Int. J. Electrochem. Sci., 7 **(2012)** 12354 - 12369

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Adsorption Capacity of Coconut *(Cocos nucifera L.)* Shell for Lead, Copper, Cadmium and Arsenic from Aqueous Solutions

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Received: 13 October 2012 / *Accepted:* 7 November 2012 / *Published:* 1 December 2012

This study explored the adsorption capacity of Coconut (*Cocos nucifera L.*) shell for Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} from aqueous solutions. The effect of various operational parameters such as concentration, pH, temperature and sorption time on the adsorption of Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} was investigated using batch process experiments. It was found that coconut shell (CNS) can be used as a low cost adsorbent for the removal of heavy metals in aqueous solution containing low concentrations of the metals. The maximum ion adsorption capacities followed the trend $Pb^{2+}>Cu^{2+}>Cd^{2+}>As^{3+}$ and the percentage adsorption was found to depend on the concentration of the adsorbent present, the solution pH, temperature and the sorption. The average values of the activation energy of adsorption for CNS were 7.99, 3.79, 10.24 and 53.977KJ/mol for Pb, Cu, Cd and As respectively. This shows that the adsorption of metal ions on the adsorbent is physical adsorption mechanism. Kinetic treatment of the results gave a pseudo-second order type of mechanism while the adsorption characteristics of the adsorbent followed the Freundlich adsorption isotherm.

Keywords: Adsorption; Coconut shell; Adsorption capacity; Aqueous solutions; Freundlich isotherm

1. INTRODUCTION

Water pollution, contamination of streams, lakes, underground water, bays or oceans by substances harmful to living things as a result of increasing technological development and industrialization has been known to disrupt and destroy the fragile ecology through indiscriminate discharge of industrial and municipal wastes into the sea. The composition of industrial waste cannot be readily characterized by a typical range of values because its makeup depends on the type of manufacturing process involved. Sewage, industrial wastes and agricultural chemicals such as fertilizers and pesticides are the main causes of water pollution. The development of industries such as paint, coating, smelting and electric battery manufacturing, alloy preparation, wood preservation, plating, tanning, corrosion inhibition has resulted in heavy metals finding its way into natural bodies of water. These metals are potentially toxic as reported by Goyer and Chisolon [1] and Assenato *et al*. [2].

In recent years, management of pollution caused by heavy metals has been a major problem especially in developing countries. The introduction of heavy metals into the body of water and subsequently the consumption of it by human and other living things lead to hazardous effects such as blood and brain disorders (especially in young children), nephropathy, colic–like abdominal pains and miscarriage, as in the case of lead [3]. Cadmium and solutions of its compound are highly toxic, with cumulative effects causing irreversible brain, liver and kidney damage [4].

Arsenic is poisonous in doses significantly larger than 65 mg (1 gram) and the poisoning can arise from a single larger dose or from repeated small doses, as for example, inhalation of arsenical gases or dust. These metals are known to progressively accumulate in our ecosystem once they are introduced, from very low levels to levels that exceed the threshold in the environment. Most of these metals such as cadmium, lead, arsenic, mercury, copper, chromium, cobalt and nickel are very toxic. They are carcinogenic and at very high concentrations, may lead to brain damage [5]. So their removals from industrial waste waters remain an important challenge.

In spite of the hazards associated with these metals, a number of industries indiscriminately dispose of their waste containing metals directly into the environment, especially in the water bodies (streams, lake, river etc). Also, through the use of domestic antiseptic soaps and pesticides on our farms, these poisonous substances are washed into the water bodies [6]. Consequently, these metals accumulate in aquatic biotas which inhabit these water bodies. Feeding on these aquatic animals such as fishes, and use of the contaminated water for drinking and cooking purposes can lead to poisoning of humans [7-8].

Unlike organic pollutants, heavy metals do not biodegrade and thus, pose a different kind of challenge for remediation. To alleviate the problem of water pollution by heavy metals, various methods have been used to remove them from waste water as chemical precipitation, coagulation, floatation, adsorption, ion exchange, reverse osmosis and electrodialysis [9-11]. The production of the sludge in the precipitation methods poses challenges in handling treatment and hand filling of the solid sludge. Ion exchange usually requires a high – capital investment for the equipment as well as high operational cost. Electrolysis allows the removal of metal ions with the advantage that there is no need for additional chemicals and also there is no sludge generation. However, it is inefficient at a low metal concentration. Membrane processes such as reverse osmosis and electrodialysis tend to suffer from the in-stability of the membranes in salty or acidic conditions and fouling by inorganic and organic substances present in waste water [12]. Most of these techniques have some pretreatments and additional treatments. In addition, some of them are less effective and require high cost [13].

It was only in the 1990s that a new scientific area, biosorption was developed that could help in the recovery of heavy metals. The first reports described how abundant biological materials could be used to remove, at very low cost, even small amounts of toxic heavy metals from industrial effluents [13-15]. Metal-sequestering properties of non-viable microbial biomass provide a basis for a new approach to the removal of heavy metals when they occur at low concentrations [13]. Therefore, many researchers have applied regenerated wastes to treat heavy metals from aqueous solutions [16-19].

According to Volesky and Holan [20], the assessment of the metal-binding capacity of some types of biomass has gained momentum since 1985. Abundant natural materials, particularly of cellulosic nature, have been suggested as potential bio-sorbents for heavy metals. Indeed, some biomass types are very effective in accumulating heavy metals. The economy of environmental remediation dictates that the biomass used for clean-up purposes should be abundantly available and must come from nature or even has to be a waste material [21]. Seaweeds, molds, yeasts, bacteria, crab shells, periwinkle shells among other kinds of biomass, have been tested for metal adsorption with very encouraging results [6, 22]. Considering the number of biomass types, metals of interest and the number of experimental or process parameters, the task of prospecting for new and potentially feasible adsorbents has a very wide scope.

The coconut palm, *Cocos nucifera*, is a member of the *plantae* order- *Arecales* of the Family *Arecaceae* (Palm family). It is only accepted species in the genus cocos. The term coconut can refer to the entire coconut palm, the seed, or the fruit which is not a botanical nut but a drupe [23]. Like other fruits it has layers: exocarp, mesocarp, and endocarp. The exocarp and mesocarp make up the husk of the coconut, and the mesocarp itself is composed of fibers called coir which have many traditional and commercial uses.

Found across much of the tropical and subtropical area, the coconut is known for its great versatility as seen in any domestic, commercial and industrial uses of its different parts. Coconut is part of the daily diet of many people. It is known as the edible flesh of the coconut; when dried it is called the copra. The oil and milk derived from it are commonly used in cooking and frying; coconut oil is also widely used in soaps and cosmetics. The clear liquid coconut water within is a refreshing drink and can be processed to create alcohol. The husks and leaves can be used as material to make a variety of products for furnishing and decorating, while the coconut coir dust have been used as raw material for activated carbon industries.

Coconut coir dust is one of the agricultural waste products often used as adsorbent in waste water treatment. It’s all year round availability and its abundance in the environment makes it a good source of adsorbent for metal ion removal from aqueous solution. It is the light, fluffy material that falls off from the thick mesocarp of coconut fruit when shredded during coir processing. The re-markable properties of coir dust that enhances its effectiveness as adsorptive/ion exchange capacities include good structural stability, high water absorptivity and high porous nature [24]]. Its constitutents include ligmin-36.15%, cellulose-33.61%, pentosana-29.27%, ash-0.61%, dry basis [25].

The other constituents are kemicelluloses and extractives. These extractives contain tannins, pectins, with polyhenolic, carboxyl and hydroxyl groups. Ligmins and cellulose in the coir affords its adsorptive/ion exchange properties. The porous structure of the coir dust allows it to absorb large amount of water but still, remain insoluble very much like any synthetic hydrogel [26].

This study was carried out using *Cocos nucifera L.* (coconut) shell powder as the adsorbents for the removal of lead, copper, cadmium and arsenic from aqueous solutions.

2. MATERIALS AND METHOD

2.1 Coconut (Cocos nucifera) shell

Coconut fruits were bought at Nsidung (beach) Market, Calabar and selectively picked and the endosperm (copra) was separated from the shell. The shell was soaked for about one hour in water, well scrubbed using a sponge and tap water and then sun dried for three (3) hours. The dried shell was then placed on a clean hard surface and broken into smaller pieces with the use of a hammer. These smaller pieces were further dried in an N53C-Genlab laboratory oven at 200^{o}C for three hours, grounded to fine particles using the manual grinding machine and sieved with sifter to obtain 120 mm (micrometer mesh) finer dust particles. The finer dust particles were re-introduced into an oven at a temperature of 30^{o}C for 30 minutes and then preserved in a sample container for future use.

2.2. Aqueous solution of heavy metal

All reagents used for this study were analytical reagent grade and were procured from Vikam Scientific Surplier, U.J Esuene Stadium, Calabar. 1000 mg/l aqueous solutions of the metals ions were prepared as stock from their salts ($CuSO_4$, AS_2O_3, $Pb(NO_3)_2$ and $CdSO_4$). From the stock, working solutions of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l were prepared from appropriate aliquots diluted to the appropriate concentration. The total concentration of each metal ion in the aqueous solution was confirmed by analysis using (Unicam thermo/solar system 2009 model) Atomic Adsorption Spectrometer (AAS).

2.3. Experimental procedure

Batch adsorption experiments were carried out to study the effect of initial metals ion concentration, contact time and temperature on the adsorption of Cu^{2+}, As^{3+}, Pb^{2+} and Cd^{2+} on coconut shell. Adsorption studies were carried out using 25 ml of each metal ion solution and 0.5 g of the adsorbent. At the end of each experiment, the content of each tube was filtered using a Whatman No 14 filter paper after which the concentration of residual metal ions in each filtrate was determined. All experiments were carefully conducted to acquire good result.

2.4.Variation of initial metal ion concentration

Batch adsorption was carried out using initial metal ion concentrations of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l each for aqueous solution of Cu, As, Pb and Cd ions. 0.5 g adsorbent (coconut shell) were weighed into each of the four (100 mls) beakers and 25 ml of 0.5 mg/l solution of each metals was measured into beakers. The adsorption mixtures were uniformly and continuously agitated with the use of a platform shaker at a fixed temperature of 30^{o}C for 30 minutes after which the content of each beaker was filtered into clean sample bottles. A thermostated water-bath was used to maintain the temperature. The concentration of residual metals ions in the filtrates was determined using AAS. The amount of metal ions adsorbed from the solution was determined by difference.

2.5.Variation of contact time

The adsorption of the metal ions on coconut shell was studied at various time intervals (0-180 min). Kinetic sorption studies were carried out using 25 ml of each metal ion solution with initial metal ion concentration of 0.5 mg/l. The metal ions solutions were measured into four labeled beakers each containing 0.5 g of the adsorbent. The mixtures were uniformly agitated at 30^{o}C for 30 minutes. The experimental setup was thereafter repeated for various time intervals of 60, 90, 120, 150 and 180 minutes. At the end of each contact time, the content of each tube was centrifuged and filtered. The concentration of metal ions in the filtrates was determined using AAS and the amount of metal ions adsorbed was calculated.

2.6. Variation of temperature

The adsorption of the metal ions on coconut shell was studied at various temperatures (30-60^{o}C) with the use of a thermostated water bath. Kinetic sorption studies were carried out using 25 ml of each metals ion solution of initial concentration 0.5 mg/l. The metal ion solutions were measured into 4 labeled beakers each containing 0.5 g of the adsorbent. The mixtures were uniformly agitated at 30^{o}C for 30 minutes. The experimental setup was repeated for 40-60^{o}C. At the end of each contact time, the content of each beaker was the filtered and the residual concentration of metal ions in the filtrates were determined using AAS and the amount of metal ions adsorbed was calculated.

2.7. Variation of pH value

The adsorption of the metal ions on coconut shell, were studied at various pH (2, 6, 8, 10). Kinetic sorption studies were carried out using 25 ml of each metal ion solution with initial metal concentration of 0.5 mg/l. The metal ion solutions were measured into four labeled beakers each containing 0.5 g of the adsorbent. The mixtures were uniformly agitated at 30^{o}C for 30 minutes.

At the end of each pH analysis, the content of each tube was centrifuged and filtered. The concentration of metal ions in the filtrates was determined using an AAS, and the amount of metal ions adsorbed was calculated.

3. RESULTS AND DISCUSSION

3.1. Effect of concentration on the removal of $Pb^{2+,}$ Cu^{2+}, Cd^{2+} and As^{3+} solutions

The effect of initial concentration of metal ions on metal ion adsorbed by CNS was studied at 30^{o}C. It was found that the concentration of metals ions adsorbed increased with increase in initial metal ion concentration as shown in Table 1. This is due to the fact that as the concentration is increased, more metal ions are available in the solution for the adsorption process [27]. Fig. 1 shows the variation of quantity of metal ions adsorbed (y_t) by CNS with concentration. It was observed that y_t increased with increase in metal ion concentration, and that the rate of adsorption with respect to concentration was uniform and progressive in all the ions except for cadmium ion in Fig 1 which had an initial slow adsorption rate probably due to a low activation energy needed to kick start the reaction, and copper ion on CNS (Fig.1) which adsorption stops even at an increase of concentration from 4 mg/l to 5 mg/l (a possibility of the surface of the adsorbent being saturated).

Table 1. Concentration of the metal ions adsorbed (Y_t) at various concentration at 30°C and ambient pH by coconut (CNS) shell

Concentration (mgl^{-1})	Y_t (mgl^{-1})			
	Pb^{2+}	Cu^{2+}	Cd^{2+}	As^{3+}
0.5	0.309	0.355	0.046	0.090
1.0	0.819	0.428	0.046	0.246
2.0	1.786	1.076	0.444	0.722
3.0	2.730	1.946	2.571	1.324
4.0	3.757	2.924	3.578	1.815
5.0	4.720	2.924	4.566	2.019

3.2.Effect of contact time on the removal of $Pb^{2+,}$ Cu^{2+}, Cd^{2+} and As^{3+} solutions

The adsorption of Cu^{2+}, Pb^{2+} , Cd^{2+} and As^{2+} CNS was studied as a function of time in order to find out the equilibrium time required for maximum adsorption of metallic ions. Table 2 and Fig. 2 show the adsorption of the metallic ions using CNS. It is observed that the concentration of metal ions adsorbed on the coconut CNS increased with time. This is also due to the migration of higher fraction of the metal ions from the bulk solution through the adsorbent boundary layer onto the active sites of the adsorbent as time progresses [6]. This enhanced sorption of the metal ion with increase in agitation time may be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in kinetic energy of the hydrated metal ions [6]. The removal of metal ions by CNS could also be due to difference in sorption processes: ion- exchange, adsorption (physisorption/chemisorptions) co-ordination, complexion as a result of the various types of ion binding groups such as hydroxyl, carboxylic, phenolic functional groups in CNS.

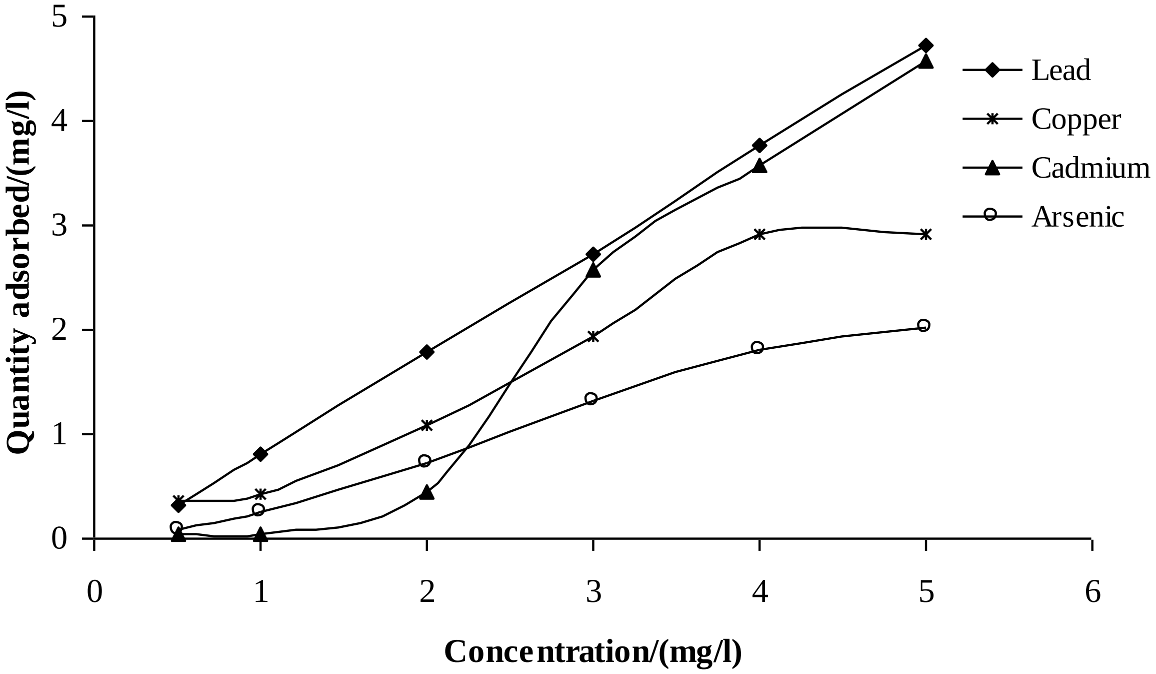

Figure 1. Variation of quantity of ion adsorbed by coconut shell with concentration of metal ions at 30°C

The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depends on the surface area of the adsorbents. The Pb^{2+} and Cu^{2+} adsorption took place at the more reactive sites. As these sites were progressively filled, the more difficult the sorption becomes, as the sorption process tend to be more unfavourable. This is the general characteristics of adsorption of metal ions [28-32]. The quantity of metal ions adsorbed follow the trend Cu^{2+} >Pb^{2+} >Cd^{2+}>As^{3+} for CNS.

Table 2. Concentration of the metal ions adsorbed (Y_t) at various time interval at 30°C and ambient pH by coconut (CNS) shell

Time (min.)	Y_t (mgl^{-1})			
	Pb^{2+}	Cu^{2+}	Cd^{2+}	As^{3+}
30	0.106	0.283	0.056	0.041
60	0.228	0.426	0.058	0.052
90	0.242	0.427	0.059	0.055
120	0.272	0.428	0.064	0.063
150	0.341	0.442	0.086	0.064
180	0.347	0.483	0.099	0.065

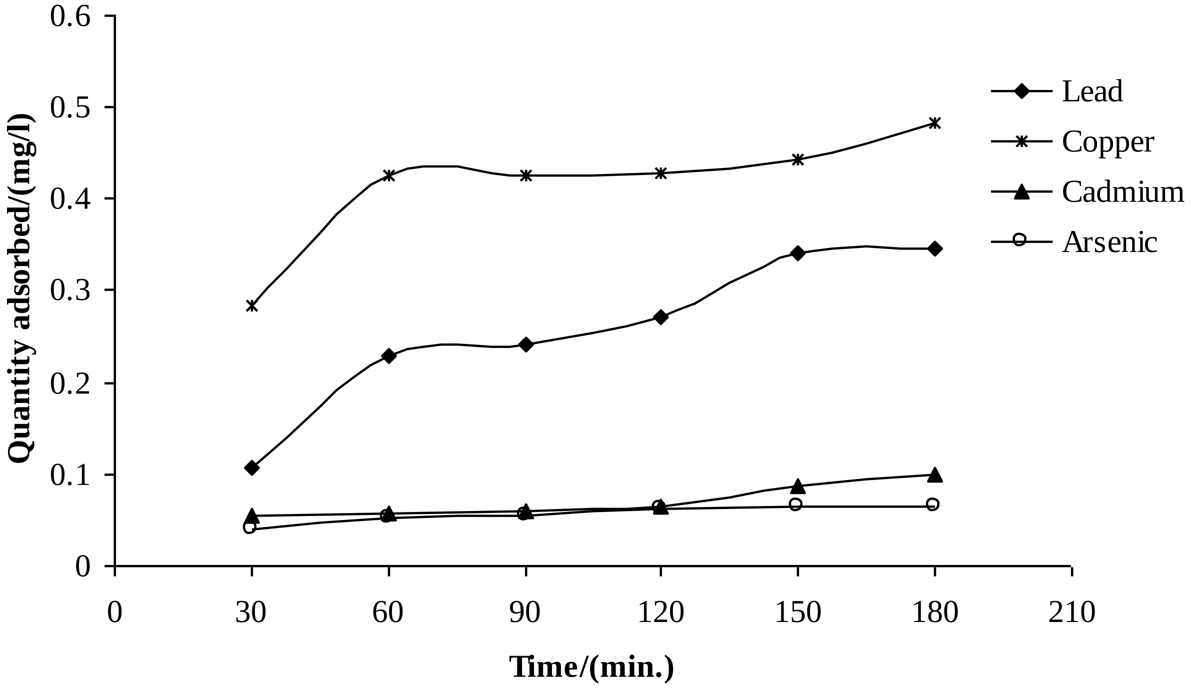

Figure 2. Variation of quantity of ion adsorbed by coconut shell with time at 30°C

3.3. Effect of temperature on the removal of Pb^{2+}, Cu^{2+}, Cd^{2+}, and As^{3+}, from solutions

Temperature can affect the adsorption behavior of metallic ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, As^{3+}) in solutions. The effect of temperature on the adsorption of Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} from solutions containing CNS was studied at a concentration of 0.5 mg/l for 30 minutes. Table 3 and FIG. 3 show that the removal of Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} from aqueous solution by CNS is temperature dependent. Increase in temperature from 30°C to 60°C was found to result in a steady increase in the removal efficiency of the adsorbent for the metal ions. This is probably due to the effect of temperature on the interaction between the shell surface and the metal ions in solution.

Table 3. Concentration of the metal ions adsorbed (Y_t) at various temperature and ambient pH by coconut (CNS) shell

Temperature (°C)	**Y_t (mgl^{-1})**			
	Pb^{2+}	Cu^{2+}	Cd^{2+}	As^{3+}
30	0.309	0.417	0.046	0.075
40	0.310	0.439	0.067	0.103
50	0.366	0.456	0.068	0.308
60	0.403	0.479	0.068	0.446

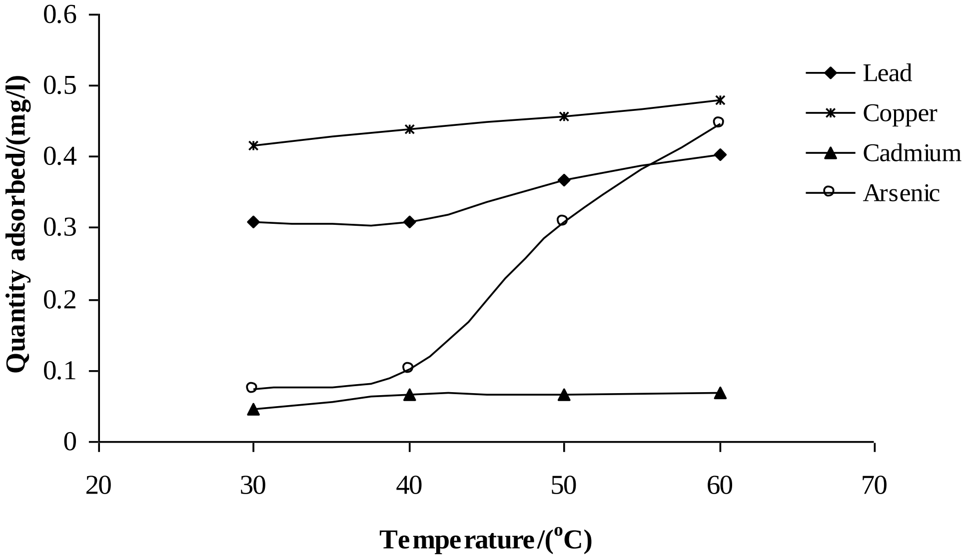

Figure 3. Variation of quantity of ion adsorbed by coconut shell with temperature

Increase in temperature probably weakens the bond formed between the metal ions and the adsorption sites on the adsorbent thereby resulting in an increase in the amount of metal ions adsorbed on the adsorbent. This implies that increase in temperature creates a wider surface area for adsorption at the adsorbent. Some researchers have suggested that sorption from aqueous solution is by a different adsorption mechanism, which may be described as either physical adsorption or chemisorption.

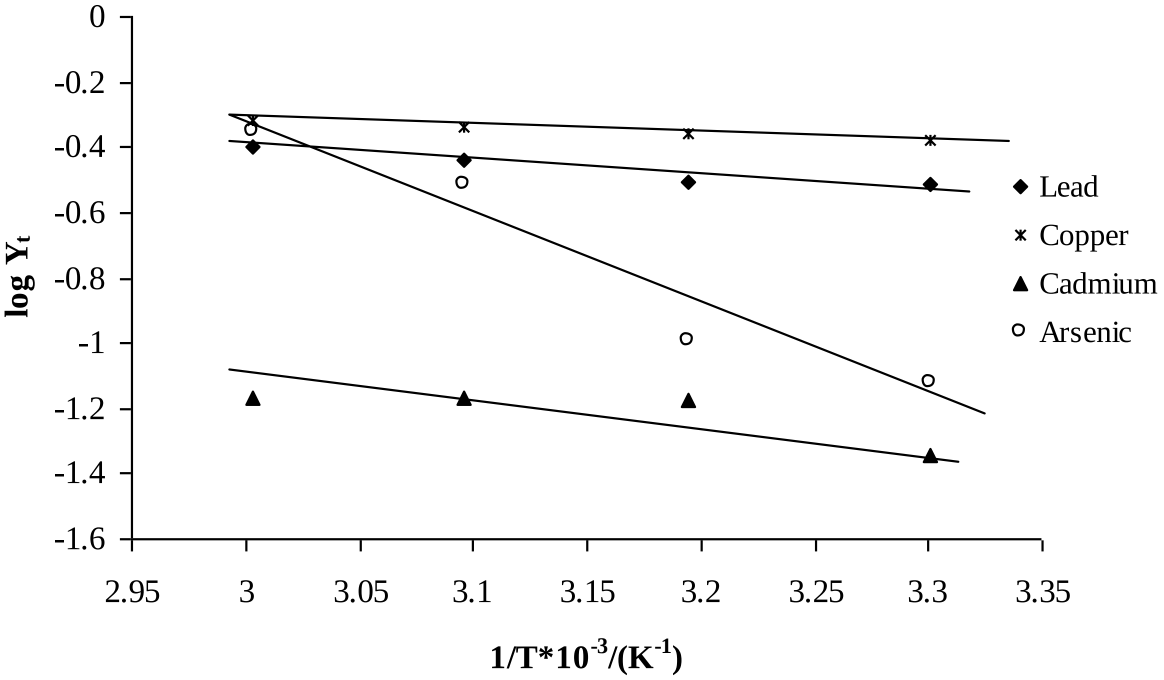

Figure 5. Arrhenius plot for the adsorption of the metal ions by coconut shell

The apparent activation energies (E_a) for the adsorption process were determined from the Arrhenius equation:

$$Y_t = A \exp -E_a/RT \qquad 1$$

where Y_t is the amount adsorbed at temperature T, A is the Arrhenius constant, E_a is the activation energy and R is the universal gas constant. From the equation, a plot of log y_t against 1/T should give a straight line from which E_a and A could be determined from the slope and intercept, respectively.Fig. 5 represents Arrhenius plots for the adsorption of the metal ions from aqueous solutions by CNS. Linear plots were obtained. The values of E_a and log A obtained from the slopes and intercepts, respectively, of the plots are presented in Table 5. The calculated E_a values for Pb^{2+}, Cu^{2+} and Cd^{2+} for the adsorption process on CNS is below 40kJ/mol while that for As^{3+} is 53.97 kJ/mol for CNS. This indicate that CNS would be a better adsorbent of As^{3+} at higher temperature than at lower temperature as observed in Fig. 3.

3.4. Effect of pH on the removal of Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} from solution

pH is an important controlling parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional group of the adsorbent and the degree of ionization of the adsorbate during reaction [33, 34]. The heavy metal cations are completely released in extreme acidic condition [35]. At lower pH values, the H^+ ions compete with the metal cation for the adsorption sites in the system [36, 37].

The effect of pH on the adsorption of Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} from solutions containing CNS was studied at a concentration of 0.5 mg/l for 30 minutes and at 30°C. Table.4 shows that the concentration of the metal ions increased as the pH moves from the acidic pH 2 to alkaline pH 10. This result of the effect of pH on the adsorption of metal ions by CNS is represented in Fig. 4. It shows that alkaline medium tend to support adsorption more than acidic medium.

According to Low *et al.* [38], at low pH values the surface of the adsorbent would be closely associated with hydroxium ions (H_3O^-), by repulsive forces, to the surface functional groups, consequently decreasing the percentage adsorption of metal. As the solution pH increases, the onset of the metal hydrolysis and precipitation begins and onset of adsorption therefore occurs before the beginning of hydrolysis [33].

When the pH of the adsorbing medium was increased from pH 2 to 10, there was a corresponding increase in the deprotonation of the adsorbent surface, leading to a decrease in H^+ ion on the adsorbent surface. This creates more negative charges on the adsorbent surface, which favours adsorption of positively charge species and the positive sites on the adsorbent surface [31, 39-40].

The hydrolysis of cations occurs by the replacement of metal ligands in the inner coordination sphere with the hydroxyl groups [34]. This replacement occurs after the removal of the outer hydration sphere of metal cations. The results obtained agreed with the findings of some researchers [29, 41]. The solubility of metals is known to be lowered at higher pH (at pH > 8) values [42].

Table 4. Concentration of the metal ions adsorbed (Y_t) at various pH at 30°C by coconut (CNS) shell

pH	Y_t (mgl^{-1})			
	Pb^{2+}	Cu^{2+}	Cd^{2+}	As^{3+}
2	0.167	0.224	0.218	0.136
6	0.306	0.432	0.238	0.178
8	0.341	0.447	0.254	0.217
10	0.353	0.450	0.279	0.368

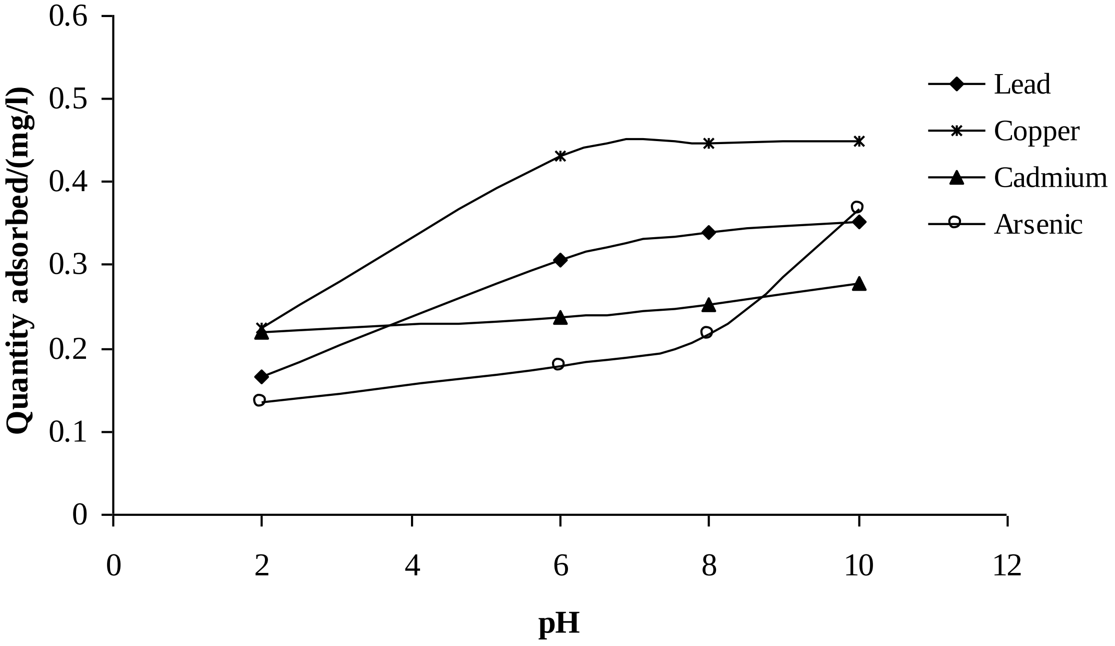

Figure 4. Variation of quantity of ion adsorbed by coconut shell with pH

3.5. Adsorption model isotherm

The result of the analysis was used to obtain metal adsorption isotherms. The adsorption isotherm was use to characterize the equilibrium between the amount of adsorbate that accumulated on the adsorbent and the concentration of the dissolved adsorbate. In this study, the experiment data set obtained was fitted using Freundlich adsorption isotherm model which may be formulated as [27]:

$$\log\ x/m = \log k + n \log c \qquad 2$$

where x/m is the concentration of metal ion adsorbed per unit mass of adsorbent (x is the amount of metal ion adsorbed, m is the mass of adsorbent), c is concentration of metal ion in solution, k and n are empirical constants. It is observed that the experimental data obtained fitted the Freundlich isotherm (Fig.6) with data reliability (R^2) of over 92% in all cases.

Value of k and n were calculated from the intercept and slope of the plot in Fig. 6. and are presented in Table 6. The Freundlich exponent n gives an indication of the favourability of adsorption. The value of n>1.0 represents a favorable adsorptions condition [43]. The values of n obtained in this study for the adsorption of Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} on CNS is greater than unity, indicating the favourable adsorption of the metal ions on CNS.

Freundlich isotherm model is indicative of surface heterogeneity of the adsorbent, i.e. the adsorptive site (surface of CNS) are made of small heterogeneous adsorption patches that are homogenous in themselves. The activation of adsorption site takes place, heading to increased adsorption probably through the surface exchange mechanism.

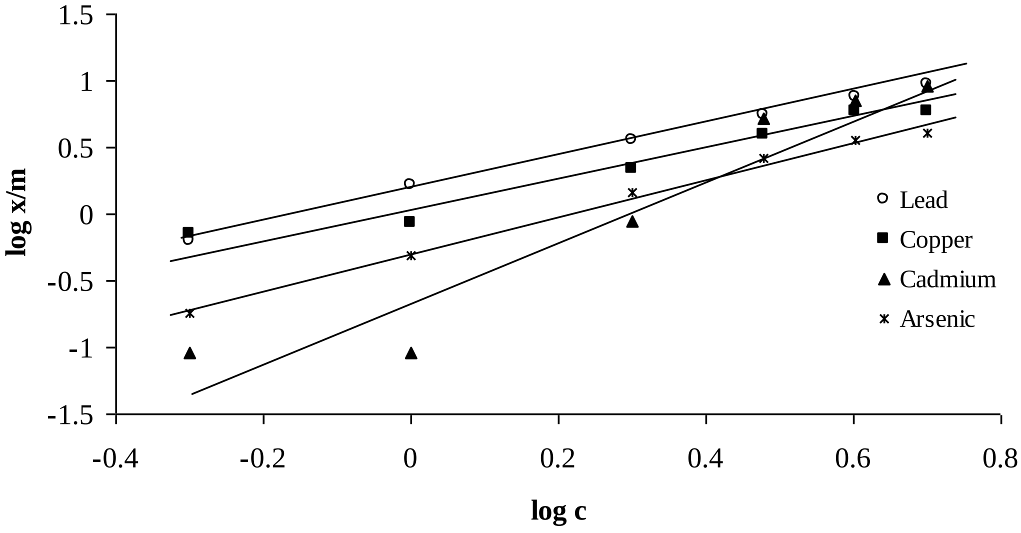

Figure 6. Freundlich adsorption isotherm for the adsorption of metal ions from solution by coconut shell

Table 6. Freundlich adsorption isotherm empirical constants

Metal ions	Coconut		
	n	*k*	R^2
Pb^{2+}	1.17	1.51	0.997
Cu^{2+}	1.04	1.16	0.956
Cd^{2+}	2.33	0.24	0.924
As^{3+}	1.41	0.50	0.993

3.6. Adsorption kinetics

The sorption kinetics of sorbent depends on the properties of the sorbate, the experimental conditions, temperature, concentrations and pH values. Each combination of sorbent and sorbate has a unique metal ion-sorbent interaction. To explain the kinetics of the adsorption of Pb^{2+}, Cu^{2+} Cd^{2+} and As^{3+} ions by CNS at 30°C, it is necessary to determine empirically which adsorption kinetic model fits best to the adsorption equilibrium date in order to determine the kinetic parameters pertaining to adsorption.

Different adsorption kinetic models have been used to determine the adsorption parameters: Pseudo-first-order kinetic model [35, 37], pseudo-second-order kinetic model [27, 34], Elovich equation [35] and intraparticle diffusion model [35]. From the results, it was found that the experimental data fitted the pseudo-second-order kinetic model. The pseudo-second-order kinetic model is expressed as:

$$t/q_t = 1/kq^2_e + t/q_e \qquad (3)$$

where q_e and q_t are the amounts of adsorbate adsorbed (mg/l) at equilibrium and at contact time t (min), respectively and k is the pseudo-second-order rate constant (min^{-1}) [35, 37]. The plots of t/q against t (min) for the adsorption of Pb^{2+}, Cu^{2+} Cd^{2+} and As^{3+} by CNS (Fig 7,) which indicates that the experiment data for the adsorption of Pb^{2+}, Cu^{2+} Cd^{2+} and As^{3+} ion by CNS fits the pseudo-second-order adsorption kinetic model. The k and q values determined from the slopes and intercept of the plots are presented in Table 7 along with the corresponding values of the correlation coefficients. From the results, it can be seen that the values of correlation efficient (R^2) implies that the adsorption of Pb^{2+}, Cu^{2+} Cd^{2+} and As^{3+} CNS could be best described by the pseudo-second-order model [35, 43].

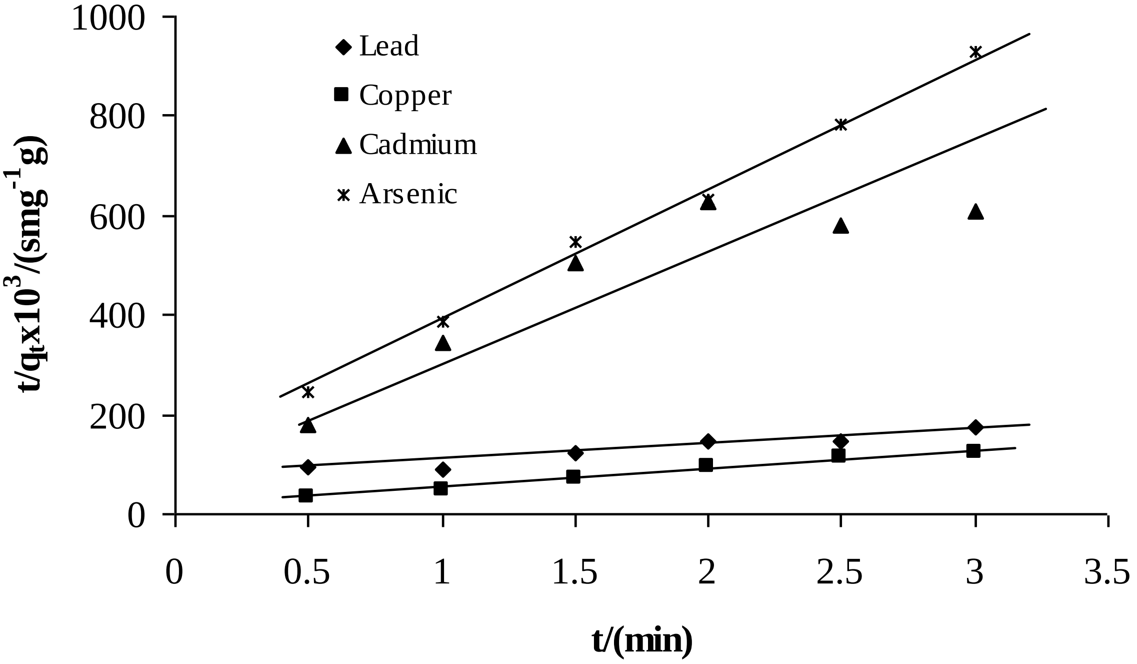

Figure 7. Pseudo-second order diffusion model for the adsorption of metal ions from solution by coconut shell

The intraparticle diffusion can be estimated by using the Weber-Morris intraparticle diffusion model.

$$q_t = k_{id}t^{1/2} + C \tag{4}$$

where q is the amount of metal adsorbed at any time, t, k_{id} is the intraparticle diffusion rate coefficient and C gives an idea about the thickness of the bounding layer i.e. the larger the intercept, the greater the contribution of surface sorption in the rate determining step [37]. The values of k_{id} and C were determined from the slopes and intercepts of the plots of q_t versus $t^{1/2}$ (Fig. 8) are presented in Table 7.

Table 7. Kinetic parameters for the adsorption of metal ions from solution on coconut shell (CNS)

	Parameters	Pb^{2+}	Cu^{2+}	Cd^{2+}	As^{3+}
Pseudo-second order models	q_e (mg g^{-1})	0.029	0.026	0.006	0.004
	k_1 (g mg^{-1} min^{-1})	16.56	104.43	164.79	604.24
	R^2	0.913	0.988	0.805	0.996
Intraparticle diffusion models	$k_{id} \times 10^{-3}$ (g mg^{-1} $min^{-1/2}$)	11.30	7.80	2.00	1.20
	C (mg g^{-1})	0.002	0.011	0.001	0.001
	R^2	0.941	0.753	0.740	0.942

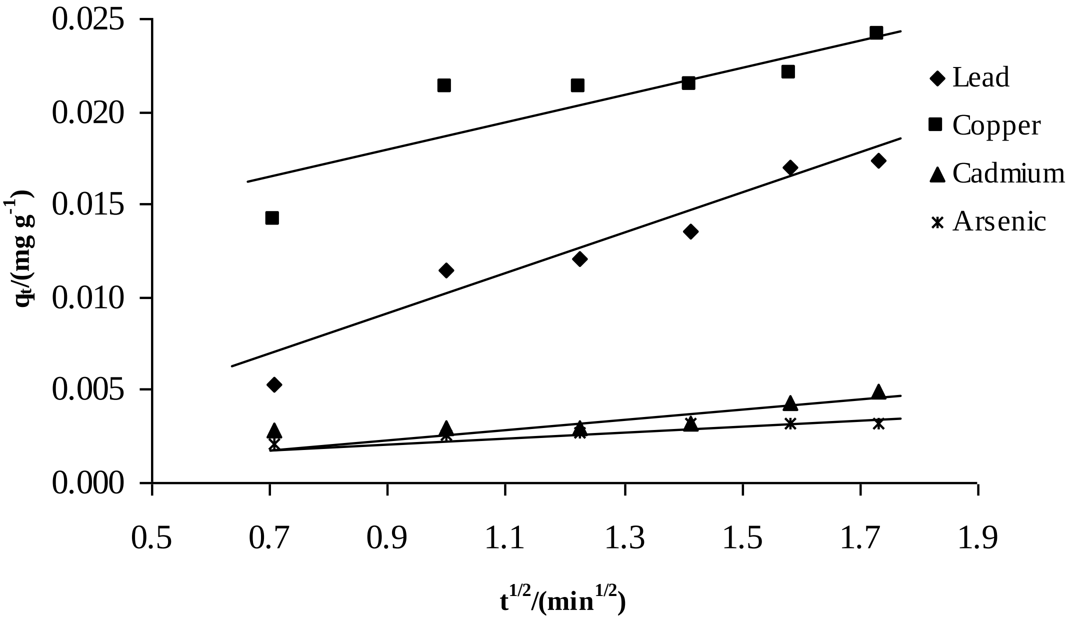

Figure 8. Intraparticle diffusion model for the adsorption of metal ions from solution by coconut shell

From the result depicted in Fig 8, it could be seen that the plots are linear but do not pass through the origin, suggesting that the adsorption of Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} involved intraparticle diffusion. And also, this deviation can now show that the pore diffusion is not the sole rate-controlling step [35, 44-45].

4. CONCLUSIONS

i. The aim of this study was to investigate the sorption capacity of coconut shell (CNS) for Pb^{2+}, Cu,$^{2+}$ Cd^{2+} and As^{3+} from aqueous solutions and the effect of contact time, initial metal ion concentration in aqueous solution, effect of temperature variation on sorption and the effect of variation of pH on aqueous solutions.

ii. The results obtained from this investigation are thereby summarized as follows:

iii. Coconut shell adsorbed Pb^{2+}, Cu,$^{2+}$ Cd^{2+} and As^{3+} ions from aqueous solutions and the concentration of the metal ions adsorbed increased with increase in concentrations, increase in contact time, increase in temperature and increases in pH for each metal.

iv. The rate of adsorption of the metal ions by coconut shell was rapid initially but decreases gradually due to the gradual blocking of the initial available uncovered surface area of the adsorbent.

v. The rate of adsorption of metal ion in aqueous solution on the active sites on the surface of the CNS is highest for Pb^{2+} and Cu^{2+} compared to those of Cd^{2+} and As^{3+}, which was at its lowest. This may be due to its larger ion size.

vi. Adsorption for the metal ions increases with increase in metal ion concentration because at low concentrations, the active site on the surface of the adsorbent are not completely covered.

vii. Analysis of the data showed that Freundlich isotherm described the date more appropriately than any other isotherm.

viii. Kinetic studies showed that the sorption of the metal ions can best be described by both pseudo-second-order and intra-particle diffusion models.

ix. It is therefore suffices to conclude that coconut shell could serve as cheap, readily available effective adsorbent for the removal of Pb,$^{2+}$ Cu,$^{2+}$ Cd,$^{2+}$ and As^{3+} from wastewater as a way of treatment before discharge into the environment.

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