Sorption kinetics and intrapaticulate diffusivity of As(III) bioremediation from aqueous solution, using modified and unmodified coconut fiber

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Abstract: The pollution and toxicity problems posed by arsenic in the environment have long been established. Hence, the removal and recovery remedies have been sought, bearing in mind the efficiency, cost effectiveness and environmental friendliness of the methods employed. The sorption kinetics and intraparticulate diffusivity of As (III) bioremediation from aqueous solution using modified and unmodified coconut fiber was investigated. The amount adsorbed increased as time increased, reaching equilibrium at about 60 minutes. The kinetic studies showed that the sorption rates could be described by both pseudo-first order and pseudo-second order process with the later showing a better fit with a value of rate constant of 1.16×10^{-4} min^{-1} for the three adsorbent types. The mechanism of sorption was found to be particle diffusion controlled. The diffusion and boundary layer effects were also investigation. Therefore, the results show that coconut fiber, both modified and unmodified is an efficient sorbent for the removal of As (III) from industrial effluents with particle diffusion as the predominant mechanism.

Keywords: arsenic; adsorption; kinetics; intraparticle diffusivity; coconut fiber.

Introduction

Efforts to minimize production of hazardous waste and to remediate existing accumulated waste have become one of the most important environmental challenges that the world faces today. Heavy metals rank as major polluting chemicals in both developed and developing countries as a result of rapid industrialization [1]. According to recent surveys, the most common contaminants reported in ground water are heavy metals. The most common metals found in wastewater that are significantly toxic to human beings (causing genetic mutations and cancer) and the ecological environment, include copper, cadmium, lead, mercury and arsenic [2,3].

Arsenic occurs naturally in a wide range of minerals, it has detrimental effects on human, plants and animals. The source of arsenic pollution is from the discharge of various industries such as smelting, petroleum-refining, and ceramic manufacturing industries [4-6]. The contamination of ground water with arsenic is a serious problem encountered in many countries especially India and Bangladesh [7]. A massive outbreak of arsenic dermatitis, observed in some parts of west Bengal State of India, is linked with

high levels of arsenic in tube well waters(0.2-2.0 mg/l)[8]. Several people were afflicted with ulcers and internal cancers. The symptoms are frightening: watery eyes, chronic indigestion, colds and stomach cramps in the early stages and swollen limbs with bleeding gangrene-like wounds in severe cases. This silent killer is arsenic. Conventional methods of arsenic removal such as coagulation-precipitation with lime, alum and ferric sulphate produce a wet bulky material and the safe disposal of the materials has not yet been solved and is not cost effective. Numerous adsorbents of different forms have been utilized in chemical techniques for the removal of toxic substances from industrial wastewater [9-15]. Some of the major draw backs in the use of these adsorbents are:

a. The high cost of the material,
b. Failure in adsorption of a range of metal ions simultaneously, and
c. Necessity of activating metal ion adsorbents with different acids or bases before use.

Therefore, inexpensive materials for removing and entrapping heavy metal wastes from contaminated water are required. Treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume followed by recovery or secure disposal. Adsorption on solid matrices is also reported to be a potential method for heavy metal removal [16, 17]. Nonspecific sorbents, such as activated carbon, metal oxides, and ion exchange, resins have been used. Specific sorbents consisting of a metal chelating ligand which interacts with the heavy metal ions specifically, and a carrier matrix which may be an inorganic material (e.g. activated carbon, alumina, silica, or glass) or polymer micro spheres (e.g., polystyrene or polymethymethacrylate) have also been reported [18, 19]. Industrial waste such as fly ash [20], bauxite, alumina, activated carbon [21], pyrite fines [22], hematite, kaolin, quartz [23] and basic yttrium carbonate [24] have been studied for the removal of arsenic. Phytoremediation, the use of plants to help clean up toxic waste sites is also being used in arsenic remediation. It is not only a growing science but also a growth industry [25].

Coconut fiber is classified as a lingo-cellulosic material made up of repeating units of β-D glucose units. The hydroxyl groups on the glucose units acts as cites of attachment for the heavy metals. Most of the works reported on the use of locally available agricultural by-products are mainly on the capacity of adsorption. In this study, we investigated the kinetics of sorption of arsenic (III) onto modified and unmodified coconut fiber. We also investigated the intraparticle diffusivity and the mechanism of arsenic (III) adsorption onto coconut fiber.

Materials and methods

Materials

All reagents used were analytical grade, purchased and used 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 obtain different sizes and activated with 2% (v/v) nitric acid overnight washed with de-ionized water and air dried.

Methods

The adsorbent was modified by method of thiolation and carboxymethylation [26, 27]. Thiolation incorporates the chelating functional group -SH (sulphydryl) where as carboxymethylation incorporates the group, -$COCH_3$ (Carboxymethyl) onto the structure of the β-D glucose units that makes up the cellulose. Various other methods of modification exists such as EDTA (ethylene diamine tetraacteic acid) modification [28,29], citric acid, tartaric acid and sodium gluconate modification [30] and Dithiophosphonate modification [31], and so on. The modification of bio-adsorbents using some of these chelating agents is because of the expected enlargements of the adsorption sites. Some of them are also used to mask and prevent a particular site on the adsorbent from adsorbing, if there is more than one functional group as site on the adsorbents. Thus, we investigated the

effect of modification by thiolation and carboxymethylation on coconut fiber.

For carboxymethylation, a portion of the adsorbent was modified by reaction with mono-chloroacetic acid. 100g of the adsorbent was added to a mixture of 650 mL ethyl alcohol and 554 mL toluene. A 50% solution of sodium hydroxide (33 mL) was added in 1 min and followed by gradual addition of 25g of mono-chloroacetic acid. The reaction mixture was kept at 65^0C for 70 min with agitation and left over night. The excess sodium hydroxide solution was neutralized with glacial acetic acid. The carboxymethylated adsorbents were filtered, washed with ethyl alcohol and purified by extraction with ethyl alcohol.

For thiolation, 25g sample of the adsorbents were thiolated with 250 mL of 1.0M solution of thiolglycolic acid for 24 hrs at 29^0C. The mixture was filtered, washed with deionized water and then with methanol. It was finally washed with deionized water and dried at 50^0C. The degree of thiolation was estimated titrimetrically by reaction of the thiolated adsorbent with iodine and back-titration of the unreacted iodine with sodium thiosulphate solution.

To determine the effect of contact time, a 2g sample of the coconut fiber (both for modified and unmodified), was put into a 100ml solution of As (III) solution of 2000 mg/l initial concentration. Different samples were left to stand for 10, 20, 30, 40, 50, 60, and 120 minutes in a rotary shaker at a constant speed of 150 rpm. At the end of each time, the samples were filtered rapidly by suction and the Arsenic content of the filtrates determined by a buck scientific flame Atomic Absorption Spectrophotometer (FAAS) model 200 A. The amount of As (III) ion adsorbed was gotten by difference. The experiment each time was maintained at a pH of 5.0 and temperature of 30^0C. The amounts adsorbed from the experiments were then divided by 2 to get the amount adsorbed in mg/g and this was used in subsequent calculations. The effects of pH and temperature on the adsorption of arsenic on coconut fiber have also been reported [32, 33]. In most of the separation methods reported, the removal of arsenic was found to be greatly dependent on pH, so that the optimum pH range is very limited [32, 35].

Results and discussion

The experimental results for the adsorption of As (III) on coconut fiber for the different parameters have been plotted and are reported below. Figure 1, shows the amount adsorbed against a fixed weight (1gram) for different particle sizes of the adsorbents. As the particle size of the adsorbent was increased, from 0.15mm to 0.85mm, the amount adsorbed also increased. From Figure 1, we can see that beyond particle size of 0.85 to 1.0 mm, the amount adsorbed is likely to decrease, i.e., from the shape of the curve. We reasoned that as the particle size increased, the number of micro pores also increases and since sorption is particle diffusion controlled (as confirmed by the intraparticle diffusivity plot in a later section), the increase in micro pores increases the number of accessible sites, hence increases the amount adsorbed. Also, from Figure 1, at particle size of 0.85, the tip of the graph is slightly bent meaning that the amount adsorbed is likely to decrease.
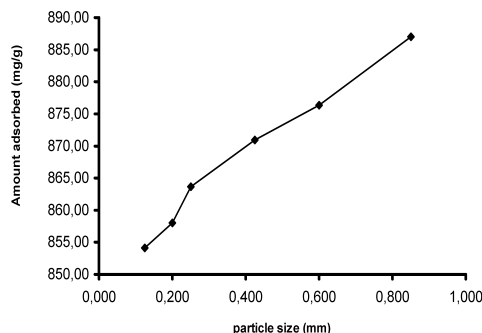

Figure 1. Amount of As (III) adsorbed (mg/g) on coconut fiber against particle size (mm).

The amount adsorbed as time increased for As (III) on unmodified, thiolated and carboxymethylated coconut fiber is shown on Figure 2. Amount adsorbed increased as time increased but began to flatten at time 60mins for unmodified and thiolated but decreased drastically for carboxymethylated. This means that equilibrium (or adsorption saturation) was reached at about

60mins for the three adsorbent types with that of carboxymethylated coconut fiber being faster than the unmodified and thiolated fiber. The unmodified showed a higher absorption capacity followed by carboxmethylated and then thiolated. The adsorption of arsenic is a complex process. For example, the oxy-anions of arsenic (V) exists in four different arsenate species as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} at the pH range <2, 3-6, 8-12 and >12 respectively [34], and that of arsenic (III) exists as H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} within the same pH range. Thus, at the pH of the experiment, that is pH of 5.0, the likely specie that would be adsorbed is $H_2AsO_3^-$. This is also similar to the results of Namasivayam and Senthilkumar (1998) [35].
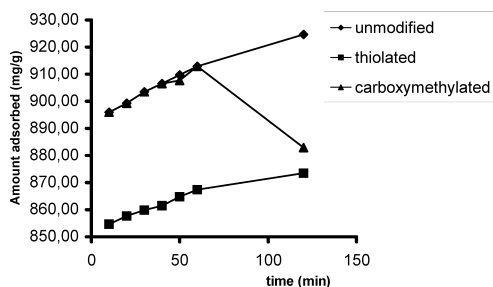

Figure 2. Amount of As (III) adsorbed (mg/g) against time(min)

Thus, the adsorbent acquires a net positive charge in the pH range and adsorption may be facilitated by columbic interactions. Grossl et al (1997) [36], have proposed a mechanism for the specific adsorption of arsenic (V) on goethite in a two- step process resulting in the formation of inner –sphere mono-dentate surface complex at low surface coverage and an inner –sphere bi –dentate surface complex at high surface coverage. A surface complexations model has also been proposed recently by Manning and Goldberg (1997) [37], for As (V) adsorption on clay minerals. Based on this, we proposed a reaction mechanism for adsorption of heavy metals on cellulose materials [32]. Extending this mechanism to the adsorption of As (III), we have the following mechanism:

Surface acid – base reactions:

$$SOH + H^+ = SOH^{2+} \qquad (1)$$
$$SOH = SO^- + H^+ \qquad (2)$$
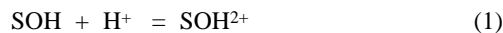
Mononuclear As (III) adsorption:

$$SOH + H_2AsO_3^- = SHAsO_3^- + H_2O \qquad (3)$$

Binuclear As (III) adsorption:

$$2SOH + H_2AsO_3^- = S_2AsO_3^- + 2H_2O \qquad (4)$$

SOH represents one reactive surface hydroxyl group bound to the glucose unit. This can also be replaced by the functional groups used in the modification process.

Thus, as said earlier, the modification by thiolation and carboxymethylation introduces the functional groups –SH and -$COCH_3$ onto the surface hydroxyl groups of the glucose units. This removes the H-atom from the surface hydroxyl group, hence affects the amount adsorbed. It is our opinion that since oxygen is more electronegative than sulphur, the unmodified and carboxymethylated will have higher adsorption capacity more than the thiolated. Then, the unmodified with –OH group is higher than the carboxymethylated group because of the methyl group. Hence, the sorption trend is unmodified > carboxymethylated > thiolated.

Figure 3 and Figure 4 shows the pseudo-first order and pseudo-second order plots for As (III) respectively. The pseudo-first order for As (III) on carboxymethylated did not give any correlation, hence was not plotted. The pseudo-second order gave a good and better fitting than the pseudo first order model. The pseudo-first order model was plotted by using equation (5) as developed by Lagergren[38]; while,

$$\log (q_e\text{-}q) = \log q_e\text{-} K_{ad} \, t/2.303 \qquad (5)$$

the pseudo-second order model as developed by Ho et al[23], was plotted using equation (6) which was derived from (7) and the rate constant for pseudo second order K_2 obtained from combination of equation (8) and the intercepts from the plots of equation (6).

$$t/q_t = 1/h_o + 1/q_e \, (t) \qquad (6)$$
$$d_q/d_t = K_2 \, (q_e - q)^2 \qquad (7)$$
$$h = K_2 \, q_e^2 \qquad (8)$$

Where t is time (min),. qt is amount adsorbed at time t, qe is the amount adsorbed at equilibrium and ho is the initial sorption rate. From Figure 3, we obtained the pseudo-first order rate constant (K_{ad}) as 7.63 x 10^{-3} min $^{-1}$ (r= 0.850) for unmodified and 8.43 x 10^{-3} min^{-1} (r = 0.824) for thiolated coconut fiber. From Figure 4, that is, for pseudo second order plot, we obtained K_2 = 1.16 x 10^{-4} min^{-1}, qe = 930.23 mg/g and ho = 100g/mg-min,(r = 0.9999). For the three adsorbent types, from the r values, we can see that the pseudo-second order is a better model than the pseudo-first order equation. Also, all three adsorbents have the same value of the pseudo-second order rate equation constants. This is confirmed from Figure 4.
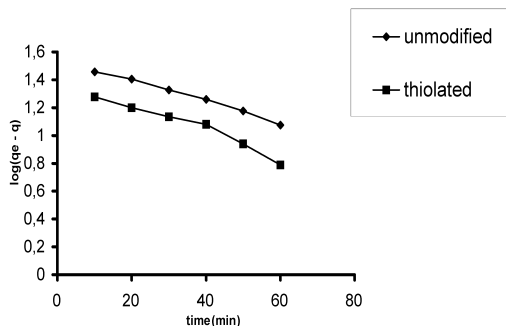

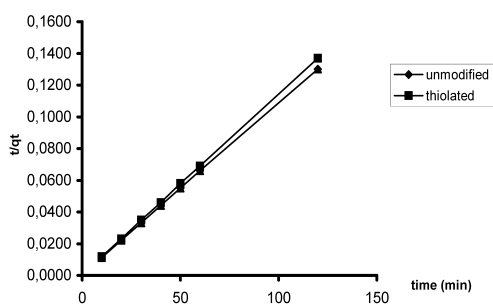**Figure 3.** Pseudo-first order rate plot for As (III) removal on unmodified and thiolated coconut fiber.

For 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: physico-chemical sorption, ion exchange, precipitation or complexation[40,41]. The first one is bulk diffusion, the second is external mass transfer resistance and the third is intraparticle mass transfer resistance. The mechanism of sorption is particle diffusion controlled when intraparticle mass transfer resistance is the rate limiting step.

The intraparticle diffusivity was estimated using equation (9),which was developed using the linear driving force concept by Chanda et al as reported by Okieimen(1991)[42].

$$\ln (1 - \alpha) = -kpt \qquad (9)$$

Where α (alpha) is the fractional attainment to equilibrium (FATE), given by equation (10) k_p is the rate constant for intraparticle diffusivity.

$$\alpha = [M]_t \, ^{n+}/ [M] \quad ^{n+} \qquad (10)$$

Where M represents As (III), n+ is the charge, i.e., amount adsorbed at time t, divided by amount adsorbed at infinity. FATE is shown on Figure 5 while intraparticle diffusivity plot is shown on Figure 6.
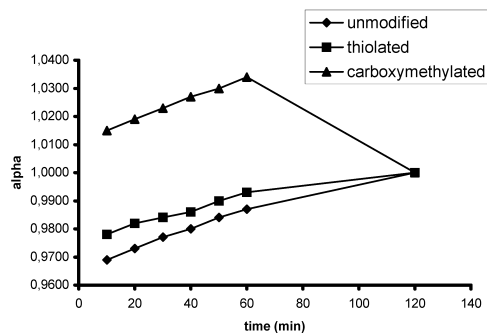

Figure 4. Pseudo-first order rate plot for As (III) removal on unmodified and thiolated coconut fiber.

Figure 5. Plot of alpha (FATE) against time for As (lll) adsorption on unmodified, thiolated and carboxymethylated coconut fiber.
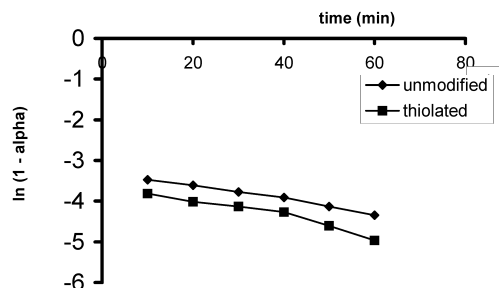
Figure 6. Intraparticule diffusivity plot for As (lll) adsorption on unmodified and thiolated coconut fiber.

The fractional attainment to equilibrium may be either film-diffusion controlled or particle diffusion controlled even though this two different mechanism may not be sharply demarcated [41, 42]. A plot of ln (1-α) against t showing a straight line confirms particle diffusion. As (III) on carboxymethylated coconut fiber did not give a straight line. This is because the adsorption of As (III) on carboxymethylated coconut fiber is predominantly film diffusion controlled. As a result, the intra-parfticle diffusion rate constant could not be calculated. The intraparticle rate constants (kp) were obtained as 9.30×10^{-2} min^{-1} and 11.40×10^{-2} min^{-1}, for unmodified and thiolated respectively.

Another type of intraparticle diffusivity equation was used to model the sorption reaction [43]. This is given by equation (11).

$$q_t = X_i + K_i \quad t \tag{11}$$

Where q_t is same as above and X_i is the boundary layer thickness. The Figure generated using equation (11) is the same shape as Figure 2. The rate constants for initial rate of sorption (K_i) were calculated as; 124.70, 118.43 and 123.32 mg/g-min$^{0.5}$ for unmodified, thiolated and carboxymethylated coconut fiber respectively. Also, the boundary layer thickness (Xi) were calculated as; 883.0, 844.0 and 883.0 mg/g respectively. Higher values of the boundary layer thickness, depicts higher adsorption capacities. This is because the initial curve portion of the plot is attributed to boundary layer diffusion effect (i.e.,

external film resistance). The boundary layer also gives an insight into the tendency of As (III) 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 As (III) ion solution diffusing across its surface.

Conclusion

The biomass of coconut fiber demonstrated a good capacity for As (III) ions bio-sorption highlighting its potential for effluent treatment processes. The incorporation of thiol and carboxymethyl groups onto the adsorbent surface affected the adsorption, especially that of carboxymethyl group which is a more bulky group, which also impacts a stearic hindrance to the adsorption process. The mechanism of sorption was found to be particle diffusion controlled except for carboxymethylated fiber which was film diffusion controlled. Thus, these results could serve as design parameters for treatment plant for the removal of arsenic from wastewater.

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