial. *Gynecology Oncology*, 100: 70-5.
- USDA (2000). Heavy metal soil contamination. United States Department of Agriculture, Soil Quality Institute, Urban Technical Note No. 3: 1-7.
- USEPA. (2000). Wastewater technology sheet: chemical precipitation. United State Environmental Protection, EPA 832-F-00-018. Available from http://www.epa.gov/own/mtb/chemical_precipitation.pdf. Accessed 07/07/2010.
- United States Environmental Protection Agency. (2007). Washington, DC. "The National Water Quality Inventory; Report to Congress for the 2002 Reporting cycle-A Profile." Fact Sheet No EPA 841-F-07-003.
- United States Environmental Protection Agency. (2007). Developing your storm water pollution Prevention plan; a guide for construction sites. EPA 833.R.06.004.
- Uzun A., Soylak M. and Elçi L. (2001). Preconcentration and separation with Amberlite XAD-4 resin; determination of Cu, Fe, Pb, Ni, Cd and Bi at trace levels in waste water samples by flame atomic absorption spectrometry. *Talanta*, 54: 197-202.
- Vaca M.V., Callejas R.L.P., Gehr R., Cisneros B.J.N. and Alvarez P.J.J. (2001). Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange. *Water Resources*, 35(2): 373-377.
- Van W. A.E. and Van W.P. (1997). *Field Guide to Trees of Southern Africa*. Struik, Cape Town.
- Varsha M., Nidhi M., Anurag M., Singh R.B. and Sanjay M. (2010). Effect of toxic metals on human health. *The Open Nutraceuticals Journal*, 3:94-99.
- Venckatesh R., Amudha T., Rajeshwari S., Chandramohan M. and Jambulingam M. (2010). Kinetics and equilibrium studies of adsorption of direct red-28 onto *Punica*



- granatum* carbon. *International Journal of Engineering Science and Technology*, 2(6): 2040-2050.
- Venter S. and Venter J.A. (1996). *Making the most of Indigenous trees*. Briza Publications, Pretoria.
- Volesky B. (2003). Sorption and Biosorption. BV-Sorbex, Inc., St.Lambert (Montreal), Quebec, Canada, pp.103-123.
- Wang X. S. and Qin Y. (2005). "Equilibrium sorption isotherms for of Cu ²⁺ on rice bran". *Process Biochemistry*, 40:677-680.
- Wang J., Qin Q.H. and Kang Y. (2005). A new meshless method for steady-state heat conduction problems in anisotropic and inhomogenous media. *Archive of Applied Mechanics*, 74(8): 563-579.
- Wen Q. L., Shao-H. X., Wen S. Z., Shao H Z. and Ai L. L. (2008). Water Pollution and Health Impact in China: A Mini Review. *Open Environmental Science Journal*, 2:3.
- Wise A. and Gilbert D.I. (1981). Binding of cadmium and lead to the calcium-phytate complex invitro. *Toxicology Letters*, 9: 45-50.
- World Health Organization, (WHO). (1991). Nickel. Environmental Health Criteria 108. 383.
- World Health Organization, (WHO). (2003). Copper in drinking water; Background document for preparation of WHO Guidelines for drinking water quality. Geneva, World Health Organization (WHO/SDE/WSH/03.04/88).
- World Health Organization, (WHO). (2007). Nickel in Drinking Water. ITS/SDE/WSH/07.08/55. Geneva: World Health Organization.
- Woźniak K. and Błasiak J. (2002). Free radicals-mediated induction of oxidized DNA bases and DNA-protein cross-links by nickel chloride. *Mutation Resources*, 514: 233-243.
- Yorifuji T., Tsada T., Takao S. and Harada M. (2008). Long-term exposure to methyl mercury and neurologic signs in Minamata and neighbouring communities. *Epidemiology*, 19(1): 3-9.
- Zoroddu M.A., Schinocca L. and Kowalik-Jankowska T. (2002). Molecular mechanisms in nickel carcinogenesis: modeling Ni (II) binding site in histone H4. *Environmental Health Perspectives*, 110: 5719-723.
- Zou H., Xu X., Zhang J. and Zhu Z. (1995). The determination of strong mutagen MX [3chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone] in Drinking Water in China. *Chemosphere*, 30(12): 2219-2225.