

Adsorption kinetics and intraparticulate diffusivities of Hg, As and Pb ions on unmodified and thiolated coconut fiber

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ABSTRACT: As, Hg and Pb are examples of heavy metals which are present in different types of industrial effluents responsible for environmental pollution. Their removal is traditionally made by chemical precipitation, ion-exchange and so on. However, this is expensive and not completely feasible to reduce their concentrations to the levels as low as required by the environmental legislation. Biosorption is a process in which solids of natural origin are employed for binding the heavy metal. It is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity. The kinetics was studied for biosorption experiments using coconut fiber for As (III), Hg (II) and Pb (II) ions adsorption. The specific surface area and surface charge density of the coconut fiber are 1.186×10^{25} (m²/g) and 5.39×10^{24} (meq/m²), respectively. The maximum adsorption capacity was found to be the highest for Pb (II) followed by Hg (II) and As (III). The modification of the adsorbent by thiolation affected the adsorption capacity. Equilibrium sorption was reached for the metal ions at about 60 min. The equilibrium constant and free energy of the adsorption at 30 °C were calculated. The mechanism of sorption was found to obey the particle-diffusion model. The kinetic studies showed that the sorption rates could be described by both pseudo first-order and pseudo second-order models. The pseudo second-order model showed a better fit with a rate constant value of 1.16×10^{-4} /min. for all three metal ions. Therefore, the results of this study show that coconut fiber, both modified and unmodified, is an efficient adsorbent for the removal of toxic and valuable metals from industrial effluents.

Key words: Adsorption kinetics, intraparticulate diffusivity, heavy metal, coconut fiber, waste management

INTRODUCTION

As, Hg and Pb have detrimental effects on human, plants and animals. The toxicity of these heavy metals to marine life and consequently to man has been established for many years. The sources of As pollution come from discharges of various industries, such as smelting, petroleum-refining, pesticides, herbicide, glass and ceramic manufacturing industries (Volesky and Holan, 1995). Pb pollution particularly results from battery manufacturing, automobile exhaust fumes and metal finishing industries. Hg pollution results from metallurgical industries, chemical manufacturing and metal finishing industries. Other sources of these heavy metals also exist and these have increased as a result of an increase in urbanization and industrialization. The chemistry of these heavy metals is complex and interesting,

especially when they find their way into human metabolism. For example, the oxy-anions of arsenate (V) exist in four different arsenate species as H_3AsO_4 , $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} in the pH range <2, 3-6, 8-10 and >12, respectively (Igwe, *et al.*, 2005a, Sadiq, 1997). Hg in the liquid form is not dangerous and it is used in a number of industries. In the vapour form, Hg becomes very poisonous. It attacks lungs, kidneys and brain. The vapour crosses blood brain barrier and gets oxidized in brain and blood stream. As affects the skin, causing skin cancer in this most severe form. A massive outbreak of arsenical dermatosis, observed in some parts of west Bengal state of India, is linked to high levels of As in tube well water (0.2-2.0 mg/L) (Muhan and Agrawal, 2006; Namasivayam and Senthilkumar, 1998). Pb is a heavy metal poison which forms complexes with oxo-groups in enzymes to affect all steps virtually in the process

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of hemoglobin synthesis and porphyrin metabolism (Ademorati, 1996). The incidence of these heavy metal occurrences in wastewater and the above implications has resulted in research on the treatment and/or recovery of these heavy metals from wastewater. The treatment of effluent water from industries and other sources can be achieved through adsorption techniques. Sorption or the removal of toxic or heavy metals from aqueous effluent has been extensively studied in recent times. The use of conventional methods has been reported such as activated carbon or activated alumina (Shim, *et al.*, 2001; Ouki, *et al.*, 1997; Monser and Adhoum, 2002) and so on. Also, the use of the ion exchange resins and precipitation methods has been the most efficient and effective method for removing heavy metals from aqueous effluents, but these are very expensive. As a result of the expensive nature of the use of the conventional methods, researches have recently focused on the use of non-conventional agricultural by-products and adsorbents of biological origin. These adsorbents are abundant and relatively cheap. These adsorbents have been used in the adsorptive removal of heavy metals such as maize cob and husk (Igwe and Abia, 2003; Igwe, *et al.*, 2005b), sunflower stalks (Gang and Weixing, 1998), chemically modified and unmodified cassava waste biomass (Abia, *et al.*, 2003), sawdust (Igwe, *et al.*, 2006), bacterial algal (Volesky and Holan, 1995, Figuererira, *et al.*, 2000), fungal biomass (Guibal, *et al.*, 1992), chitosan and N-carboxymethyl chitosan (Guibal, *et al.*, 1998; Ngah and Liang, 1998), Pillared clay (Vinod and Anirudhan, 2001), sago waste (Quek, *et al.*, 1998), banana pith (Low, *et al.*, 1995), sawdust (Raji and Anirudhan, 1997), Medicago sativa (Alfalfa) (Gardea-Torresdey, *et al.*, 1998), spagnum peat moss (Ho, *et al.*, 1995) and so on. In the present study, the kinetics of sorption of Hg (II) As (III) and Pb (II) onto modified and unmodified coconut fiber was studied at the optimum pH 7.5 and the temperature 30 °C. The fractional attainment to the equilibrium (FATE), the mechanism of sorption, the equilibrium rate constant, the order of the reaction and hence the standard Gibbs-free energy for the reaction at 30 °C were established. The adsorbent was modified by thiolation to find the effect of modification on the adsorptive capacity of the adsorbent.

MATERIALS AND METHODS

All of the used reagents were analytical grade, purchased and applied without further purification. The coconut used was obtained from a local market in Okigwe, Imo State Nigeria. The fibrous part was removed, crushed in a mill, washed with de-ionized water and air-dried. This was sieved to different sizes and activated with 2% (v/v) nitric acid for 24 h., washed with de-ionized water and air-dried. The air-dried adsorbent was divided into two parts, one part was modified and the other left unmodified. The surface characteristics of the unmodified coconut fibre were carried out by the method of Santamarina, *et al.*, (2002). Parameters such as specific surface area (S_{AA}), surface charge density (SCD), pH of slurry, bulk density, pore volume, particle density, porosity, particle size and cation exchange capacity (CEC) were determined. The specific surface area was determined by the methylene absorption test method. The bulk density was determined as the ratio of the bulk mass of the test sample to its bulk volume. The cation exchange capacity was determined by the ammonium acetate saturation method. An initial metal ion concentration of 2000 mg/L was prepared for the three metal ions. To determine the effect of contact time, a 2 g sample of the coconut fiber (half modified and half unmodified) was put into a 100 mL solution of the metal ion of initial concentration of 2000 mg/L. Different samples were left to stand for 10, 20, 30, 40, 50, 60 and 120 min. at a pH 7.5 and a temperature of 29 °C. At the end of each time, the samples were filtered rapidly and the metal content of the filtrates determined using a UNICAM 919 solar atomic absorption spectrometer (AAS). The blank solutions were also prepared and analyzed. The amounts of the metal ions adsorbed were found by the difference in the average results of triplicate readings. The intra-particulate diffusivities were then calculated. The development of the used particle sizes and the modification method by thiolation were essentially the same as those described previously (Igwe and Abia, 2003; Gang and Weixing, 1998; Okeimen and Okundaye, 1986).

RESULTS AND DISCUSSION

The surface characteristics of the unmodified coconut fiber used in this study is shown on Table 1. The specific surface area (S_{AA}) and the surface charge density (SCD) were found to be high for coconut fiber.

This suggests high sorption capacity. The experimental results of the adsorption of Hg (II), As (III) and Pb (II) ions on the coconut fiber waste biomass are reported. Fig. 1 shows the amount adsorbed against a fixed weight (1 g) of different particle sizes of the adsorbent. The amount of the metal ions adsorbed against time is shown in Fig. 2 for the unmodified coconut fiber. For the thiolated coconut fiber, it is shown on Fig. 3. As the particle size of the adsorbent increased from 150 μm to 850 μm , the adsorbed amount also increased and that of Pb (II) ion was higher than Hg (II), which then followed by As (III) ion. It was observed that there is a slight flattening of the lines as the particle size 850 μm is approached. This means that beyond this point, even when the particle sizes are increased, the adsorbed amount remains constant. As a result, the particle size of 850 μm was used in the subsequent experiments of this work.

In Figs. 2 and 3, it was observed that the amount of Pb (II) adsorbed is higher, followed by Hg (II) and then As (III) ion. Again, the thiolation of the adsorbent resulted in a decrease and a relatively flattening of the curves. The introduction of thiol groups (-SH) must have adjusted the surface characteristics of the adsorbent by replacing some or all of the functional groups such as -OH on the β -D-glucose units of the cellulosic adsorbent. This makes the reaction more complex. These findings are similar to the results of the previous studies (Abia, *et al.*, 2003). The adsorption of metal ions on cellulosic materials can be attributed to two main terms: intrinsic adsorption and columbic interaction (Gang and Weixing, 1998). The columbic term results from the electrostatic energy of interaction between the adsorbents and adsorbates. The charges on substrates as well as softness or hardness of charge are mostly responsible for the intensity of the interaction. Columbic interaction can be observed from adsorption of cationic species versus anionic species

Table 1: Surface characteristics of unmodified coconut fiber

| SN | Parameter | Value |
|----|--|---|
| 1. | Bulk density | 0.062 (g/cm ³) |
| 2. | Particle density | 0.256 (g/cm ³) |
| 3. | Pore volume | 3.9 (cm ³ /g) |
| 4. | Cation exchange capacity | 64.0 (mg/100g) |
| 5. | Porosity | 18.14 (%) |
| 6. | Specific surface area (S _{AA}) | 1.186 x 10 ²⁵ (m ² /g) |
| 7. | Surface charge density (SCD) | 5.39 x 10 ²⁴ (meq/m ²) |
| 8. | Particle size | 250-500 μm |
| 9. | pH | 5.35 |

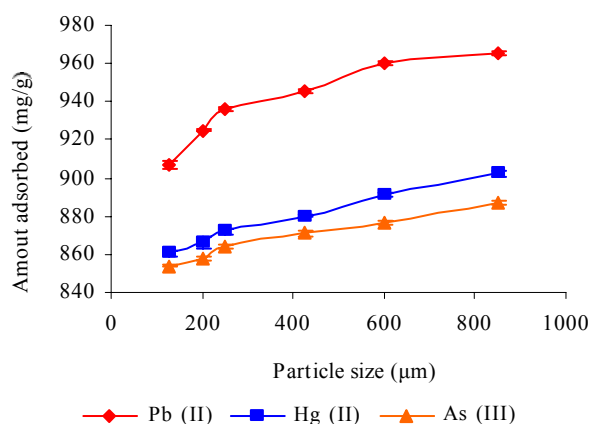
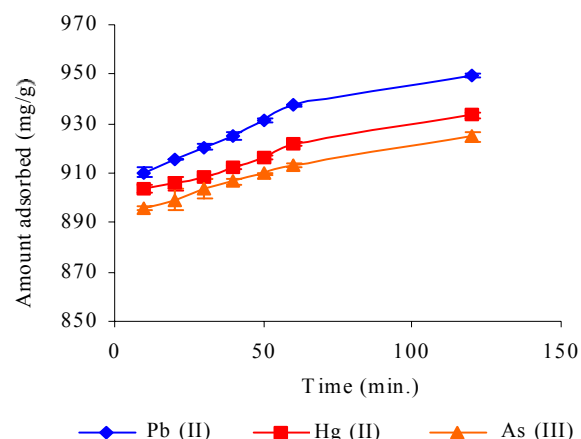
Fig. 1: Amount adsorbed (mg/g) against particle size (μm) for Pb (II), Hg (II) and As (III) ions adsorption onto unmodified coconut fibre

Fig. 2: Amount adsorbed (mg/g) against time (mins) for Pb (II), Hg (II) and As (III) ions adsorption onto unmodified coconut fibre

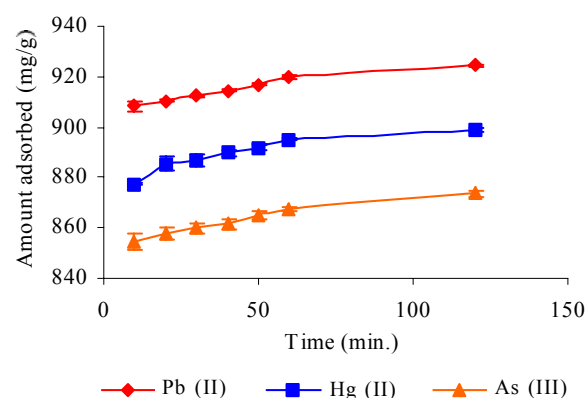


Fig. 3: Amount adsorbed (mg/g) against time (mins) for Pb (II), Hg (II) and As (III) ions adsorption onto thiolated coconut fibre

on adsorbents (Gang and Weixing, 1998). The intrinsic adsorption of the materials is determined by their surface areas, which can be observed by the effect of different sizes of adsorbents (Igwe and Abia, 2003).

Also, both intrinsic and columbic interaction could interact at the same time. Again, the transfer of a proton to the hydroxyl groups on the surface of the adsorbent is also possible (Ghosh and Yuan, 1987). Specific adsorption (ligand exchange mechanism) or chemisorptions of As on Fe-oxide/hydroxide surfaces has been reported as taking place by this method (Sadiq, 1997). Also, Grossl, *et al.*, (1997) have proposed a mechanism for the specific adsorption of As (V) on goethite (α -FeOOH) in a two-step process resulting in the formation of an inner-sphere mono-dentate surface complex at low surface coverage and an inner-sphere bi-dentate surface complex at high surface coverage. To analyze the sorption rates of Pb (II), Hg (II) and As (III) metal ions onto the biomass, two simple kinetic models were tested.

Pseudo-first-order model

The pseudo-first order rate expression, popularly known as the Lagergren equation, is generally described by the following equation (Lagergren, 1898):

$$dq/dt = k_{ad} (q_e - q_t) \quad (1)$$

where, q_e is the amount of the metal ions sorbed at equilibrium per unit weight of sorbent (mg/g); q is the amount of metal ions sorbed at any time (mg/g). Besides, k_{ad} is the rate constant/min. Integrating and applying boundary conditions, $t = 0$ and $q_t = 0$ to $t = t$ and $q_t = q_t$, Eq. 1 takes the form.

$$\log(q_e - q_t) = \log q_e - k_{ad} t/2.303 \quad (2)$$

In order to obtain rate constants, the straight-line plots of $\log(q_e - q)$ against t (time) were made (Fig. 4). This gave fairly straight lines for all three metal ions on the unmodified and thiolated. The intercept of this plot should give $\log q_e$. However, if the intercept does not equal to the equilibrium uptake of metal ions, the reaction is not likely to be first-order even if this plot has high correlation coefficient with the experimental data (Ho and McKay, 1998). The correlation coefficients were found to be between 0.9125 and 0.9884. The correlation coefficients are shown on Table 2 together with the Lagergren rate constants calculated from the slope of Eq. 2.

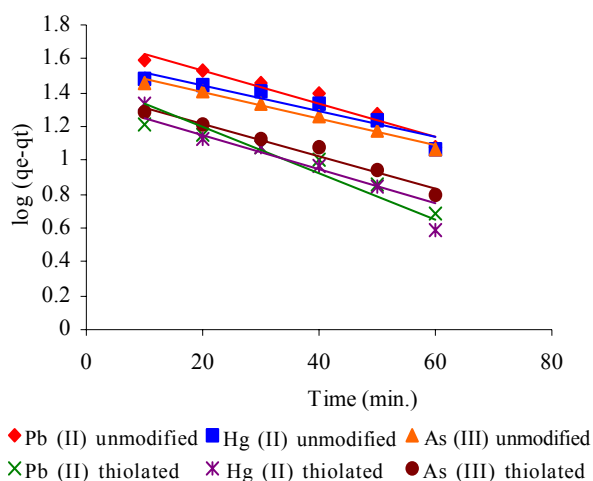


Fig. 4: Lagergren rate equation plot for Pb (II), Hg (II) and As (III) ions adsorption onto unmodified and thiolated coconut fibre

Table 2: Lagergren rate equation constants and Pseudo second-order rate equation constants for Pb^{2+} , Hg^{2+} and As^{3+} adsorption on unmodified and thiolated coconut fiber

| Metal ions | | Unmodified | | | Thiolated | | | |
|------------------|-----------------------|---|----------------------------|-----------------------|-----------------------|-----------------------|----------------------------|----------------|
| | | Lagergren rate equation constants | | | | | | |
| | K _{ad} /min. | q _c (mg/g) | R ² | K _{ad} /min. | q _c (mg/g) | R ² | | |
| Pb ²⁺ | 0.022 | 53.30 | 0.9440 | 0.024 | 22.74 | 0.9498 | | |
| As ³⁺ | 0.018 | 35.98 | 0.9884 | 0.022 | 25.28 | 0.9621 | | |
| Hg ²⁺ | 0.018 | 39.93 | 0.9125 | 0.031 | 29.15 | 0.9596 | | |
| | | Pseudo second-order rate equation constants | | | | | | |
| | h _o /min. | q _c (mg/g) | K ₂ (g/mg-min.) | R ² | h _o /min. | q _c (mg/g) | K ₂ (g/mg-min.) | R ² |
| Pb ²⁺ | 769.2 | 909.09 | 9.31x10 ⁻⁴ | 0.9999 | 2000.0 | 909.09 | 2.42x10 ⁻³ | 0.9999 |
| As ³⁺ | 1666.7 | 909.09 | 2.02x10 ⁻³ | 0.9999 | 3333.3 | 909.09 | 4.03x10 ⁻³ | 0.9999 |
| Hg ²⁺ | 1666.7 | 909.09 | 2.02x10 ⁻³ | 0.9999 | 1666.7 | 909.09 | 2.02x10 ⁻³ | 0.9999 |

Pseudo-second-order model

The sorption data was also analyzed in terms of a pseudo-second order mechanism (Ho and McKay, 1998) given by

$$dq/dt = K_2 (q_e - q_t)^2 \quad (3)$$

where, k_2 is the equilibrium rate constant (g/mg.min.). Integrating the above equation and applying boundary conditions, i.e. $t = 0$ and $q_t = 0$ to $t = t$ and $q_t = q_t$, gives:

$$t/q = 1/h_0 + 1/q_e(t) \quad (4a)$$

where, h_0 is the initial sorption rate. If the second-order kinetics is applicable, the plot of t/q against t in equation 4 should give a linear relationship from which the constants q_e and h_0 can be determined. This was plotted and Fig. 5 shows it. The plots gave a good fit to the experimental data. This means that the sorption can be described by a pseudo-second order rate equation, hence q_e and h_0 were evaluated and are presented in Table 2. The R^2 values are the same for all three metal ions and the two adsorbents with a value of 0.9999. When t tends to 0, h_0 is defined as (Horsfall, *et al.*, 2004):

$$h = K_2 q_e^2 \quad (4b)$$

where, k_2 is the pseudo-second-order rate constant (g/mg/min). K_2 was calculated for the three metal ions and is shown on Table 3. The results obtained are similar to a previous study (Horsfall, *et al.*, 2004).

Equilibrium and thermodynamic treatment of sorption process

The removal efficiency (E) of the metal ions on the adsorbent can be calculated from the equation below:

$$E = C_i/C_o \quad (5)$$

where, C_t is concentration at time t and C_o is the initial concentration. This was used to generate Table 3 and it is a modified method of that by Saifuddin and Kumaran (2005). Therefore, it is easy to see from Table 3 that the percentages could be calculated. Again, another related quantity, that is, the fractional attainment to equilibrium (FATE) represented by α , was used to analyze the equilibrium data. The equation is given as:

$$\alpha = [M]_t/[M]_{\infty} \quad (6)$$

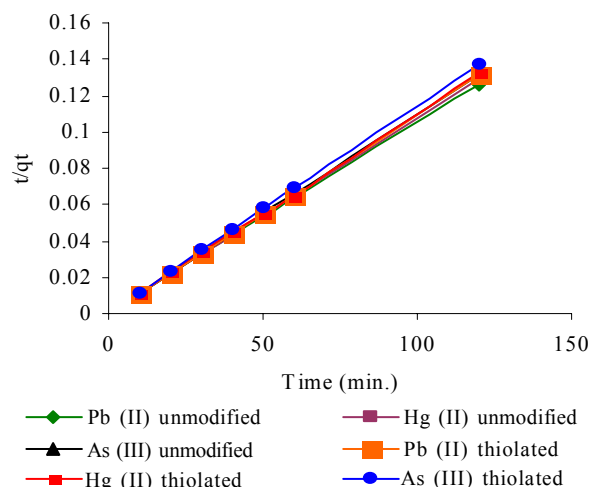


Fig. 5: Pseudo second-order plot for Pb (II), Hg (II) and As (III) ions adsorption onto unmodified and thiolated coconut fibre

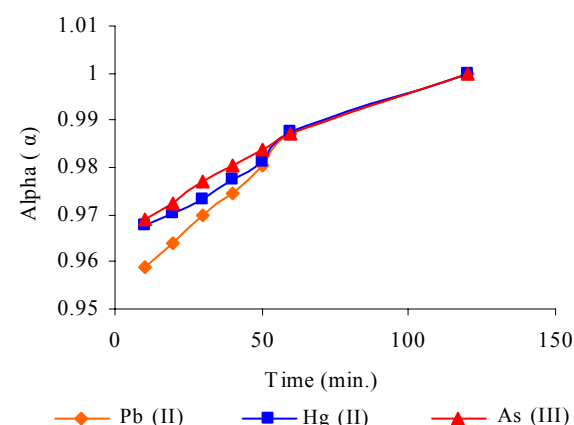


Fig. 6: Alpha (FATE) against time (min) for Pb (II), Hg (II) and As (III) ions adsorption onto unmodified coconut fibre

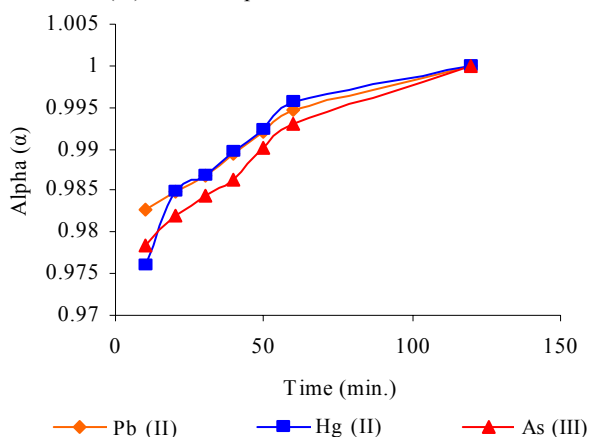


Fig. 7: Alpha (FATE) against time (mins) for Pb (II), Hg (II) and As (III) ions adsorption onto thiolated coconut fibre

where, $[M]_t$ is the concentration of metal ion at any time t and $[M]_{\infty}$ is the concentration at infinity, that is, equilibrium. The plot of α (alpha) against time for the unmodified coconut fibre is shown in Fig. 6 and that of the thiolated coconut fiber is shown in Fig. 7. From Figs. 6 and 7, it was observed that the fractional attainment to equilibrium for As^{3+} was higher than that of Hg^{2+} preceding that of Pb^{2+} ion. In the two figures, the alpha value converges to 1.0. There was a sharp increase in alpha value from 0 to about 0.99 and then all converge to 1.0. This is similar to alpha results obtained in the previous study (Abia and Igwe, 2005). Thermodynamic parameters such as change in free energy (ΔG°) was determined using the equation:

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

where, R is the universal gas constants, 8.314 J/(gmol k) ; T is absolute temperature. K and K_c are the thermodynamic equilibrium constant, which was calculated using Eq. 8 (Namasivayam and Senthilkumar, 1998):

$$K_c = C_{Ad}/C_e \quad (8)$$

where, C_{Ad} is the amount of the metal ion (mg) adsorbed on the adsorbent per liter of the solution at equilibrium and C_e is the equilibrium concentration (mg/L) of the metal ion in the solution. The values of ΔG° and K_c for the metal ions are shown on Table 4.

From Table 4, we see that the thermodynamic treatment of the sorption data indicates that ΔG° values were negative for all the metal ions. The

negative values of ΔG° indicate the spontaneous nature of adsorption of the metal ion by the biomass (Horsfall and Spiff, 2005).

It has been reported that ΔG° up to -20 kJg/mol are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while ΔG° values more negative than -40 kJg/mol involve charge sharing or transfer from the biomass surface to the metal ion to form a coordinate bond (chemical adsorption) (Horsfall and Spiff, 2004). The ΔG° values obtained in this study for the three metal ions are $< -10 \text{ KJg/mol}$, which indicates that physical adsorption was the predominant mechanism in the sorption process. This is similar to the results of Abdel Ghani and Elchaghaby, (2007). The values of the thermodynamic equilibrium constant range from 0.76 to 0.86. This shows that a greater amount of the heavy metals was removed because their values were greater than 0.5. The other thermodynamic parameters ΔH° and ΔS° could not be evaluated because the temperature does not vary in this work.

Intraparticle diffusivity

The sorption rate is known to be controlled by several factors including the following: (i) diffusion of the solute from the solution to the film surrounding the particle, (ii) diffusion from the film to the particle surface (external diffusion), (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and (iv) uptake which can involve several mechanisms such as physico-chemical sorption, ion exchange, precipitation or complexation (Findon, *et al.*, 1993; Weber and Digiano, 1996).

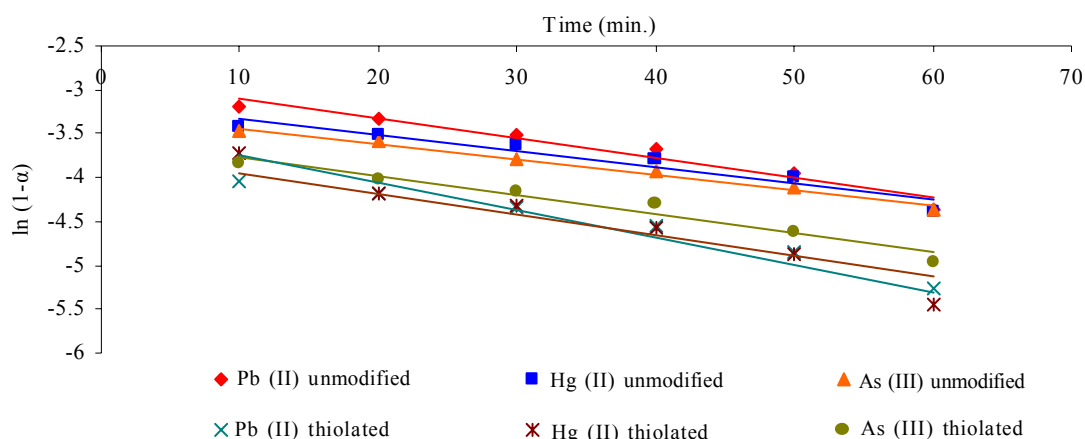


Fig. 8: Intraparticle diffusivity plot for Pb (II), Hg (II) and As (III) ions adsorption onto unmodified and thiolated coconut fibre

Table 3: Fraction of the amount adsorbed for Pb²⁺, Hg²⁺ and As³⁺ ions on coconut fiber

| Time (min.) | Ct/Co | | | | | |
|-------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | Unmodified | | | Thiolated | | |
| | Pb ²⁺ | Hg ²⁺ | As ³⁺ | Pb ²⁺ | Hg ²⁺ | As ³⁺ |
| 10 | 0.455 | 0.452 | 0.448 | 0.454 | 0.439 | 0.427 |
| 20 | 0.458 | 0.453 | 0.450 | 0.455 | 0.443 | 0.429 |
| 30 | 0.460 | 0.454 | 0.452 | 0.456 | 0.444 | 0.430 |
| 40 | 0.463 | 0.456 | 0.453 | 0.4567 | 0.445 | 0.431 |
| 50 | 0.466 | 0.458 | 0.455 | 0.459 | 0.446 | 0.432 |
| 60 | 0.469 | 0.461 | 0.456 | 0.460 | 0.448 | 0.434 |
| 120 | 0.475 | 0.467 | 0.462 | 0.462 | 0.450 | 0.437 |

Table 4: Equilibrium constant (Kc) standard Gibbs free energy (ΔG^0) and Rate coefficient Kp/min for particle-diffusion controlled sorption for the adsorption of Pb²⁺, Hg²⁺ and As³⁺ on unmodified and thiolated coconut fibre at 30 °C

| Kc | | | | | |
|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Unmodified | | | Thiolated | | |
| Pb ²⁺ | Hg ²⁺ | As ³⁺ | Pb ²⁺ | Hg ²⁺ | As ³⁺ |
| 0.86 | 0.84 | 0.83 | 0.80 | 0.76 | 0.84 |
| ΔG^0 (J/mol) | | | | | |
| 379.94 | 439.22 | 469.39 | 439.22 | 562.13 | 691.35 |
| Kp/min | | | | | |
| 2.25x10 ⁻² | 1.81x10 ⁻² | 1.77x10 ⁻² | 2.34x10 ⁻² | 3.11x10 ⁻² | 2.15x10 ⁻² |
| R ² | | | | | |
| 0.9517 | 0.9420 | 0.9906 | 0.9502 | 0.9622 | 0.9571 |

Table 5: Rate constants (K_i) for the initial rate of sorption controlled by intraparticle diffusion for Pb²⁺, Hg²⁺ and As³⁺ on coconut fiber and boundary layer thickness (X_i)

| K _i (mg/g-min ^{0.5}) | | | | | |
|---|------------------|------------------|------------------|------------------|------------------|
| Unmodified | | | Thiolated | | |
| Pb ²⁺ | Hg ²⁺ | As ³⁺ | Pb ²⁺ | Hg ²⁺ | As ³⁺ |
| 127.54 | 125.70 | 124.70 | 125.56 | 122.27 | 118.43 |
| X _i (mg/g) | | | | | |
| 896.0 | 887.0 | 883.0 | 901.0 | 866.0 | 844.0 |

The first one is bulk diffusion, the second is external mass transfer resistance and the third is intraparticle mass transfer resistance. Mass transfer is governed by several relationships, taking into account the diffusion mechanisms and their related equations, the coupling between liquid and solid phases and the initial and boundary conditions. Therefore, it means that the rate of attainment to equilibrium may be either film-diffusion controlled or particle-diffusion controlled, even though these two different mechanisms cannot be sharply demarcated (Abia and Igwe, 2005). The linear driving force concept was used to develop the relationship for particle-diffusion controlled sorption as reported by Igwe and Abia (2005) and shown by Eq. 9.

$$\ln(1-\alpha) = -K_p t \quad (9)$$

α was defined earlier by Eq. 6. K_p is the rate coefficient for particle-diffusion controlled process corresponding

to the particle size of the sorbent; t is time and $\ln(1-\alpha)$ is a measure of the intra-particulate diffusivity. If a plot of $\ln(1-\alpha)$ versus time results in a linear relationship, the sorption process is particle-diffusion controlled and the diffusivity of the metal ions onto the adsorbent surface is independent of the extent of sorption. Eq. 9 was used to analyze the data and it is shown in Fig. 8. From the figure, it was observed that the adsorption process tested was particle diffusion controlled. The values of K_p from the slope of the graph and the coefficient of regression (R^2) are shown on Table 4.

Higher values of K_p indicate that the particle diffusion mechanism predominates. This means an increase in the adsorption rate. Also, the result of McKay and Poots, (1980) were used to analyze the experimental data. They observed that the fraction of solute adsorbed could be expressed in terms of the square root of time. A plot of fraction of solute adsorbed against $t^{0.5}$ may be used to estimate the intraparticle

diffusion rate in the linear range. This mathematical dependence of concentration in the solid on $t^{0.5}$ has been deduced by considering the sorption mechanism to be controlled by diffusion in the sorbent (as spherical particles) and convective diffusion in the solution (Guibal, *et al.*, 1998). The solution of the diffusion equations leads to a relationship between the concentration in the solid and the parameter $(Dt/a^2)^{0.5}$. Since D and a are considered constant during the experiment, the concentration varies as a function of $t^{0.5}$ as given by Eq. 10:

$$q_{(t)} = x_i + K_i t^{0.5} \quad (10)$$

The slope of the linear part of the curve (uptake capacity versus square root time) gives the initial rate of sorption (here taken between 10 and 30-60 min.) controlled by intraparticle diffusion K_i ($\text{mg/g} \cdot \text{min}^{-0.5}$) (McKay and Poots, 1980). The linear plots (not shown) have the same shapes as those in Figs. 2 and 3 for unmodified and thiolated, respectively. They confirm that the sorption is particle-diffusion-controlled. The values of K_i are shown on Table 5. The initial curve portion of the plot is attributed to boundary layer diffusion effect (i.e. external film resistance). The extrapolation of the linear straight lines gives the intercepts X_i , which are proportional to the boundary layer thickness. The values are also shown on Table 5. The boundary layer also gives an insight into the tendency of the metal ions to adsorb to the adsorbent phase or remain in solution. Since diffusion takes place, the boundary layer is looked upon as a viscous drag existing between the adsorbent surface and the metal ion solution diffusing across its surface. Therefore, higher values of X_i , i.e. the boundary layer thickness, depict higher adsorption capacities. It has been reported that at a high temperature, the thickness of the boundary layer decreases due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase, which results in a decrease in adsorption as the temperature increases (Aksu, 2001). As shown on Table 5, the boundary layer thickness varies from 844.0 to 927.7 mg/g . This shows high tendency for adsorption capacity. In conclusion, the biomass of the coconut fiber demonstrated a good capacity of Pb (II), Hg (II) and As (III) ions biosorption, highlighting its potential for effluent treatment processes. The amount of the adsorbed metal ions increased as the time lapses, similar to that reported by Gueu, *et al.*, (2007). The

incorporation of the thiol groups onto the adsorbent surface affected the adsorption. The kinetics of sorption followed both the pseudo first-order and pseudo second-order rate equations, with the second order giving a better fit than the first order. The coefficient of determination (R^2) for the pseudo second-order rate equation was found to be the same (i.e. 0.9999) for all of the three metal ions. The sorption process also followed the particle diffusion process. The experimental data gave linear plots to both the McKay and Poots, (1980) plots and the fractional attainment to the equilibrium concept. The boundary layer thickness was also evaluated. Thus, this process will help to keep our environment clean. The use of waste from coconut processing small-scale industries to clean up metal bearing effluents is feasible and environment-friendly. This may also provide an affordable technology for small and medium scale industries.

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