

Selected operational factors effects on adsorption kinetics of Arsenic

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ABSTRACT

This paper presents a report on the statistical assessment of factors that impacted the adsorption kinetic of arsenic (Asc) onto powdered eggshell (PDEs). The elemental compositions of the PDES were monitored using standard procedures. Adsorption kinetics of Asc onto PDES was monitored using standard adsorption kinetics models. Effects of pH, particle size, mass adsorbent, and initial Asc concentrations on the kinetics of Asc adsorption onto PDEs were studied and analysed using analysis of variance (ANOVA). The study revealed that moisture content (M_{cc}) and volatile solids (V_s) at 550°C of the PDEs were 0.894 %, and 2.014 % (1.96 % based on the dried weight), and volatile solids at 1200°C were 20.594 % (20.41 % based on the dried weight). Statistical assessment revealed that substantial factors that had impact on adsorption kinetics of Asc onto PDEs were time ($F = 2.477$, $p = 0.022$), initial concentration of Asc ($F = 98.625$, $p = 2.0 \times 10^{-17}$), pH ($F = 66.174$, $p = 4.78 \times 10^{-14}$), particle size of the adsorbent ($F = 129.828$, $p = 1.35 \times 10^{-12}$) and mass of the adsorbent ($F = 144.390$, $p = 2.24 \times 10^{-13}$) at 95 % confidence level. It was concluded that PDEs can adsorb arsenic ions and the presence of metallic ions (Fe, Al and Ca) aided arsenic removal. Mass of adsorbent, pH, particle size, and initial Asc concentration are substantial factors that impacted the adsorption kinetic of Asc onto PDEs.

Keywords: arsenic; adsorption kinetics; statistical evaluation; significant factors, analysis of variance

1. Introduction

Arsenic (Asc) is a teratogen and carcinogen substance that can traverse placental barriers, yield fetal death and malformations in many types of mammals [1,2]. Most Asc wastes are produced originated from agronomic products (insecticides, fungicides, herbicides, wood preservatives, algicides, and growth stimulants for plants and animals, 3, 4). Living things are exposed to Asc by way of atmospheric discharges from smelters and smelter wastes, arsenical herbicide sprays, coal-fired power plants, water polluted by mine tailings, and natural mineralization; and from the diet (consumption of marine biota, 1 - 4). Asc concentrations are usually low (<1.0 mg/kg wet mass) in several living organisms but are higher in marine biota (in which Asc arises as arseno-betaine and postures little threat to organisms or their consumer) in plants and animals

from parts that are naturally arseni-ferous or that are near industries and users of arsenical wastes. Asc is bio-concentrated by organisms, but is not bio-magnified in the food chain [1, 2]. Asc occurs in four oxidation statuses, as in-organic or organic systems. Its bio-availability and toxic properties are considerably modified by many biological and abiotic factors. In general, in-organic forms of Asc compounds are additional toxic than organic Asc compounds, and trivalent types are more deadly than pentavalent types. Asc may be absorbed by assimilation, inhalation, or through permeation of skin or slimy membranes; cells take up Asc through a dynamic transport structure usually used in phosphate transportation. The mechanisms of Asc toxicity differ greatly among chemical species, although all appear to cause similar signs of poisoning [1 – 4]. Scientists and engineers had identified several methods and

techniques suitable for Asc removal from water and wastewaters. Some of the scientific methods and techniques that have been useful in Asc reduction are coagulation/flocculation and sedimentation, pH adjustment and sedimentation, ion-exchange, filtration, reverse-osmosis, electrochemical, precipitation, adsorption and electro-dialysis [2, 5 – 22]. With the expectation of adsorption and filtration, the present Asc removal technologies mentioned above are not sustainable for rural communities in developing countries because of extraordinary capital cost and high maintenance required by skilled

MATERIALS AND METHODS

Unboiled, Natural and unprocessed eggshells (chicken) were collected from Obafemi Awolowo University, Ile-Ife, Nigeria. The eggshells were cleaned using distilled water (to remove impurities and sand), air-dried, pulverised into powder and separated into various sizes using British Standard sieves. Powdered eggshell with sieve sizes of lower than $63 \times 10^{-6}m$ (PDES₁), between 63.0×10^{-6} and $75.0 \times 10^{-6} m$ (PDES₂) and between 75.0×10^{-6} and $150.0 \times 10^{-6}m$ (PDES₃) were separated and stored in desiccators. The elemental contents of the PDES were determined using Atomic Absorption Spectrophotometer (AAS) after acid digestion of a known mass of the samples [23, 24]. The microstructure was examined using a scanning electron microscope (Carl Zeiss Smart Evo 10). This was carried out with the aid of the backscattered electron detector, providing compositional contrast and the secondary electron detector providing topographical information. Energy Dispersive Spectroscopy (EDS) was used to confirm the elemental composition of identified phase while examinations were done in the high vacuum mode. Selected physical and chemical properties of the PDEs were determined using standard methods as follows:

Determination of Moisture Content of the PDEs:

A well and an adequate mixed sample of the PDEs was dried in an initially weighed dish at 105°C to a

labours, thus making adsorption treatment technique the most inexpensive and easy to device for Asc removal. In this study, powdered eggshell was used to adsorb Asc from aqueous solution (the material is easily available and economical, [1 - 3; 25 – 28] and because it had been used as an adsorbent to remove other heavy metals [29 – 31]. The primary objective of this study was to scrutinize adsorption properties of PDEs with particular attention to adsorption kinetics models, and effects of selected factors on the adsorption kinetic models.

constant weight in an oven [23] and the moisture content (M_c) of PDEs was computed as follows:

$$M_c (\%) = 100 \left(\frac{W_1 - W_2}{W_1} \right) \tag{1}$$

Where: M_c is the moisture contents, W₁ and W₂ are the initial and final weights of the PDEs after oven-dried at 105°C

Determination of As and Volatile Contents of the PDEs:

A known weight of the dried PDEs samples used for the determination of moisture content was placed in crucibles of known masses and transferred into a muffle furnace (Brother Furnace, XD 1220N). The muffle furnace was heated to 550°C and 1200°C for 2 hours respectively. The PDEs samples were allowed to cool in desiccators to room temperature, and the final weights of the crucibles and the PDEs were determined. Volatile solid and ash contents of the PDEs were computed as follows:

$$V_s (\%) = 100 \left(\frac{W_2 - W_3}{W_2} \right) \tag{2}$$

$$V_{sd} (\%) = \left(\frac{V_s}{1 + M_c} \right) \tag{3}$$

$$A_{sh} (\%) = 100 \left(\frac{W_3}{W_1} \right) \tag{4}$$

$$A_{shd} (\%) = \left(\frac{A_{sh}}{1 + M_c} \right) \tag{5}$$

Where: W_3 is the final weight of the PDEs after 2 hours burnt in the muffle furnace at 550 and 200°C, A_{sh} and V_s are the ash and volatile solid contents of the PDEs.

Determination of Water and Acid Solubilities of the PDEs: Known dried masses of the PDEs samples were soaked in a known volume (300 mL) of distilled water and a known volume (300 mL) of 0.25 M of HCl individually for 24 hours. The PDEs samples were filtered using pre-dried and weighed filter paper (Whatman). The PDEs samples and the filter paper were dried in the oven at 105° C for 24 hours and allowed to cool in desiccators to room temperature, and the final weights were determined. The water (W_s) and acid solubilities (A_s) of the PDEs were computed as follows [32]:

$$W_s (\%) = 100 \left(\frac{W_2 - W_4}{W_2} \right) \quad (6)$$

$$W_{sd} (\%) = \left(\frac{W_s}{1 + M_c} \right) \quad (7)$$

$$A_s (\%) = 100 \left(\frac{W_2 - W_5}{W_2} \right) \quad (8)$$

$$A_{sd} (\%) = \left(\frac{A_s}{1 + M_c} \right) \quad (9)$$

Where: W_s is the water solubility of the PDEs, A_s is the acid solubility of the PDEs, W_4 and W_5 are the dry weight of the PDEs after being soaked in the distilled-water and the 0.25 M of HCl acid for 24 hours respectively.

Determination of Elemental Contents of the PDEs: A known mass of the PDEs was digested using the trioxo-nitrate (V) acid digestion method as stated in Standard Methods for Water and Wastewater Analysis [23]. The chemical properties of the PDEs were determined using standard methods [23] and the total metal concentrations (M_{cc}) were determined using AAS method. Metal

concentrations in the PDEs were computed as follows:

$$M_{cc} (mg / L) = \left(\frac{A \times B}{W_1} \right) \quad (10)$$

Where: B is the dilution factor, A is the concentration of the metals (mg/L) in the PDEs obtained from the reading and M_{cc} is the actual concentration of the metal in the PDEs (mg/l).

Determination of Adsorption Performance of the PDEs: Adsorption kinetics of the PDEs were determined using synthetic lead ion aqueous solutions (stock solutions) prepared using the standard method [23, 24]. Working solutions of Asc were regularly prepared from the stock solution. Adsorption capacities of the PDEs were studied on synthetic wastewaters prepared by dissolving 14.63 grams of $Na_2HAsO_4 \cdot 7H_2O$ in distilled water [23]. Specifically, known masses (1, 0.85 and 0.75 gram) of the adsorbent were added into beakers containing 300 ml of a known concentration (2.5 mg/L) of Asc. The mixtures were thoroughly stirred at 60 revolutions per minute (rpm) for 3 minutes and allowed to settle for 18 hours. The supernatants of the samples were filtered through a filter paper (Whatman) to remove suspended solids and arsenic ion concentrations in the filtrates were determined. The procedures were repeated for natural water collected to ascertain the applicability of the process. In order to determine the adsorptions equilibrium and dynamic, known quantities of the PDEs were added to 300 ml of a solution containing 1.5 mg / L Asc solution, stirred for 3 minutes, and allowed to settle. The supernatants of these aqueous solutions were filtered through a filter paper at an interval of 1 hour and the filtrates were analysed for arsenate. For adsorptive rates of natural waters (raw water from Aponmu river, an artificial lake in Elizade University, Ilara - Mokin), water samples were collected weekly for four months and subjected to similar treatments as the synthetic

wastewaters. The amount of solute removed (adsorbed) was computed using equation (11).

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (11)$$

Where: q_e is the adsorption capacity of the PDEs at equilibrium (mg/g), C_0 is initial the concentration of Asc ion in the solution (mg/l), C_e is the experimental concentration of Asc ion in the solution at equilibrium (mg/l). The percentage of Asc removed (R_t %) from the solution was calculated using equations (12 and 13).

$$R_t(\%) = 100 \left(\frac{(C_0 - C_t)}{C_0} \right) \quad (12)$$

$$q_t = \left(\frac{(C_0 - C_t)}{M} \right) V \quad (13)$$

Where: q_t is the adsorption capacity of the PDEs at time t (mg/g), C_0 is initial the concentration of lead in the solution (mg/l), C_t is the experimental concentration of the As ion in the solution at time t (mg/l), and R_t is the percentage of the Asc ion adsorbed (%). Impact of pH on the adsorption of Asc from synthetic wastewaters and water samples individually was investigated using PDES of particle size below 63×10^{-6} m at different pH values (the pH of the solutions were adjusted with either 0.01 M of HCl or 0.01 M of NaOH), at an initial Asc ion concentration of 1.00 mg / L. The influence of particle size on the Asc removal from solution by adsorption experiments was investigated using various particle sizes of the PDEs (PDEs₁, PDEs₂ and PDEs₃) at pH 7.2 and at an initial Asc concentration of 1.5 mg / L. The effect of initial concentrations on the adsorptive rate adsorption capacity of Asc onto the PDEs using batch adsorption experiments was investigated at initial concentrations between 0.5 mg / L and 1.5 mg / L at particle size below 63×10^{-6} m (PDEs₁) and pH 7.2.

The laboratory analyses of pH and Asc ion concentrations in both synthetic and natural water used were conducted as specified in APHA [23]. Adsorption kinetics of Asc unto PDEs was monitored and analysed using standard techniques (first and second-order pseudo, Elovich, and intra-particle diffusion kinetic models). Microsoft Excel Solver was used for the determination of the adsorption kinetics parameters based on availability at no additional cost. The procedure used for Microsoft Excel solver can be summarized as follows [33 -35]:

- a. Excel solver was added in the Microsoft Excel,
- b. Target $((K_p - K_t)^2 = 0)$, operation and changing cells were set, Where; K_p is the experimental adsorption capacity and K_t is the calculated adsorption capacity; and Microsoft Excel Solver was allowed to iterate at 200 iterations with 0.005 tolerance (Figure 1).

Adsorption kinetics of Asc onto PDEs were monitored through standard adsorption kinetics models as follows:

- a) The second-order pseudo adsorption kinetic equation is expressed as shown in equation (14):

$$q_t = \frac{k_2(q_e)^2 t}{1 + k_2(q_e)t} \quad (14)$$

Where: q_e is the equilibrium solid phase concentration of sorbate (mg/mg), t is the time, k_2 is the rate constant of second-order pseudo adsorption.

- b) The pseudo first-order equation is generally expressed as follows:

$$q_t = q_e \left(1 - Exp^{-\frac{k_1 t}{2.303}} \right) \quad (15)$$

- c) Erhan *et al.* [36], Oke *et al.*[37], Ismail *et al.*[38] simplified Elovich equation as follows:

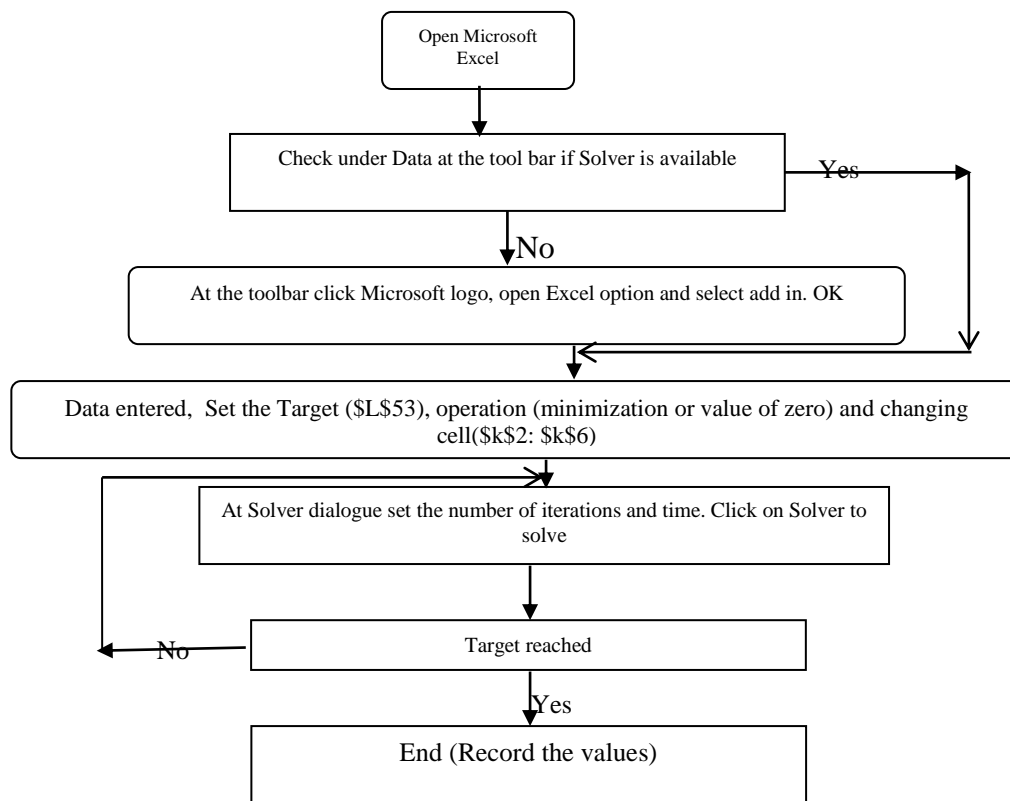


Figure 1: Procedure for using Microsoft Excel Solver in the computation of the parameters

$$q_t = \frac{1}{\beta} \log_e(\alpha\beta) + \frac{1}{\beta} \log_e(t) \quad (16)$$

Where: β is the desorption constant during any experiment and α is the initial adsorption rate

d) The intra-particle diffusion model is based on the theory proposed by Weber and Morris [36]. It was tested to identify the diffusion mechanism. It is an empirical functional relationship and common to the most adsorption processes. The theory states that the uptake varies proportionally with $t^{0.5}$ rather than with the contact time t . According to this theory the equation can be expressed as follows [39 – 41]:

$$R = k_p(t)^{0.5} + C \quad (17)$$

e) The other form of intra-particle diffusion model found in literature can be expressed as equation (18) as follows:

$$R = k_{id}(t)^a \quad (18)$$

Where: R is the percentage of the pollutant adsorbed (%), ‘ a ’ is the gradient of linear plots and k_{id} is the intraparticle diffusion rate constant (/h).

Chrastil’s diffusion model describes sorption kinetics in diffusion-controlled systems. The model can be expressed by the following equation [41]:

$$q_t = q_e \left(1 - \text{Exp}^{-k_c A_0 t}\right)^n \quad (19)$$

where k_c is a rate constant ($\text{dm}^3/\text{g}\cdot\text{min}$), which depends on diffusion coefficients and the sorption capacity of biosorbent, A_0 is the dose of biosorbent (g/dm^3), and n is a heterogeneous structural diffusion resistance constant, which can range from 0 to 1. Constant n is independent of the sorbate concentration, sorbent concentration A_0 , q_e , and temperature [41 – 44]. Parameters in these adsorption kinetics models were computed through Microsoft Excel Solver and evaluated statistically

using analysis of variance (ANOVA), total error, and Akaike Information Criterion (AIC).

The total error, which is the sum of the squares of the errors between the calculated adsorption capacity and the expected adsorption capacity can be interpreted as a measure of variation in the values expected left unexplained by the values obtained. Lower value of total error indicates higher the accuracy, validity and good fitness of the device. Total error (Err^2) can be computed using equation (20):

$$Err^2 = \sum_{i=1}^n (Y_{obsi} - Y_{cali})^2 \quad (20)$$

Where; Y_{obsi} is observed concentration and Y_{cali} is calculated concentration. The AIC was derived from the Information Criterion of Akaike [37]. It allows a direct comparison among models with a different number of parameters. The AIC presents the information on a given set of parameter estimates by relating the coefficient of determination to the number of parameters. The AIC was determined using Equation (21) as follows:

$$AIC = n \left(\ln \sum_{i=1}^n (Y_{obsi} - Y_{cali})^2 \right) + 2p \quad (21)$$

The Schwartz Criterion (SC) is defined by the formula in equation (22).

$$SC = n \left(\ln \sum_{i=1}^n (Y_{obsi} - Y_{cali})^2 \right) + p \ln(n) \quad (22)$$

RESULTS AND DISCUSSION

The composition of the PDEs: The result of the composition determination revealed that moisture content and volatile solids at 550°C of the PDEs were 0.894 %, and 2.014 % (1.96 % based on the dried weight), and volatile solids at 1200°C were 20.594 % (20.41 % based on the dried weight). Ash contents of the PDEs were 97.941 % (97.07 % based on the dried weight), and 79.943 % (79.722 % based on the dried weight) at 550°C and 1200°C

respectively. Acid solubilities were 6.481 % and 6.423 % based on the wet and dried weights respectively, and water solubilities were 0.454 % and 0.430 % based on the wet and dried weights respectively. The mineral contents were 22.65 mg/g of iron as Fe^{2+} , 12.75 mg /g of aluminium as Al^{3+} and 448 mg /g of Calcium as Ca^{2+} . The results of the scanning electron microscope, backscattered electron detector and secondary electron detector are as presented in Figure 2. The results revealed that the PDEs is a calcium salt (calcite material). It has been suggested that in the presence of water aluminium, calcium and iron salts undergo displacement reactions [38 – 40]. Figure 2 presents the micrograph structure of PDEs. The figure revealed that there are pores on the PDEs. These pores gave rooms for the adsorption of arsenic. Figure 3 presents a similar micrograph structure of eggshells from literature [45]. Figure 4 presents a similar micrograph structure of eggshells from literature [46]. Literature such as Kuh and Kim [25]; Elkady *et al.*, [26]; Tsai *et al.*, [27]; Zulfikar, *et al.*, [28], Hess *et al.* [50], Anastasija *et al.* [48], Lin *et al.* [47] and Krzytof *et al.* [49] established the composition and structure of eggshells.

Effect of initial pH on adsorption of Asc: The previous studies on the effect of pH on metal biosorption from aqueous solutions using various adsorbent indicate that the solution pH has a large effect on the uptake of metal ions [1, 22]. In the present study (Figure 5a), there was continuous decrease in the percentage of adsorption when pH was increased initially from 3.2 to 11.5 in a fixed experimental condition (an environment of unchanging As concentration and PDEs dose). The increase in pH value leads to Asc precipitation and Asc accumulation within the pores. It may be attributed to the fact that the Asc reacts with OH^- and forms insoluble Asc hydroxide which decreases the amount of Asc adsorption. Tables 1a and b

present statistical evaluation of the effects of pH on adsorption of Asc for both synthetic wastewaters and raw water respectively, which indicate that pH is a significant factors that influence Asc adsorption onto PDEs at 95 % confidence level for both synthetic wastewaters ($F = 66.17352$ and $p = 4.78 \times 10^{-14}$) and raw water ($F = 4.780522$ and $p = 0.007108$) respectively.

Effect of Asc concentration on adsorption of Asc onto PDEs: Figure 5b presents the effect of Asc concentration on adsorption of Asc onto PDEs. The figure reveals that the proportion of the Asc adsorbed was tended to increase with decreasing Asc concentration. Since the available adsorption sites were restricted because of fixed adsorbent dose, when it achieves equilibrium, the percentage removal of Asc shows a constant decrease due to the non-availability of more adsorption sites. Tables 2a and b present statistical evaluation of effects of Asc concentration on adsorption of Asc for both synthetic wastewaters and raw water respectively, which indicate that Asc concentration is a significant factors that influence Asc adsorption onto PDES at 95 % confidence level for both synthetic wastewaters ($F = 98.62457$ and $p = 2.0 \times 10^{-17}$) and raw water ($F = 73.57468$ and $p = 2.0 \times 10^{-15}$) respectively.

Effect of particle size of PDEs on adsorption of Asc onto PDEs: Figure 5c presents effect of particle size of PDEs on adsorption of Asc onto PDEs. The figure reveals that as particle size of PDEs decreases the surface area of PDEs tended to increase with decreasing particle size of PDEs. Since the available adsorption sites were increased with surface area because of fixed adsorbent dose, when it achieves equilibrium, the percentage removal of Asc shows a constant decrease due to the non- availability of more adsorption sites due to small surface areas in larger particle size of PDEs.

Tables 3a and b present statistical evaluation of effects of particle size of PDEs on adsorption of Asc for both synthetic wastewaters and raw water respectively, which indicate that particle size of PDEs (adsorbent) is a significant factors that influence Asc adsorption onto PDEs at 95 % confidence level for both synthetic wastewaters ($F = 129.8277$ and $p = 1.35 \times 10^{-13}$) and raw water ($F = 43.16467$ and $p = 2.42 \times 10^{-8}$) respectively

Effect of PDEs mass on adsorption of Asc onto PDEs: Figure 5d presents adsorption of Asc onto PDEs at various Adsorbent masses. At a fixed Asc concentration and pH of the aqueous solution, with increase in PDEs dosage ranging from 0.75 to 1.0, the percentage of adsorption increases to a certain level due to the increase in surface area and active centers of adsorbent, after that diminishes due to saturation of the adsorbate with the ample amount of adsorbent. The available adsorption sites were increased because of increased PDEs dose, when it achieves equilibrium, the percentage removal of Asc shows a constant increase due to the availability of more adsorption sites (Figure 5d). A similar effect of adsorbent was reported by other authors in literature such as Beltra'n-Heredia *et al.* [51] Bozbas and Boz [52] and Tural *et al.* [53]. Tables 4a and b present statistical evaluation of effects of PDEs mass on adsorption of Asc for both synthetic wastewaters and raw water respectively, which indicate that Asc concentration is a significant factors that influence Asc adsorption onto PDEs at 95 % confidence level for both synthetic wastewaters ($F = 144.3896$ and $p = 2.24 \times 10^{-13}$) and raw water ($F = 73.02916$ and $p = 1.93 \times 10^{-10}$) respectively. Tables 1 to 4 revealed that time was a significant factor that influence adsorption of Asc onto PDEs at various conditions of aqueous solutions.

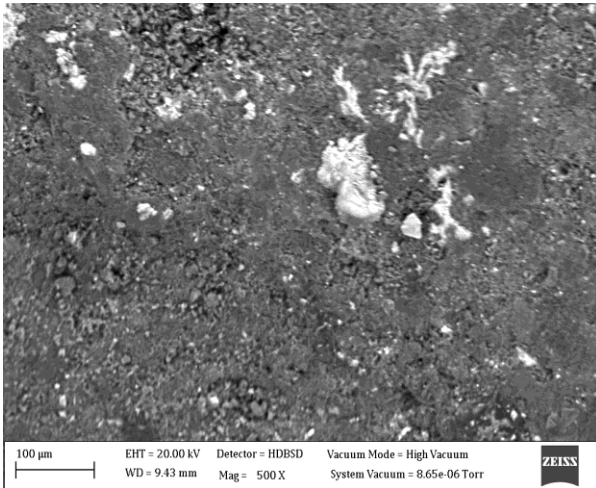


Figure 2a: SEM of PDEs magnitude 500 X

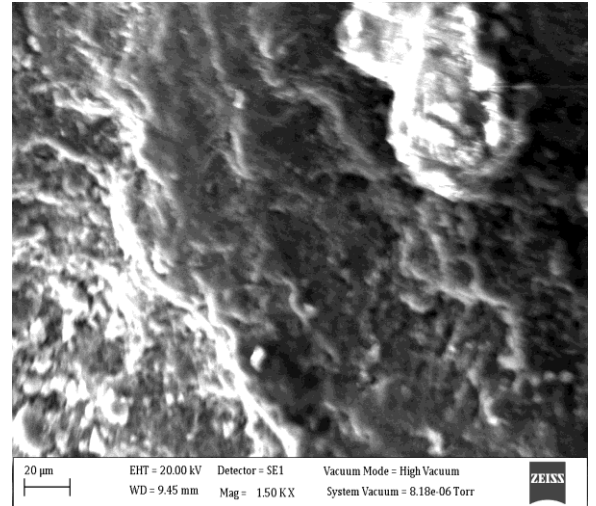


Figure 2b: SEM of PDEs magnitude 150 X

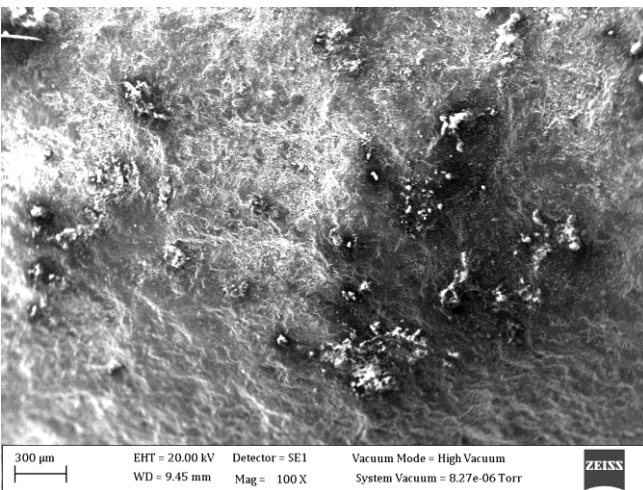


Figure 2c: SEM of PDEs magnitude 100 X

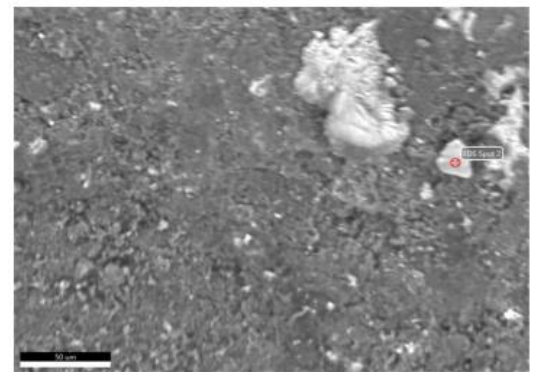


Figure 2d: Spot A SEM of PDEs for



Figure 2f: Spot B SEM of PDEs for composition

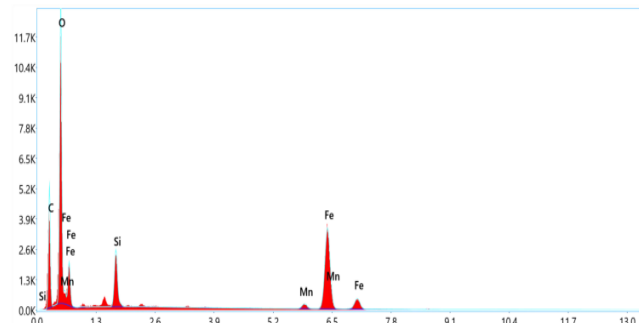


Figure 2e: Spot A EDS of PDEs for composition

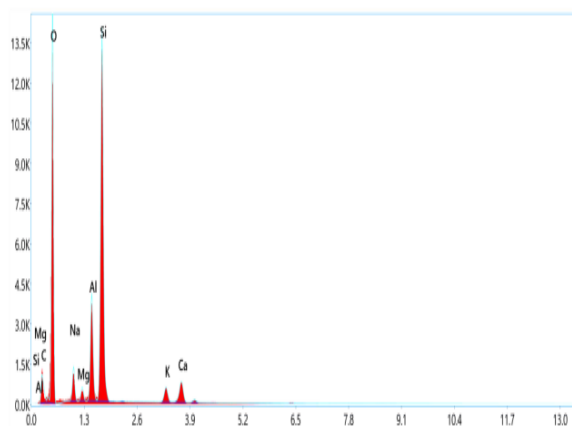


Figure 2g: Spot B EDS of PDEs for composition

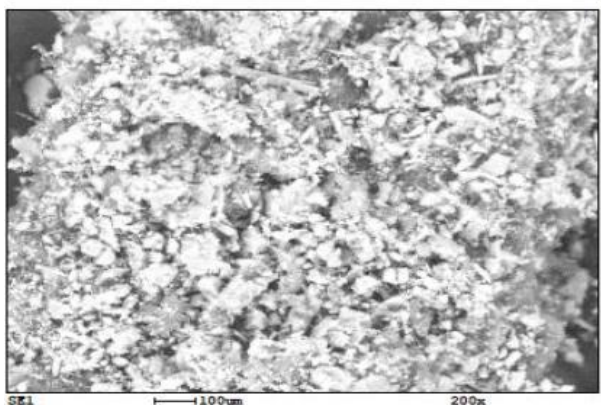


Figure 3a: A Similar SEM of PDEs (Source: Ajala *et al.*, [45])

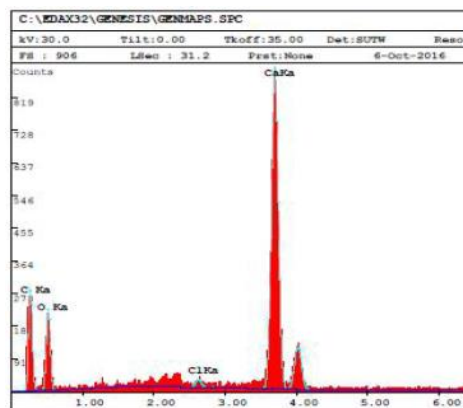


Figure 3b: A Similar EDS of PDEs (Source: Ajala *et al.*, [45])

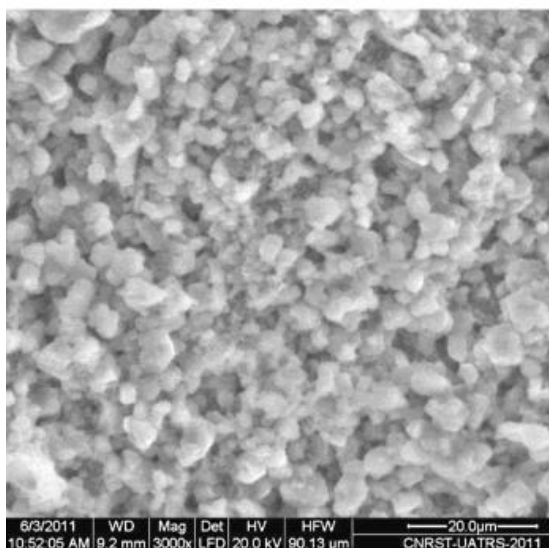


Figure 4: A Similar SEM of PDEs (Source: Slimani *et al.*, [46])

Regeneration and Desorption of PDEs: Once the sorbent is used, it needs to be regenerated. Desorption processes are important from two points of view as follows:

- a) to recover metal ion and its subsequent use in industrial, and
- b) in the regeneration of sorbent for new use processes.

The amount of Asc released from the adsorbent was calculated from pH variation. Percentage of Asc desorbed and amount of hydroxyl concentration were calculated as follows:

$$As_{des} = 100 \left(\frac{C_{6.5} - C_{11.5}}{C_{6.5}} \right) \quad (23)$$

where: $C_{7.2}$ is the Asc concentration at pH of 6.5 and $C_{11.5}$ is the Asc concentration at pH of 11.5,

$$OH^- = X_{ab} - X_{ac} \quad (24)$$

where: X_{ab} is the OH⁻ concentration at pH of 11.5 and X_{ac} is the OH⁻ concentration at pH of 6.5
The results of desorption computation revealed that 45.2 % of Asc/ mg of initial concentration was desorbed at 8 hours with a particle size of PDEs of 0.063 mm and PDEs mass of 0.85 g with 0.0033 moles of OH⁻/ dm⁻³

Estimated Cost of Producing PDEs: Costs of producing PDEs were based on 95% yield from every 1 kilogram PDEs collected, assuming that 320 days per year, collected eggshells were waste materials, 1000 kg of PDEs were produced per shift day public energy source will be used and three men per a shift of 8 hours. The average cost of producing a kilogram of PDEs was found to be 0.426 USD at

the rate of ₦660 per USD. It could then be said that the study has identified the estimated cost of 0.426 USD / kg of PDEs. The cost is cheaper compared to the cost of producing empty fruit bunches (0.50 USD/kg, [20, 21], activated carbons (0.504USD) and chemical activation carbon (24.003 USD), grape fruit (pencon shell based activated carbon (2.72 USD/kg) 0.068 USD/kg of powdered corn cob and sugar cane based granular activated carbon by steam (3.12 USD/kg) 20 – 22].

CONCLUSION

This study concluded that

- a. arsenic could be removed by an inexpensive waste product – the powdered eggshell - with an equilibrium time of 8 hours.
- b. PDEs contains Ca, Al, and Fe, which aided in arsenic ion removal from water and wastewaters.
- c. PDEs can adsorb arsenic ion and the presence of metallic ions (Fe, Ca and Al aided arsenic removal) and
- d. Mass of adsorbent, pH, particle size, and initial Asc concentration are significant factors that influence the adsorption kinetic of Asc onto PDEs.

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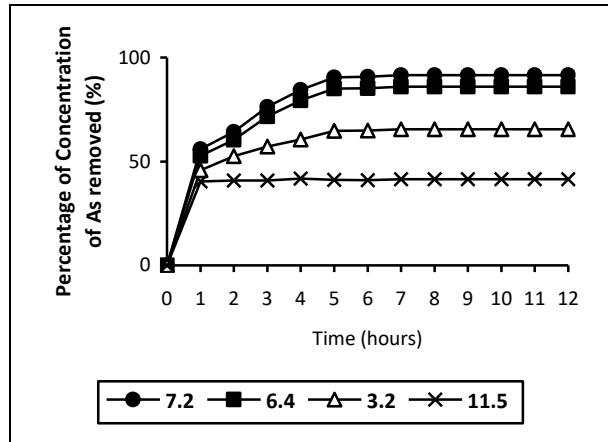


Figure 5a: Adsorption of Asc onto PDEs at various pH of aqueous solution

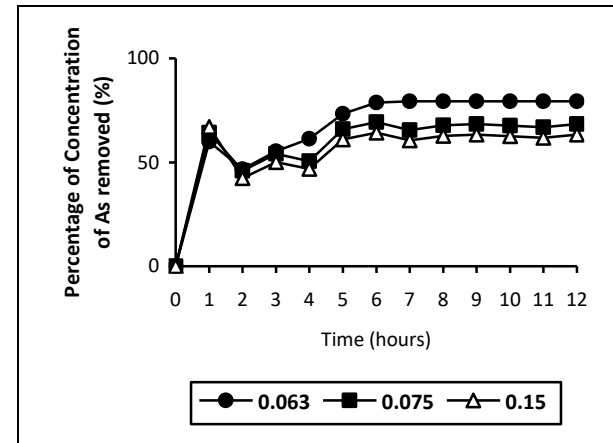


Figure 5c: Adsorption of Asc onto PDEs at various Particle sizes of PDEs

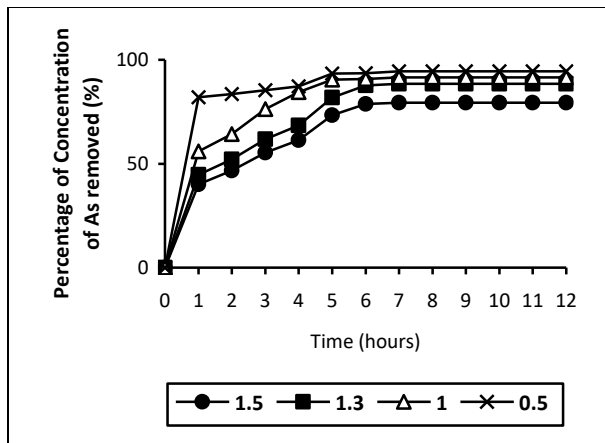


Figure 5b: Adsorption of Asc onto PDEs at various initial concentration of Asc (mg/l) in aqueous solution

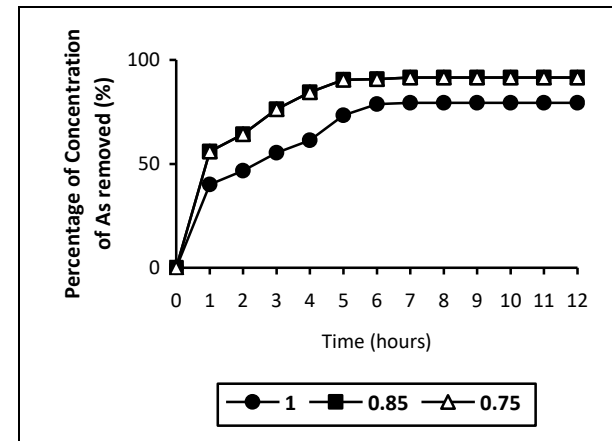


Figure 5d: Adsorption of Asc onto PDEs at various Adsorbent masses

Table 1a: Effect of pH on adsorption of Asc onto PDEs synthetic wastewater

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Time	43.2383	11	3.930755	2.476714	0.021748
pH	315.069	3	105.023	66.17352	4.78×10^{-14}
Error	52.3738	33	1.587085		
Total	410.6811	47			

Table 1b: Effect of pH on adsorption of Asc onto PDEs raw water

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Time	1.924877	11	0.174989	501.4881	2.1×10^{-33}
pH	0.005004	3	0.001668	4.780522	0.007108
Error	0.011515	33	0.000349		
Total	1.941396	47			

Table 2a: Effect of Asc concentration on adsorption of Asc onto PDEs synthetic wastewater

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Time	1.118213	12	0.093184	9.011335	1.25×10^{-7}
Initial Concentration	3.059571	3	1.019857	98.62457	2.0×10^{-17}
Error	0.372269	36	0.010341		
Total	4.550052	51			

Table 2b: Effect of Asc concentration on adsorption of Asc onto PDEs raw water

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Time	0.670251	12	0.055854	9.759723	4.61×10^{-8}
Initial Concentration	1.263189	3	0.421063	73.57468	2.0×10^{-15}
Error	0.206026	36	0.005723		
Total	2.139465	51			

Table 3a: Effect of particle size on adsorption of Asc onto PDEs synthetic wastewater

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Time	2.045513	12	0.170459	56.35804	1.38×10^{-14}
Particle Sizes	0.785349	2	0.392674	129.8277	1.35×10^{-13}
Error	0.07259	24	0.003025		
Total	2.903451	38			

Table 3b: Effect of particle size on adsorption of Asc onto PDEs raw water

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Time	0.777165	11	0.070651	19.67298	6.9×10^{-9}
Particle Sizes	0.310034	2	0.155017	43.16467	2.42×10^{-8}
Error	0.079008	22	0.003591		
Total	1.166207	35			

Table 4a: Effect of PDEs mass on adsorption of Asc onto PDEs synthetic wastewater

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Time	2.828988	11	0.257181	33557.79	8.36×10^{-44}
Adsorbent mass	0.002213	2	0.001107	144.3896	2.24×10^{-13}
Error	0.000169	22	7.66×10^{-6}		
Total	2.831369	35			

Table 4b: Effect of PDEs mass on adsorption of Asc onto PDEs raw water

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Time	32.17564	11	2.925058	1.403833	0.239298
Adsorbent mass	304.3305	2	152.1652	73.02916	1.93×10^{-10}
Error	45.8397	22	2.083623		
Total	382.3458	35			

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