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Mechanism and Activation Energy of Arsenic Removal From Aqueous Solutions

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Abstract. This paper presents the mechanism and activation energy adsorption of arsenic (A_{se}) onto powdered eggshells (PWDEs). The essential compositions and micrograph structure of the PWDEs were determined using standard methods. Adsorption kinetics of A_{se} onto PWDES were monitored using standard adsorption kinetics models.

Effects of pH, particle size, and initial A_{se} concentrations on the kinetics of A_{se} adsorption onto PWDES were studied and analysed using analysis of variance (ANOVA).

The study revealed acid solubilities were 6.048 % and 6.383 % based on the wet and dried weights respectively, and water solubilities were 0.450 % and 0.536 % based on the wet and dried weights respectively. ΔS° and E_a become more negative or positive with decreasing initial concentration indicating that changes in the selected factors favour the removal process.

It was concluded that in the presence of water aluminium, calcium and iron salts undergo displacement reactions. Average cost of producing a kilogram of PDEs was found to be 0.426 USD at the rate of ₦660 per USD.

Keyword. Arsenic; Adsorption kinetics; Adsorbents; Aqueous solution; Adsorption mechanisms

INTRODUCTION

Arsenic and its compounds (A_{se}) are notorious poisonous substances. These notorious poisonous substances are now known to be among the world's extreme environmental threats, which are threatening the lives of numerous hundred million people (Ravenscroft et al., 2009; Mosaferi et al., 2014).

In numerous countries, communities, and regions of the world, biogeochemical progressions have resulted in a release of naturally arising Ase into groundwater and surface water (Bhattacharya et al., 2007). On the other hand, unrestrained anthropogenic actions (mining, smelting of metal ores, fossil fuels burning, use of wood preservatives, pesticides, and Ase seasonings to livestock feed) can discharge A_{se} directly to the environment (Choong et al., 2007; Mohan and Pittman, 2077; Sharma and Sohn, 2009).

Introduction to A_{se} is a key concern to public health in mutually developing and developed countries and elimination of A_{se} from drinking water and wastewaters is a worldwide priority and vital (Dastgiri et al., 2010).

Contact to elevated A_{se} concentrations has been accredited to adverse health connected issues in humans. These health connected issues are alterations in skin pigmentation, lung ailments, diabetes, cancers of the kidney, kidney diseases and bladder (WHO, 2011). With reference to its momentous toxicity, the World Health Organization has recognized a value of $10\ 10^{-6}$ g A_{se} /L as the extreme contaminant concentrations for total A_{se} in potable water (WHO, 2011; Luther et al., 2012).

It is a crucial and urgent need to produce and supply an A_{se} free environment and drinking water in the world. It is well recognized that Ase exists in the usual environment mostly in the forms of arsenite (A_{se} (III)) and arsenate (A_{se} (V)).

Arsenite is more portable and toxic than arsenate. Supreme removal technologies for water and wastewater treatment are competent when the element is in the pentavalent state (Mishra and Ramaprabhu, 2011; Triszcz et al., 2009).

Elimination of Ase contamination from water and wastewater can be accomplished by a variety of conversation and emerging techniques namely: coagulation (Song et al., 2006; Kumar et al., 2004), adsorption and absorption (Daus et al., 2004; Singh and Pant, 2004), ion exchange, filtration, reverse-osmosis, electrochemical, precipitation (An et al., 2011), membrane filtration, electro-dialysis (Shih, 2005; Ningh, 2002) and biological process (Katsoyiannis and Zouboulis, 2004).

A substantial problem faced in the removal of A_{se} from groundwater aquifers, surface water and municipal water systems is the existence of A_{se} in both A_{se} states of A_{se} (III) and A_{se} (V). A_{se} (III) compounds are mainly non-ionic whereas A_{se} (V) compounds are ionic in natural (raw) water pH (Olyaie et al., 2012; Oke et al., 2014). With the exception of adsorption and filtration A_{se} removal technologies stated above are not sustainable for rural communities in developing countries due to high capital cost and maintenance by skilled labourers, thus creating adsorption the most economical and easy to implement for A_{se} removal.

In comparison with other removal techniques, adsorption can remove both A_{se} (V) and A_{se} (III) without previous oxidative pre-treatment and does not necessitate the use of additional chemical products, since some adsorbents are used for the continual production of colloidal hydrous ferric oxides (Triszcz et al., 2009).

Adsorption kinetics and equilibrium that heighten removal of A_{se} from aqueous solution do offer some insight into the scale of application, factors energetic process selection and difficulties that may have ascended in practice.

The accessibility of adsorption kinetic and equilibrium on removal recital at laboratory and full-scale treatment are severely limited. The rapid improvements in information technology and consequent elimination of technical obstructions to sharing information and knowledge of adsorption kinetics and equilibrium should allow the development of an international, accessible database or even a metadata portal for mechanism and activation energy for A_{se} removal that would offer the potential to advantage from past and ongoing experience in practice.

More on A_{se} removal, adsorption kinetic, adsorption equilibrium and treatment can be established in An et al., (2011); Analia et al., (2019); Bozas and Boz (2016), Doina et al., (2019), Ravenscroft et al., (2009), Alam et al., (2018), Nena et al., (2018); Shih (2005); Zunaira and Zhu (2015); Ningh (2002); Mirjana et al., (2012); Morgada et al., (2009); Largittea and Pasquierta (2016); Seda et al., (2017) and Tural et al., (2017). The prime objective of this study was to examine the adsorption properties of PWDEs with particular attention to the adsorption mechanism and activation energy of A_{se} reactions and provide recovery rate and cost estimated in the production PWDEs.

MATERIALS AND METHODS

Unprocessed (unboiled) eggshells (chicken) were collected from Obafemi Awolowo University, Ile-Ife, Nigeria. These raw 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. These powdered raw eggshells with sieve sizes of lower than 63.0 10^{-6} m ($PWDEs_1$), between 63.0 10^{-6}m and 75.0 10^{-6}m ($PWDEs_2$) and between 75.0 10^{-6}m and 150.0 10^{-6}m ($PWDEs_3$) were separated and stored in desiccators.

The elemental contents of the PWDEs were determined using Atomic Absorption Spectrophotometer (AAS) after acid digestion of a known mass of the samples (Rice and Bridgewater, 2012; van Loosdrecht et al., 2016).

The microstructure was examined using a scanning electron microscope (Carl Zeiss Smart Evo 10). This was conducted with the aid of the backscattered electron detector, providing compositional contrast, and the secondary electron detector providing topographical information. Energy Dispersive Spectroscopy was used to confirm the elemental composition of the identified phase while examinations were done in the high vacuum mode. Selected physical and chemical properties of the PWDES were determined using standard methods as follows:

Determination of Moisture Content of the PWDEs

A well and an adequate mixed sample of the PWDEs was dried in an initially weighed dish at 105°C to a constant weight in an oven (Rice and Bridgewater, 2012; van Loosdrecht et al., 2016; Fehintola et al., 2015) and the moisture content (M_c) of PWDEs was computed as follows:

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

M_c is the moisture contents, W_1 and W_2 are the initial and final weights of the PWDES after oven dried at 105°C

Determination of As and Volatile Contents of the PWDEs

A known weight of the dried PWDES 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 PWDEs samples were allowed to cool in desiccators to a room temperature, and the final weights of the crucibles and the PWDEs were determined. Volatile solid and ash contents of the PWDES were computed as follows:

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

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

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

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

W_3 is the final weight of the PWDES after 2 hours burnt in the muffle furnace at 550 and 1200°C, A_{sh} and V_S are the ash and volatile solid contents of the PWDEs.

Determination of Water and Acid Solubilities of the PWDEs

Known dried masses of the PWDEs 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 PWDEs samples were filtered using pre-dried and weighed filter paper (Whatman). The PWDEs samples and the filter paper were dried in the oven at 105° C for 24 hours and allowed to cool in desiccators to a room temperature, and the final weights were determined.

The water (W_s) and acid solubilities (A_s) of the PWDEs were computed as follows (Fehintola et al., 2015):

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

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

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

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

W_S is the water solubility of the PWDES, A_S is the acid solubility of the PWDES, W_4 and W_5 are the dry weight of the PWDES after soaked in the distilled water and the 0.25 M of HCl acid for 24 hours respectively.

Determination of Elemental Contents of the PWDES

A known mass of the PWDES was digested using trioxo-nitrate (V) acid digestion method as stated in Standard Methods for Water and Wastewater Analysis. The chemical properties of the PWDES were determined using standard methods and the total metal concentrations (M_{cc}) were determined using AAS method (Rice and Bridgewater, 2012).

Metal concentrations in the PWDES were computed as follows:

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

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

Determination of Adsorption Performance of the PWDES

Adsorption kinetics of the PWDEs were determined using synthetic lead ion aqueous solutions (stock solutions) prepared using standard methods (Rice and Bridgewater, 2012; van Loosdrecht et al., 2016).

Working solutions of As were regularly prepared from the stock solution. Adsorption capacities of the PWDEs were studied on synthetic wastewaters prepared by dissolving 14.63 grams of $Na_2HAsO_4.7H_2O$ in distilled water (Rice and Bridgewater, 2012).

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 arsenic ion.

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, kinetic and activation energy, a known quantity of the PWDEs was added to 300 ml of a solution containing 1.5 mg/l arsenic 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 from natural waters (raw water from Aponmu river, 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 equations (11 and 12).

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

q_e is the adsorption capacity of the PWDEs at equilibrium (mg/g), C_0 is initial the concentration of A_{se} in the solution (mg/l), C_e is the experimental concentration of A_{se} in the solution at equilibrium (mg/l).

$$q_t = \frac{(C_0 - C_t)}{M} V \quad (12)$$

q_t is the adsorption capacity of the PWDEs at any time t; (mg/g), C_0 is initial the concentration of A_{se} in the solution (mg/l), C_t is the experimental concentration of A_{se} in the solution at equilibrium (mg/l).

Impact of pH on the adsorption equilibrium of arsenic from synthetic wastewaters and water samples individually was investigated using PWDEs of particle size 63.0 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 arsenic ion concentration of 1.00 mg/l.

The influence of particle size on the arsenic removal from solution by adsorption equilibrium was investigated using various particle sizes of the PWDEs ($PWDEs_1$, $PWDEs_2$ and $PWDEs_3$) at pH 7.2 and at an initial arsenic concentration of 1.5 mg/l. The effect of initial concentrations on the adsorption capacity of arsenic onto the PWDEs using batch adsorption equilibrium was investigated at initial concentrations between 0.5 mg/l and 1.5 mg/l at particle size 63.0 10^{-6}m ($PWDEs_1$) and pH 7.2.

The laboratory analyses of pH and arsenic ion concentrations in both synthetic and natural water used were conducted as specified in APHA (Rice and Bridgewater, 2012).

Thermodynamic parameters (enthalpy, ΔH^o, entropy, ΔS^o, and free Gibbs energy ΔG^o) of adsorption kinetics of A_{se} onto PWDES were computed using Microsoft Excel Solver based on experiments performance in a batch system at time between 1 and 12 hours as follows (Devi and Mishra, 2019; Slimani et al., 2021; Singh and Pant, 2004):

$$\ln(1000K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{Rt} \quad (13)$$

$$K_d = \frac{q_t}{C_t} \quad (14)$$

$$\Delta G = \Delta H^o - T\Delta S^o \quad (15)$$

R is the universal gas constant (8.314 J mol^{-1} k^{-1}), T is the temperature (303K). K_d is the distribution coefficient. The activation energy of the adsorption process (E_a) was obtained from the slope of linear plotting of ln(1–θ) against 1/t (modified Arrhenius equation):

$$\ln(1-\theta) = \frac{\Delta S}{R} - \frac{\Delta E_a}{Rt} \quad (16)$$

$$\theta = \left(1 - \frac{C_t}{C_0}\right) \quad (17)$$

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 summarised as follows (Oke et al., 2016; 2017): - Excel solver was added in the Microsoft Excel; - Target ($(K_p-K_t)^2=0$), operation and changing cells were set, 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 (Fig. 1).

Effects of selected factors on activation energy were analysed statistically using analysis of variance (ANOVA).

RESULTS AND DISCUSSION

The composition of the PWDEs and Adsorption Mechanism

The result of the composition determination revealed that moisture content and volatile solids at 550^{o}C of the PWDEs were 0.899 %, and 2.002 % (1.113 % based on the dried weight), and volatile solids at 1200^{o}C were 20.760 % (20. 041 % based on the dried weight). Ash contents of the PWDEs were 97.998 % (98.887 % based on the dried weight), and 79.240 % (79.959 % based on the dried weight) at 550^{o}C and 1200^{o}C respectively. Acid solubilities were 6.048 % and 6.383 % based on the wet and dried weights respectively, and water solubilities were 0.450 % and 0.536 % based on the wet and dried weights respectively.

The mineral contents were 22.465 mg/g of iron as Fe^{2+}, 12.545 mg /g of aluminium as Al^{3+} and 418 mg /g of Calcium as Ca^{2+}.

Figure 2 presents the micrograph structure of the PWDEs. It revealed that there are pores on the PWDEs. These pores gave room for the adsorption of arsenic.

The results of the scanning electron microscope, backscattered electron detector and secondary electron detector are as presented in figures 3-9 present similar micrograph structures of eggshells from literature such as Ajala et al., (2018), Slimani et al., (2021), Kuh and Kim (2000); Elkady et al., (2011); Tsai et al., (2006); Zulfikar et al., (2012), Hess et al., (2018), Smirnova et al., (2016), Lin et al., (2020) and Krzytof et al., (2017), which established the composition and structure of eggshells.

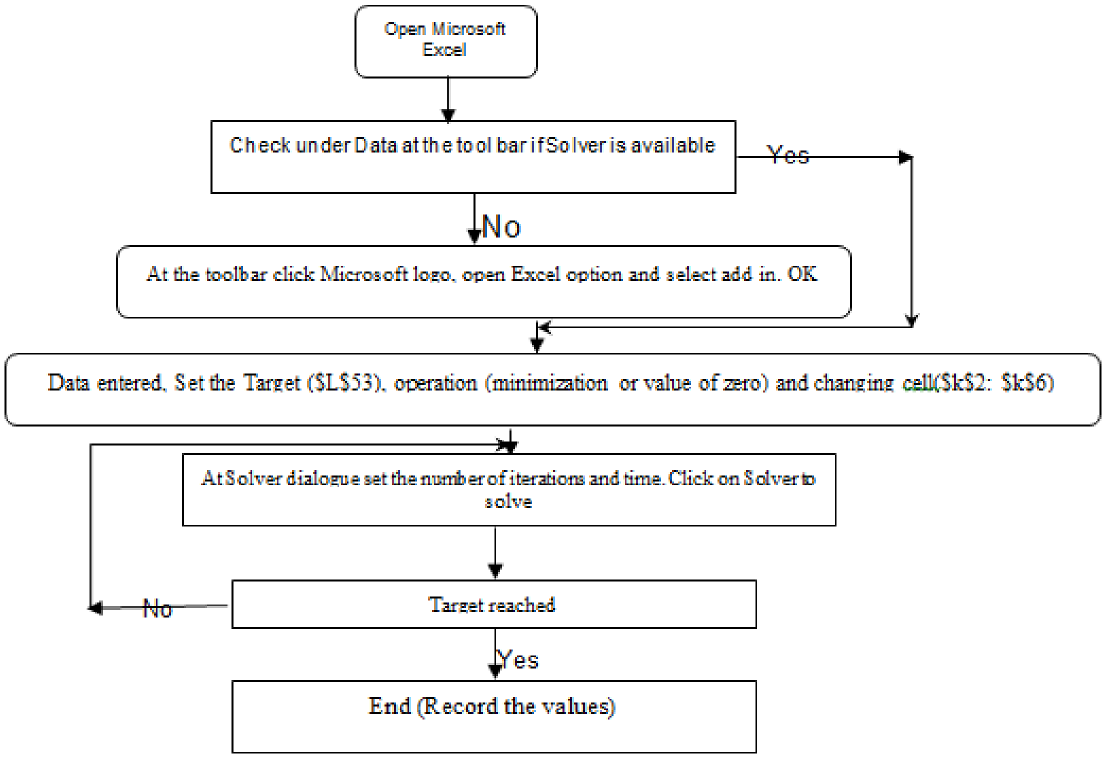


Fig.1. Procedure for using Microsoft Excel Solver in the computation of the parameters.

The results revealed that the PWDEs is a calcite material (calcium salt). It has been suggested that in the present of water aluminium, calcium and iron salts undergo displacement reactions as indicated in equation (18) as follows (Jassim, 2012; Nakano et al., 20013):

$$Al^{3+} + 3H_2O \rightarrow \frac{3}{2}H_2 + Al(OH)_3 \quad (18a)$$

$$Al^{3+} + 2H_2O \rightarrow \frac{3}{2}H_2 + AlO(OH) \quad (18b)$$

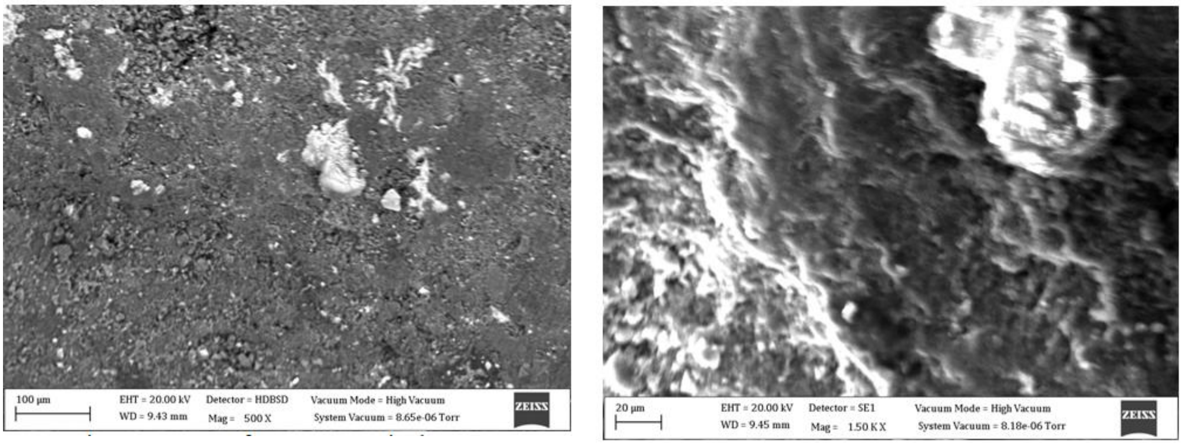
$$Al^{3+} + \frac{3}{2}H_2O \rightarrow \frac{3}{2}H_2 + Al_2(O)_3 \quad (18c)$$

$$Fe^{2+} + 2H_2O \rightarrow H_2 + Fe(OH)_2 \quad (18d)$$

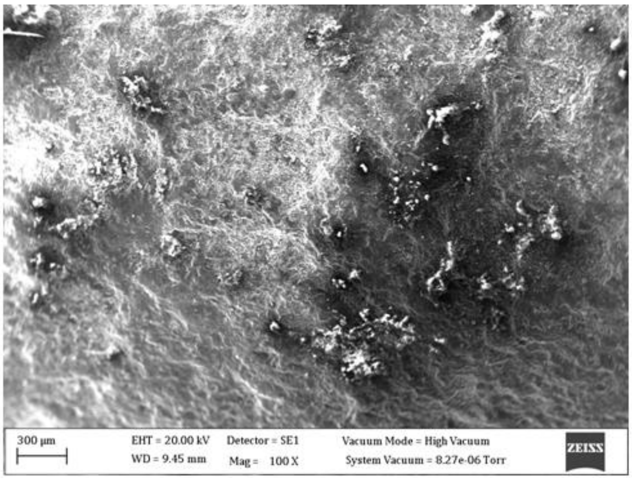
$$Ca^{2+} + 2H_2O \rightarrow H_2 + Ca(OH)_2 \quad (19e)$$

The first reaction (18a) forms the aluminium hydroxide bayerite ($Al(OH)_3$) and hydrogen, the second reaction (18b) forms the aluminium hydroxide boehmite (AlO(OH)) and hydrogen, and the third reaction (18c) types of aluminium oxide and hydrogen. All these reactions of aluminium salts are thermodynamically favourable from room temperature past the melting point of aluminium (660^0C). All are also highly exothermic. From room temperature to 280^0C, $Al(OH)_3$ is the most stable product, while from 280-480^0 C, AlO(OH) is the most stable. Above 480 ^{0}C, Al_2O_3 is the most stable product.

This result shows that the PWDEs underwent the reaction in equation (19) with A_{se}, which altered the pH value and the product formed react with arsenic ion to precipitate the pollutant as calcium, aluminium and iron salts (Fehintola et al., 2015):



a)Magnitude 500 X b)Magnitude 150 X



c)Magnitude 100 X

Fig. 2. SEM of PWDEs .

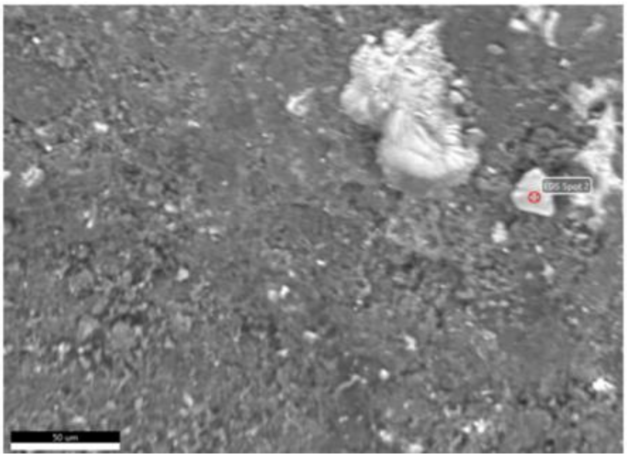


Fig. 3. Spot 2 PWDEs composition

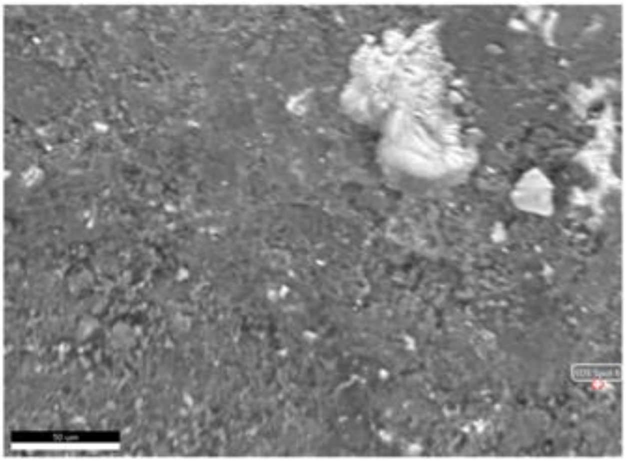


Fig. 4. Spot 6 PWDEs composition.

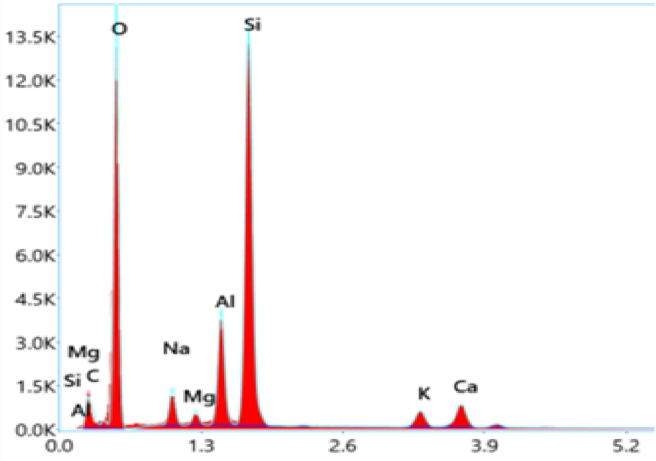


Fig. 5. Spot 2 Elemental composition.

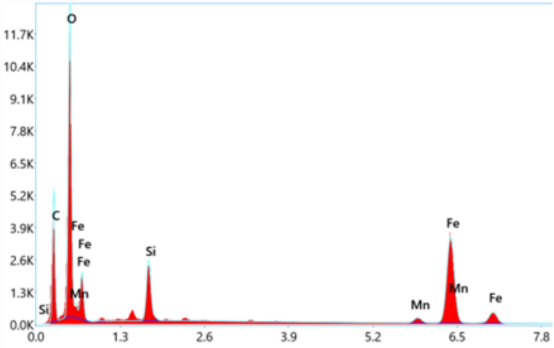
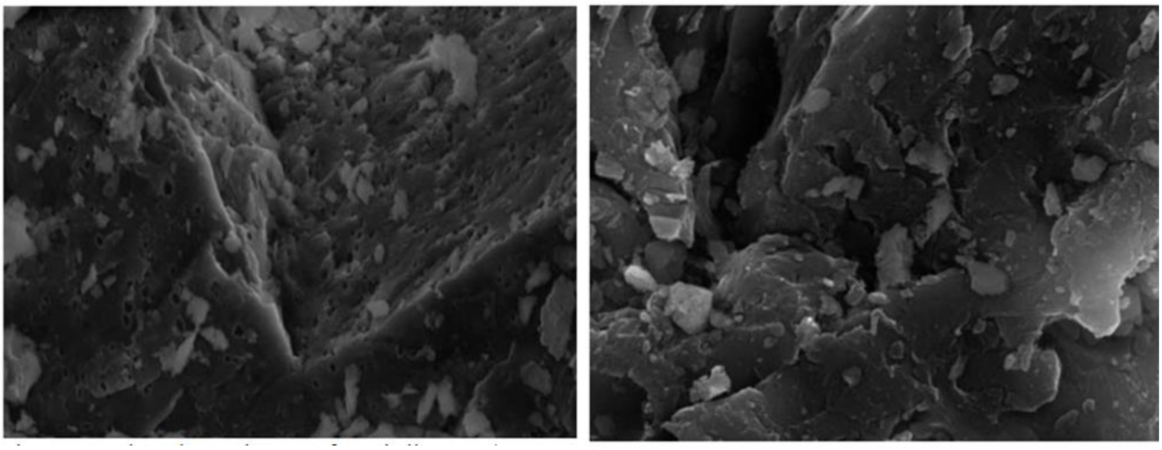
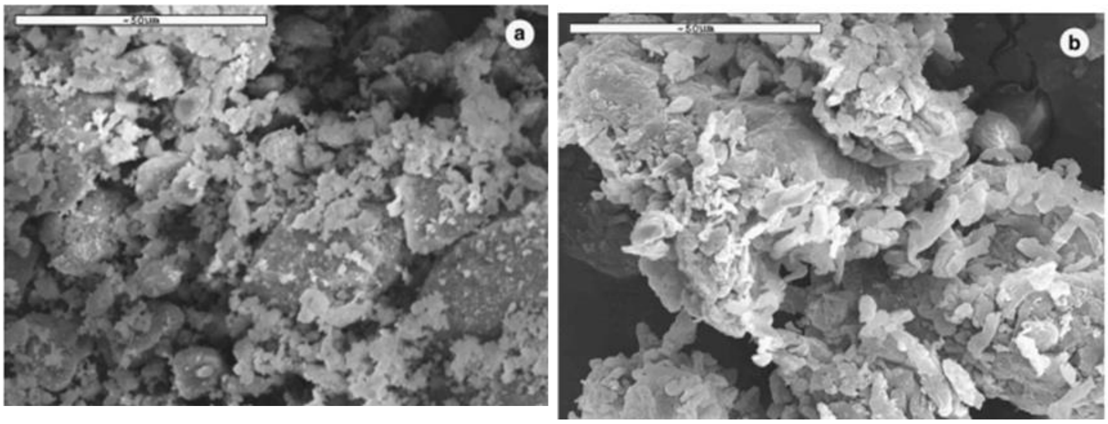


Fig. 6. Spot 6 Elemental composition



a)at 500 b) at 1000

Fig. 7. Selected SEM images of eggshell (Kuśmierek et al., 2017).



a) of (a) eggshell b) of eggshell membrane particles

Fig. 8. SEM photographs (·1000) (Tsai et al., 2006).

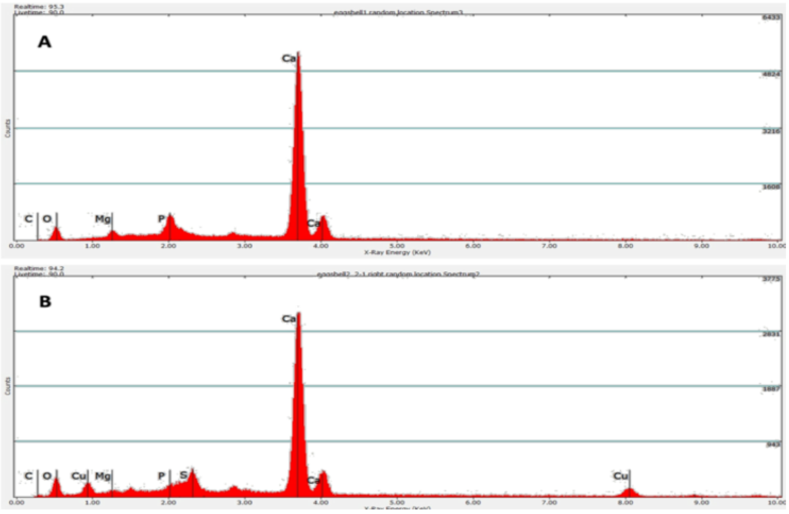


Fig. 9. EDS spectra of raw eggshell (A) and spent eggshell (B) (Hess et al., 2018).

$$Ca(OH)_2 \quad + X_2HAsO_4 \quad \rightarrow \quad CaHAsO_4 + 2XOH \qquad (19a)$$

$$Fe(OH)_2 \quad + X_2HAsO_4 \quad \rightarrow \quad FeHAsO_4 + 2XOH \qquad (19b)$$

$$Al(OH)_3 \quad + 3X_2HAsO_4 \quad \rightarrow \quad Al(HAsO_4)_3 + 6XOH \qquad (19c)$$

Mehmood et al., (2009) reported that arsenic oxidation state governs its toxicity, chemical form, and solubility in natural and disturbed environments. There are two inorganic arsenic forms dominant in nature (arsenate and arsenite), the latter (arsenite) is more mobile and toxic than the former (arsenate).

Arsenate and phosphate (PO$_3$-4) are chemically similar. These two compounds (Arsenate and phosphate) or ions tend to compete for potentially arsenic-bearing phases of aqueous solutions. The concentration of phosphate (PO$_4$) is one of the significant factors that affects the adsorption of arsenic ion negatively.

Organic matter (OM) has a negative effect on the adsorption of arsenic ion adsorption from water, aqueous solutions, and wastewaters. It has been stated that OM and PO$_4$ have a competition for adsorption sites with arsenate.

pH of the aqueous solution changes (increases or decreases) adsorption of arsenic ion depending on the type of adsorbent and form of arsenic ion (Reilly *et al.*, 2001).Thermo-dynamically, the pentavalent arsenic species (HAsO$_4$ $^{2-}$ > H$_2$AsO^{4-}) are more abundant in solutions and are oxidised more at pH greater than 9. The trivalent arsenic forms (H$_3$AsO$_{30}$, HAsO$_{20}$, H$_2$AsO^{3-}, AsO^{2-}) are relatively anoxic solutions with pH less than 7 (Fehintola et al., 2015).

Oxides and hydroxides of iron in solutions are major constituents which control adsorption of arsenic ions in acidic and in an alkaline environment (Taggart *et* al., 2004).

The surface of oxides and hydroxide of aluminium and silicate materials such as kaolinite, montmorillonite play a role in the adsorption of arsenic ion in acidic solutions.

The carbonate minerals are expected to adsorb arsenic ions in calcareous solutions. The functions of manganese oxides and biogenic particles in the adsorption of arsenic ions in solutions are limited to acidic solutions.

All these reactions and the presence of pores revealed that iron, aluminium and calcium present in the PWDEs aided in the removal of arsenic from water and wastewaters. Chemisorption of arsenate and arsenite on colloid surfaces, especially those of iron oxides, hydroxides and carbonates have a common mechanism for arsenic ion solid phase formation (Yang and Donahoe, 2007).

It has been reported that silicate materials retain arsenic ion by inner sphere surface complexation and strong specific ion attraction (Fehintola et al., 2015).

At extremely low arsenic ion concentration, a ligand exchange reaction of H$_2$AsO$_4$$^{2-}$ with surface OH groups form the monodentate complex.

At high concentrations, the removal of arsenate from water and wastewaters by the adsorbents are controlled by the development of bidentate superficial complexes (Gao et al., 2006). CaCO$_3$ forms precipitation in solutions with arsenic ions and forms an inner-sphere complex at the calcite surface, whereby AsO$_4$ units link through the corner- distribution to calcium octahedral.

Thermodynamic Parameters

The thermodynamic and activation energy parameters provide in-depth information about the energetic changes associated with the adsorption process (Yunusa et al., 2020; Inyinbor et al., 2016). Values standard Gibbs energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) for the adsorption of the A_{se} onto PWDEs were determined. Tables 1 and 2 present calculated values of activation energy parameters.

The negative ΔS° values at different times and selected factors indicate the spontaneous nature of the adsorption of A_{se} on PWDEs.

Positive values of E_a indicate the non-spontaneous nature of the adsorption process.

The values of ΔS° and E_a become more negative or positive with decreasing initial concentration indicating that changes in the selected factors favour the removal process.

Table 1 revealed there are good and fair correlations between these parameters for synthetic (with error, CD and R ranging from 0.00207 to 0.96341, 0.52624 to 0.99996 and 0.72542 to 0.99998, respectively), and raw water (with error, CD and R ranging from 0.3633 to 1.5056, 0.1725 to 0.9267 and 0.4154 to 0.9626, respectively), respectively.

Tables 3-10 revealed that effects of these factors were not significant on both E_a and ΔS°.

Table 1. Values of ΔS° and E_a calculated for A_{se} removal from Synthetic wastewater.

Factors		**Slope**	**Intercept**	**ΔS°**	**Ea**	**Error**	**CD**	**R**
Initial Ase concentration	1.5	-1.62578	-1.38155	-11.48067	13.51023	0.17060	0.88698	0.94179
	1.3	-2.35562	-2.04270	-16.97487	19.57519	0.27959	0.85794	0.92625
	1.	-3.00551	-2.11993	-17.61664	24.97577	0.19568	0.94901	0.97417
	0.5	-4.01167	-1.52636	-12.68405	33.33695	0.21682	0.97124	0.98551
pH	7.2	-3.00551	-2.11995	-17.61681	24.97581	0.19568	0.94901	0.97417
	6.4	-2.48532	-1.56396	-12.99647	20.65298	0.12951	0.96590	0.98280
	3.2	-1.51678	-0.55576	-4.61838	12.60443	0.03477	0.98854	0.99425
	11.5	-0.94166	-0.02098	-0.17434	7.82521	0.00207	0.99996	0.99998
Particle size of PWDEs	0.063	-1.62578	-1.38156	-11.48073	13.51024	0.17060	0.88698	0.94179
	0.075	-2.53496	-2.35180	-19.54347	21.06551	0.33966	0.82220	0.90675
	0.15	-5.56553	-5.94623	-49.41314	46.24951	0.96341	0.52624	0.72542
Mass of PWDEs	0.75	-3.00551	-2.11993	-17.61664	24.97578	0.19568	0.94901	0.97417
	0.85	-3.10055	-2.13199	-17.71687	25.76558	0.16949	0.94193	0.97053
	1.	-1.62578	-1.50019	-11.48077	13.51027	0.17060	0.88698	0.94179

Table 2. Values of ΔS° and E_a calculated for A_{se} removal from raw water.

Factors		**Slope**	**Intercept**	**ΔS°**	**E_a**	**Error**	**CD**	**R**
Initial A_{se} concentration	1.05	-6.5019	-7.9056	-65.6954	54.0308	1.4037	0.2443	0.4942
	5.02	-1.3873	-3.2563	-27.0598	11.5285	0.8742	0.2461	0.4961
	10.01	1.0375	-1.1160	-9.2742	-8.6214	0.3633	0.9267	0.9626
	0.005	-13.5559	-10.5004	-87.2580	112.6492	2.3287	0.2894	0.5380
pH	7.2	-6.6498	-7.8572	-6.6498	-7.8572	1.5056	0.1725	0.4154
	6.4	-6.8713	-7.9486	-66.0532	57.1008	1.4972	0.2017	0.4491
	3.2	-6.7693	-7.8266	-65.0391	56.2532	1.4510	0.2351	0.4849
	11.5	-6.7134	-7.8639	-65.3491	55.7882	1.4206	0.2596	0.5095
Particle size of PWDEs	0.063	-6.5019	-7.9056	-65.6951	54.0307	1.4037	0.2443	0.4942
	0.075	-4.9872	-5.6638	-47.0660	41.4436	0.7290	0.7122	0.8439
	0.15	-4.9872	-5.6638	-47.0660	41.4436	0.5254	0.7210	0.8491
Mass of PWDEs	0.75	1.0375	-1.1160	-9.2744	-8.6213	0.3633	0.9267	0.9626
	0.85	-6.6498	-7.8572	-65.2933	55.2600	1.5056	0.1725	0.4154
	1	-6.5019	-7.9056	-65.6951	54.0307	1.4037	0.2443	0.4942

Table 3. Effects of Initial A_{se} Concentration of synthetic wastewater on ΔS° and E_a.

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Between ΔS° and E_a	112.6032	3	37.5344	0.050959	0.982733
Within ΔS° and E_a	2946.249	4	736.5622		
Total	3058.852	7			

Table 4. Effects of pH of synthetic wastewater on ΔS° and E_a.

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Between ΔS° and E_a	0.098484	3	0.032828	7.94E-05	0.999999
Within ΔS° and E_a	1653.517	4	413.3793		
Total	1653.616	7			

Table 5. Effects of adsorbent particle size of synthetic wastewater on ΔS° and E_a.

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Between ΔS° and E_a	8.196949	2	4.098475	0.002152	0.997851
Within ΔS° and E_a	5712.491	3	1904.164		
Total	5720.688	5			

Table 6. Effects of mass of adsorbent of synthetic wastewater on ΔS° and E_a.

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Between ΔS° and E_a	10.85191	2	5.425953	0.00752	0.992527

Within ΔS° and E_a	2164.694	3	721.5648		
Total	2175.546	5			

Table 7. Effects of Initial A_{se} Concentration of raw water on ΔS° and E_a.

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Between ΔS° and E_a	622.6106	3	207.5369	0.029761	0.99204
Within ΔS° and E_a	27893.35	4	6973.338		
Total	28515.96	7			

Table 8. Effects of pH of raw water on ΔS° and E_a.

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Between ΔS° and E_a	11.13131	3	3.710437	0.000666	0.999972
Within ΔS° and E_a	22277.23	4	5569.308		
Total	22288.36	7			

Table 9. Effects of adsorbent particle size of raw water on ΔS° and E_a.

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Between ΔS° and E_a	12.16875	2	6.084377	0.001217	0.998784
Within ΔS° and E_a	15001.1	3	5000.368		
Total	15013.27	5			

Table 10. Effects of mass of adsorbent of raw water on ΔS° and E_a.

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	F-Value	P-value
Between ΔS° and E_a	17.21774	2	8.608869	0.001789	0.998213
Within ΔS° and E_a	14433.9	3	4811.3		
Total	14451.12	5			

Regeneration and Desorption of PWDEs

Once the sorbent is used, it needs to be regenerated. Desorption processes are important from two points of view as follows: - to recover metal ion and its subsequent use in industrial; - in the regeneration of sorbent for new use processes.

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

$$As_{des} = 100\left(\frac{C_{6.5} - C_{11.5}}{C_{6.5}}\right) \quad (16a)$$

$C_{6.5}$ is the As concentration at pH of 6.5 and $C_{11.5}$ is the As concentration at pH of 11.5,

$$OH^- = X_{ab} - X_{ac} \quad (16b)$$

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 As/ mg of initial concentration was desorbed at 8 hours with particle size of PWDEs of 0.063 mm and PWDEs mass of 0.85 g with 0.0033 mole of OH^-/ dm^{-3}.

Estimated Cost of Producing PWDEs

Costs of producing PWDEs 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 PWDEs 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) (Inyinbor et al., 2016; Hong et al., 2018; Gao et al., 2006), activated carbons (0.504USD) and chemical activation carbon (24.003 USD), grapefruit (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) (Hong et al., 2018; Gao et al., 2006).

CONCLUSION

This study concluded that :

- A_{se} can be removed by an inexpensive waste product – the powdered eggshell - with an equilibrium time of 8 hours.
- PWDEs contain Ca, Al, and Fe, which aids in arsenic ion removal from water and wastewaters.
- Desorption computation revealed that 45.2 % of As/ mg of initial concentration was desorbed at 8 hours with particle size of PWDEs of 0.063 mm and PWDEs mass of 0.85 g with 0.0033 mole of OH^-/ $dm^{-3.}$
- The average cost of producing a kilogram of PDEs was found to be 0.426 USD at the rate of ₦660 per USD.

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