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Adsorption kinetics for arsenic removal from aqueous solutions by untreated powdered eggshell

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Abstract The batch removal of arsenic from aqueous solution using low-cost adsorbent (powdered eggshell) under the influences of initial arsenic ion concentrations (0.50 to 1.50 mg/L), pH (3.2 to 11.5) and particle size of eggshells (63 to 150 µm) were investigated. Eggshells were collected from Obafemi Awolowo University, Ile-Ife, washed with distilled water, air dried, ground into powder and sieved into different sieve sizes using British standard sieve. Powdered eggshells were stored in a desiccator for use. Adsorption isotherms and dynamics of arsenic onto PES were studied. The study revealed that there was a slight reduction in the rate of adsorption of arsenic ion onto the larger particle size, but adsorption capacity and parameters were unaffected. Powdered eggshell with particle size of 63 µm removed up to 99.6% of the 1.5 mg/L of arsenic ion in synthetic water within the first 6 hours but decreased to 98.4% and 97.4% when the powdered eggshell particle sizes were increased to 75 and 150 µm respectively. The pH optimum for arsenic removal was 7.2. The adsorption isotherms and adsorption dynamic kinetic studied through the use of graphical method revealed that Freundlich, activated sludge adsorption and pseudo second-order kinetic models correlate significantly with the experimental data with correlation coefficient of not less than 0.964.

Keywords Arsenic · Adsorption kinetics · Low-cost adsorbents · Solution · Adsorption isotherms

Abbreviations

q_e	the adsorption capacity at equilibrium (mg/g)
q_t	the adsorption capacity at time t (mg/g),
k_i	the rate constant of pseudo first-order adsorption.
k_2	the rate constant of pseudo second-order adsorption.
α	the initial adsorption rate
β	the desorption constant during any one experiment.
R	the per cent pollutant adsorbed (%)
t	the contact time (h)
a	the gradient of linear plots
a_L	the Langmuir adsorption constant
k_{id}	the intraparticle diffusion rate constant (/h)
C_0	initial concentration of arsenic in the solution (mg/l)
C_e	experimental concentration in the solution at equilibrium (mg/l)
C_t	experimental concentration in the solution at time t (mg/l)
X	adsorbed concentration (mg/l)
M	mass of the adsorbent added (g)
N	constants related to equilibrium concentration of the solute
a_L	constant related to adsorbent and adsorbate
b_L	constants related to adsorbent only
V	volume of the sample used (300 ml) = 0.3 L
K_f	Freundlich constant (l/g)
K_m	constant for activated sludge model t (l/g)
N_m	exponential constant for activated sludge model (mg/g)

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N_f exponential constant for Freundlich sludge model (mg/g)

1 Introduction

Pollutants such as heavy metals, volatile organic compounds and dissolved solids are found in wastewaters. They are removed on adsorbents such as activated carbon, clay and sediments in riverbeds and in suspension. Over the years, the role of adsorption in wastewater and water treatment had been critically investigated. Adsorption of heavy metals onto suspended particles had been studied as a model of transportation of metals in rivers and sea (Sheindorf et al. 1982). The effects of chemical composition and particle size on adsorption by suspended particles had also been studied. Adsorption of phenol, parabromophenol and benzenesulphonate by carbon had been examined by Sheindorf et al. (1982). Adsorption of colloid by activated sludge and adsorption of bovine serum albumin by activated sludge had been investigated (Banerji et al. 1968a,1968b; Crombie-Quilty and McLoughin 1983). Johannes and Johan (2002) reported the performance of granular activated carbon at three South African water treatment plants while Michele and Johannes (2004) gave practical experiences with granular activated carbon at the Rietvel water treatment plant.

Attention had mostly been on carbon as adsorption materials and indeed Erhan et al. (2004) had documented not less than 37 sources of carbon, which had been studied as adsorbents for the removal of water pollutants. Three problems associated with the use of carbon for the adsorption of pollutants in a regular volume of waters are:

(i) Its relatively high cost in making renovation of water by this means very expensive.
(ii) The fragility of present types of activated carbon makes the regeneration and reuse of activated carbon difficult.
(iii) Activated carbon is virtually limited to the removal of non-polar materials (Schroeder 1977).

Eckenfelder (1989) reported that arsenic and its compounds are present in waters from the metallurgical industries, glassware and ceramic production, tannery operation, dyestuff, pesticide manufacture, some organic and inorganic chemical manufacturing, petroleum refining and the rare earth industries. Arsenic contamination of subsurface waters is believed to be geological and from industrial wastewaters. High arsenic concentrations may result from dissolution of, or desorption from iron oxide, and oxidation of arsenic pyrites (Thirunavukkarasu et al. 2003). Population-based studies have shown that arsenate may adversely affect several organs in the human body (Subramanian and Kosnet 1998; Karim 2000) including cancer of the skin, lung and urinary bladder. Although, literature (Joshi and Chaudhuri 1996; Thirunavukkarasu et al. 2001; Viraraghavan et al. 1994) have documented possible methods for arsenic removal, it makes sense to develop arsenate treatment process such as adsorption at the lowest initial and operational costs. Also the disadvantage of activated carbon for removal of pollutants such as arsenic have been documented in literature (Peavy et al. 1988; Metcalf and Eddy Inc. 1991; Tebbutt 1991). Therefore there is a need to continue the search for materials that may be more suitable than carbon for water treatment either because of lower initial cost or because of the potentially greater ease of regeneration while still possessing its desirable adsorptive characteristics. The main aim of this study was to investigate adsorption properties of powdered eggshell.

2 Materials and Methods

Eggshells (chickens), collected within the Obafemi Awolowo University, Ile-Ife, Nigeria campus were washed with distilled water, air-dried, ground into powder and classified using British Standard (BS) sieve. Powdered eggshell was selected on the basis of its availability and its lower initial cost of production. Powdered eggshell with sieve sizes of 63 µm (PES_1), 75 µm (PES_2) and 150 µm (PES_3) were separated and stored in desiccators. The mineral content of PES was determined by using AAS after acid digestion of 2 g samples (APHA 1998).

Adsorption capacities of powdered eggshells (PES) were examined on synthetic wastewaters prepared by dissolving 4.63 grams of $Na_2HAsO_4 \cdot 7H_2O$ in distilled water (APHA 1998). Specifically, known masses (1, 0.85, 0.75, 0.50, 0.40, 0.35, 0.30 and 0.25 grammes) of the adsorbent were added into beakers containing 300 ml of a known concentration (2.5 mg/L) of arsenic ion. The mixtures were stirred at 60 revolutions per minutes (rpm) for 3 minutes and allowed to stand for 18 hours (at which equilibrium concentration might have been reached). The supernatants were filtered through a filter paper Number 40 (Whatman) to remove suspended solids and arsenic ion concentration in the filtrate was determined. The procedures were repeated for natural water collected. The amount of solute remove (adsorbed) was computed using (1).

$$q_e = \frac{(C_0 - C_e)}{M} V \tag{1}$$

In order to determine the adsorptions dynamic, known quantities of PES were added to 300 ml of solution containing 1.5 mg/L arsenic solution, stirred for 3 minutes and allowed to settle. The supernatants were filtered through a filter paper at an interval of 1 hour and the filtrates were then analysed for arsenate. For adsorptive rates of natural waters, water samples were collected weekly for four months (March,

Table 1 Some properties and components of powdered eggshell

Parameters	Mean	Maximum	Minimum	Standard deviation
Ash content (%)	97.58	99.36	95.32	1.84
Moisture content (%)	1.06	1.498	0.7261	0.36
Calcium as Ca^{2+} (g/g)	0.401	0.411	0.399	0.0032
Aluminium as Al^{3+} (g/g)	0.01245	0.0127	0.0121	0.0001
Iron as Fe^{2+} (g/g)	0.0224	0.0235	0.0216	0.0020

April, August and September, 2004), prior to its treatment, from the Opa reservoir of the Obafemi Awolowo University and subjected to a similar treatment as for the synthetic wastewaters. The amount of solute remove (adsorbed) was computed using (2a). The percentage of arsenic ion removed (R%) from the solution was calculated using (2b).

$$q_t = \frac{(C_0 - C_t)}{M} V \tag{2a}$$

$$R = \frac{(C_0 - C_t) \times 100}{C_0} \tag{2b}$$

Influence of pH on the removal of arsenic from synthetic wastewater was investigated using PES of particle size 63 µm (PES_1) at different pH values (the pH of the solutions were adjusted with either 0.01 M HCl or NaOH), at an initial arsenic concentration of 1.00 mg/L. The influence of particle size on the arsenic removal from solution by batch adsorption experiments was investigated using various particle sizes of PES (PES_1, PES_2 and PES_3) at pH 7.2 and at an initial arsenic concentration of 1.5 mg/L. The effect of initial concentrations on the adsorptive rate of arsenic using batch adsorption experiments was investigated at initial concentrations between 0.5 mg/L and 1.5 mg/L at particle size 63 µm (PES_1) and pH 7.2.

The laboratory analyses of pH and arsenic concentrations in both synthetic and natural water used were carried out as specified in APHA (1998) using the Alpha 4 Atomic Absorption Spectrophotometer (AAS) (Chem Techn Analytical) at the Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria for arsenic concentrations. The adsorption capacities of the adsorbent were analyzed through the use of graphs for Langmuir, Freundlich and activated sludge models. The adsorption dynamic kinetics of arsenic adsorption on to PES of particle size 63 µm (PES_1) were analyzed using pseudo first-order, pseudo second-order, Elovich, and intra-particle diffusion kinetic models through the use of Microsoft excel. The conformity between experimental data and the model was expressed as the correlation coefficient (R^2).

3 Results and Discussion

Result of the digestion indicates that one gram of PES contained 22.4 mg Fe, 12.45 mg aluminium as Al^{3+} and 401 mg Ca as Ca^{2+} (Table 1) and it is well known that eggshell contains $CaCO_3$ as the major components (up to 95% $CaCO_3$). It has been postulated that in the present of water calcium salts undergo displacement reaction as indicated in (3). This shows that the PES underwent the reaction in (3a) with arsenic ion, which can reduce the pH and the end product can reacted with arsenic ion to precipitate the pollutant as calcium salt.

$$CaCO_3 + 2H_2O \rightarrow H_2O + CO_2 + Ca(OH)_2 \tag{3}$$

$$\begin{aligned} &H_2O + CO_2 + Ca(OH)_2 + X_2HAsO_4 \\ &\quad \rightarrow H_2O + CO_2 + CaHAsO_4 + 2XOH \end{aligned} \tag{3a}$$

By expressing the mass of PES in terms of Fe, Ca^{2+} and Al^{3+} contents 0.010 mole of Ca^{2+}, 4.0×10^{-4} mole of Fe^{2+} and 4.611×10^{-4} mole of Al^{3+} could be found in one gram of PES.

The nature of the adsorption reaction can be described by relating the adsorption capacity (mass of solute adsorbed per unit mass of adsorbent) to the equilibrium concentration of the solute remaining in the solution, such a relation is known as an adsorption isotherm. There are many basic isotherms models, which include: Langmuir, Freundlich, BET, Temkin, Redlich-Peterson, Nerst and activated sludge isotherms. The first three isotherms are common, but the first two are commonly used for adsorption parameters.

The Langmuir isotherm is based on three assumptions, namely: adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate at most one adsorbed atom; and the ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites. The Langmuir isotherm is expressed as (Tebbutt 1991):

$$q_e = \frac{a_L b_L C_e}{1 + a_L C_e} \tag{4}$$

Rearranging (4) can linearise, the equation in three different possible forms (e.g. (4a) and (4b)), from which the values of

Table 2 Adsorption parameters for synthetic wastewaters

Langmuir model			Freundlich model			Activated sludge model		
a_L (L/g)	b_L (g/mg)	R^2	K_f (mg/g)	$1/N_f$ (L/mg)	R^2	K_m (mg/g^2)	$1/N_m$ (L/mg·g)	R^2
30.76	1.92	0.879	2.82	0.343	0.978	1.93	0.245	0.988

“a” and “b” can be determined from slope and intercept by plotting 1/qe vs. 1/Ce.

$$\frac{1}{q_e} = \frac{1 + a_L C_e}{a_L b_L C_e} \tag{4a}$$

$$\frac{1}{q_e} = \frac{1}{b_L} + \frac{1}{a_L b_L} \frac{1}{C_e} \tag{4b}$$

The estimated adsorption parameters by the Langmuir model are shown in Table 2. The Langmuir constants “a” and “b” (30.76 and 1.92 respectively) and the square of regression coefficient ($R^2 = 0.8794$) suggested that the adsorption of arsenic could not be modelled perfectly by the Langmuir isotherm. The value of b greater than 1 indicates that PES as an adsorbent would be effective when initial concentrations of arsenic are higher. These values of a and b are lower than the values obtained for HSAC at pH of 1, 1.5, 2.0 and 3 but higher than values for pH of 6 and 8 (Kobya 2004), which indicates that PES is a valuable adsorbent as HSAC (hazelnut shell activated carbon). It is well documented that the essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless parameter (R_l). R_l has been defined (Saswati and Ghosh 2005) as the isotherm shape that predicts if an adsorption system is favourable or unfavourable. Mamdouth et al. (2004) stated that R_L indicates the isotherm shape according to the following adsorption characteristics, $R_L > 1$ (is unfavourable), $R_L = 1$ (linear adsorption), $R_L = 0$ (is irreversible) and $0 < R_L < 1$ (is favourable). It has been expressed as follows:

$$R_l = \frac{1}{1 + b_L C_0} \tag{5}$$

For synthetic wastewater the R_L was 0.172 ($0 < R_L < 1$) indicating that adsorption of arsenic on PES is favourable (Saswati and Ghosh 2005).

The Freundlich isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data (Tebbutt 1991). It can be expressed as shown in (6). Figure 1 shows Freundlich model of the adsorption.

$$q_e = K_f C_e^{1/N_f} \tag{6}$$

The values of K_f and N_f can be obtained by plotting logarithms of adsorption capacity against equilibrium concentration. The estimated adsorption parameters by the Freundlich model are shown in Table 2. The high level of K_f and a low $1/N_f$ values (less than 1) from the Freundlich isotherm (Table 2) suggested that the adsorption capacity of PES was high and that any large change in the equilibrium concentration of arsenic would not result in a remarkable change in the amount of arsenic adsorbed by PES (at higher values of As concentration change in the root of the concentration will be approximately zero). The correlation coefficient (R^2) for Freundlich isotherm was 0.978, representing a good fit of the observed data. This high correlation coefficient confirms Tebbutt (1991) statement on Freundlich isotherm. The values of K_f and N_f are different from the values documented in Mamdouth et al. (2004) and in Kobya (2004), which indicate that adsorption onto carbon is different from adsorption onto PES.

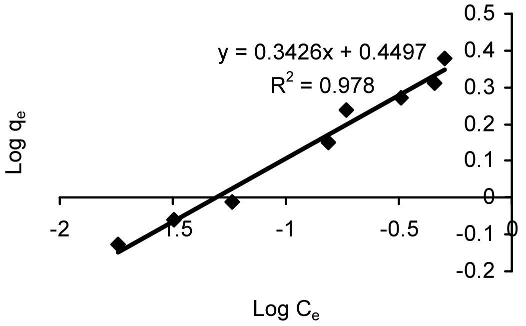

Fig. 1 Freundlich model of arsenic ion adsorption onto PES

Literature on the evaluation of heavy metals removal by adsorption onto PES is relatively scarce, but previous studies by Findon et al. (1993), Mckay et al. (1989) and Udaybhaskar et al. (1990) provide data on the Langmuir and Freundlich isotherms constant for the adsorption of Cu(II) ion on chitosan. Schmuhl et al. (2001) provided data on the adsorption of Cu(II) ions and Cr(VI) ions onto chitosan. These values as well as the values obtained from this study (adsorption of As onto PES) are presented in Table 2a. For copper ion the adsorption results onto chitosan have been described with the Langmuir and Freundlich isotherms, but arsenic ion adsorption in this study could be described better with Freundlich isotherm only. This may mean that the PES have more heterogenous types of adsorption sites. Although, the Freundlich adsorption constants are difficult to compare with Langmuir adsorption isotherm but the maximum capacity q_{max} is comparable with the values in literature.

Table 2a Langmuir and Freundlich constants from previous studies

Sources	Adsorbents	Langmuir model			Freundlich model			Pollutants
		a_L (dm^3/g)	b (dm^3/g)	C_{mac} (mg/g)	K_f (g/dm^3)	$1/N_f$ (mg/g)	C_{mac} (mg/g)	
Findon et al. (1993)	chitosan	1.17	0.02	59	2.44	1.64		Copper
Mckay et al. (1989)	chitosan	6.83	0.03	288				Copper
Udaybhaskar et al. (1990)	chitosan	34.9	0.62	56.3				Copper
Schmuhl et al. (2001)	chitosan	0.29	0.0037	70	0.12	0.98	>80	Copper
	chitosan	0.21	0.004	50	0.98	0.64	>80	Chromium
Mamdouth et al. (2004)	Maize cob	0.3502	0.1399	2.5	0.104	3.9		Iron
	Palm FB	0.3217	0.1622	1.9	0.078	4.8		Iron
	Maize cob	0.4731	0.2077	2.88	0.132	5.7		Manganese
	Palm FB	0.4197	0.190	2.21	0.122	3.8		Manganese
Saswati and Ghosh (2005)	chitosan	3.48	0.941		1.48	3.206		Chromium
Kobya (2004)	HSAC	17.0	0.071		22.61	0.382		Chromium
		103.84	0.022		7.82	0.418		Chromium
		60.39	0.032		14.19	0.209		Chromium
		52.25	0.010		4.98	0.339		Chromium
		30.03	0.041		6.61	0.242		Chromium
		19.27	0.014		3.73	0.236		Chromium
		10.36	0.014		2.85	0.178		Chromium

The adsorption rate constants for arsenic ion are 2.82 and 1.34 mg/g seems to be higher that values for copper II ions adsorption on to non-cross linked chitosan (Table 2a), indicating that adsorption of arsenic (As) onto PES is influence by the kinetic. The Freundlich constants ($1/N_f$) for copper II ion are 1.64, 0.64 and 0.98 for chitosan, non-cross linked chitosan and cross linked chitosan (Table 2a) and for As ion onto PES the values are 0.297 and 0.393 (mg/g) for natural water and synthetic wastewater, which indicates that 1 kilogram of PES is required to remove 297 mg of As from a litre (1 kg of PES will remove 0.297 mg of As from 1000 litres of water) as against 1640, 640 and 980 mg of As from a litre by 1 kg of chitosan, non-cross linked chitosan and cross linked chitosan respectively. This means that economically PES would be cheaper than chitosan, non-cross linked chitosan and cross linked chitosan for heavy metal removal when compared the cost of producing or generating any form of chitosan.

The third isotherm was developed by Crombie-Quilty and McLoughin (1983), it described floc formation at an equilibrium concentration. Crombie-Quilty and McLoughin (1983) describes the model which is known as activated sludge model. The activated adsorption equation is as shown in (7).

$$q_e = K_m \left(\frac{C_e}{M}\right)^{1/N_m} \tag{7}$$

The values of K_m and N_m can be obtained by plotting logarithms of adsorption capacity against equilibrium concentration. The estimated adsorption parameters by the activated adsorption model are shown in Table 2. A low level of K_m (1.94) from the activated sludge isotherm suggests that the tendency of floc formation is possible but low. A lower $1/N_m$ value (less than 1) from the activated sludge isotherm suggests that any large change in the equilibrium concentration of arsenic would not result in a remarkable change in the amount of arsenic floc formation by PES. The correlation coefficient (R^2) for activated sludge isotherms (0.988) also represents an excellent fitness of the observed data.

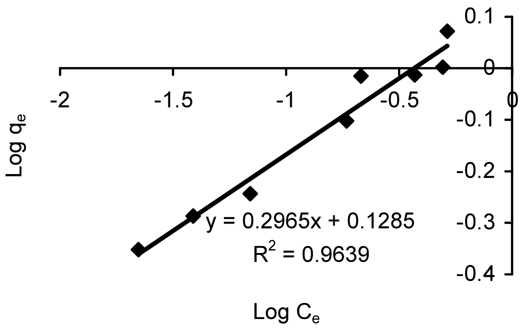

Fig. 2 Freundlich model for natural water

The results of isotherm studies, of natural water at 8 h equilibrium determined at pH 6.8, were also fitted into the Freundlich (Fig. 2), the Langmuir and the activated sludge adsorption models. The model parameters and correlation coefficients are given in Table 3. The estimation of Freundlich and activated sludge isotherms parameters such as

Table 3 Adsorption parameters for natural water

Langmuir model			Freundlich model			Activated sludge model		
$a_{L\ (L/g)}$	b_L (g/mg)	R^2	K_f (mg/g)	$1/N_f$ (L/mg)	R^2	K_m (mg/g^2)	$1/N_m$ (L/mg·g)	R^2
30.76	1.92	0.879	1.34	0.297	0.964	4.57	1.422	0.997

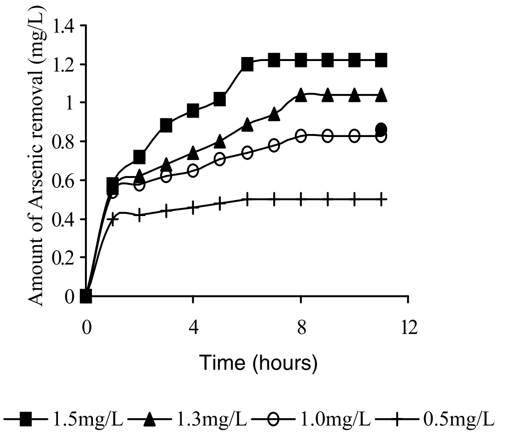

Fig. 3 As adsorption onto PES with various initial concentrations

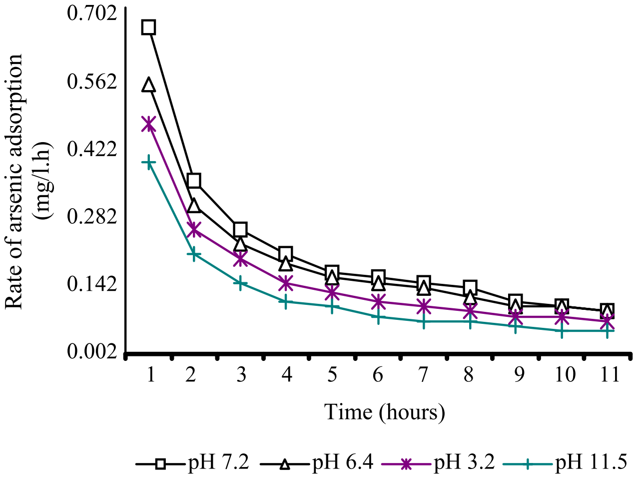

Fig. 4a Rate of As adsorption onto PES

'K_f and K_m' values (1.34 L/mg and 4.57/L), $1/N_f$ and $1/N_m$ value (0.297 L/mg and 1.422/L) confirms that the adsorption capacity of PES was high ($K > 1$) and the removal of arsenic by PES was aided by floc formation ($1/N_m > 1$). Thirunavukkarasu et al. (2003) obtained K_f for arsenic adsorption onto GFH to be 10.3 and 18.0 L/µg. These changes in the value could be attributed to other pollutants in natural water unlike synthetic wastewater. The differences in the values of K_f and N_f for both synthetic and natural water indicate that arsenic adsorption onto PES is likely to be affected by the presence of other pollutants in the solution. For natural water the R_l was 0.160 ($0 < R_l < 1$), Thirunavukkarasu et al. (2003) obtained R_L for arsenic adsorption onto GFH to be 0.33 and 0.14 indicating that adsorption of arsenic on PES is favourable (Saswati and Ghosh 2005). It can be said here that applicability of these isotherms models for the present experimental data follows the order of activated sludge > Freundlich > Langmuir for both synthetic wastewater and natural water.

The adsorption of arsenic from synthetic wastewater by PES of particle size 63 µm at initial arsenic concentration range of 0.50 mg/L to 1.5 mg/L occurred in two stages (Fig. 3). Adsorption rate (which was determined using changes in the adsorption divided by changes in the time) was higher during the initial 3-hour period compared to the final 3-hour second stage prior to the establishment of equilibrium. It is well known that calcium in water gives calcium compounds, which are known for pollutants removal therefore, adsorption at the first stage may be attributed to co-precipitation of Ca [as $Ca(OH)_2$] with a ferric hydroxide floc (all from PES) that tied up arsenic and removed it from the solution. It has been established that colloidal material (floc) increases in diameter with time (type 2 settling). It can be said that adsorption at the second stage can be attributed to Type 2 settling which can be attributed to settlement of flocs through charged particle attraction. Figure 3 also indicates that more than 50% of the arsenic concentration was removed in 3 h of contact time at initial concentrations between 0.5 and 1.50 mg/L of arsenic ion at an equilibrium time of eight hours. The most efficient arsenic adsorption on to PES occurred at a concentration of 1.50 mg/L, with 0.58 mg/L of arsenic removed within 1 h and 1.20 mg/L removed at the equilibrium time of 8 h. It is an evidence from Fig. 3 that the amount of arsenic adsorbed by PES at lower initial arsenic ion concentration was smaller than the amount of arsenic adsorbed at the higher initial arsenic ion concentration. This seems to indicate that arsenic adsorption by PES is a function of the adsorbate initial concentration.

The removal of arsenic from synthetic wastewater by PES of particle size 63 µm (PES_1) at different pH and at an initial concentration of 1.00 mg/L is presented in Figs. 4a and 4b. Adsorption of arsenic again occurred in two stages and the amounts of arsenic adsorbed varied with pH levels. Figures 4a and 4b indicate that the removal of arsenic from the solution was pH-dependent especially at pH between 6.4 and 7.6 where 44% arsenic removed in 3 hours and less than 10% of initial arsenic concentration remained at an equilibrium time of eight hours. Effective arsenic ad-

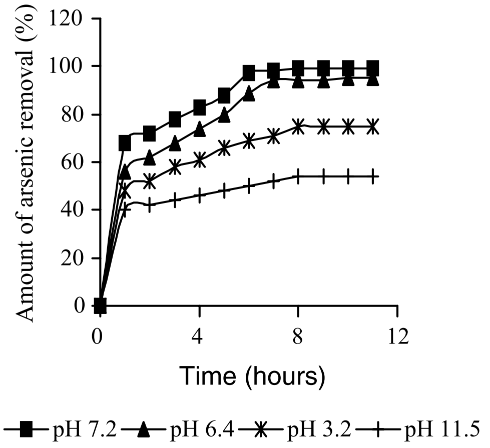

Fig. 4b As adsorption onto PES at different pH

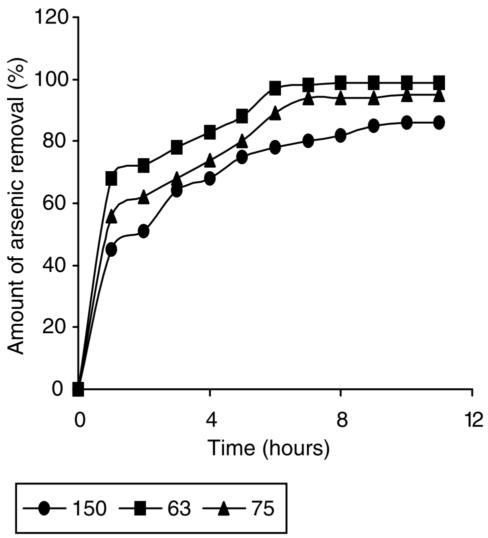

Fig. 4c As adsorption onto PES at different particle sizes

sorption on to PES occurred at pH 7.2, with 99.0% arsenate removed at the equilibrium time of 8 h (Fig. 4b). Earlier studies (Pierce and Moore 1980, 1982; Hsia et al. 1994; Wilkie and Hering 1996) had also shown that the adsorption of arsenic (III) on to amorphous ferric hydroxide increases as the pH increases; with maximum adsorption occurring at pH 7 and a maximum removal (99.7%) at an equilibrium time of 6 h). In the study by Hsia et al. (1994) with hydrous ferric hydroxide, close to 100% arsenic removal was observed in the pH range of 4 to 8. Based on these earlier studies, it could be assumed that the variation observed in the adsorption of arsenate at the pH range in the present study could be ascribed to the influence of calcium and iron, which are components of PES. The removal of arsenic ion increased while equilibrium time decreased with a decrease in particle size of PES (Fig. 4c). The relatively higher adsorption rate with smaller PES particle size may be attributed to the fact that the smaller particles produced a larger surface area. The removal of arsenate in solution increases as its initial concentration increases. The relatively higher adsorption with higher initial concentration of arsenic ions may be attributed to the fact that the rate of collision between the adsorbent and adsorbate increased at higher arsenic ion concentration.

3.1 Adsorption dynamics

Adsorption dynamics describes the solute uptake rate, which controls the residence time of adsorbate uptake at the solid-solution interface. In order to establish kinetic of arsenic adsorption, adsorption dynamic of PES was investigated by using pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion kinetic models. The adsorption dynamic kinetics of arsenic on the PES was analyzed using pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2). A relatively high correlation coefficients (R^2) value indicates that the model successfully describes the kinetics of arsenic adsorption.

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

$$\frac{dq}{dt} = k_i(q_e - q_t) \tag{8}$$

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of (8) becomes (Erhan et al. 2004):

$$\log_e(q_e - q_t) = \log_e(q_e) - \frac{k_i}{2.303}t \tag{9}$$

The values of $\log_e(q_e - q_t)$ were linearly correlated with t. The plot of $\log_e(q_e - q_t)$ vs. t should give a linear relationship from which k_i and q_e can be determined from the slope and intercept of the respectively. Figure 5, Tables 4, 5 and 6 show the pseudo-first order model and their values respectively.

The pseudo second-order adsorption kinetic rate equation is expressed as shown in (10):

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

integrating (10) and rearrangement gives (11) and let h (mg/g·h) is $h = k_2(q_e)^2$

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}t \tag{11}$$

The plot of (t/qt) and t of (11) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot respectively. Figure 6, Tables 4, 5 and 6 show more about the model.

Table 4 The adsorption kinetic model rate constants for the synthetic wastewater at different pH

Initial pH	Pseudo first-order			Pseudo second-order				Elovich model			Intraparticle diffusion		
	k_1 (l/h)	q_e (mg/g)	R^2	k_2 (g/mg·h)	h (mg/g·h)	q_e (mg/g)	R^2	β (g/mg)	α (mg/g·h)	R^2	k_{id} (l/h)	A (%/h)	R^2
3.2	0.497	0.163	0.952	3.345	0.334	0.316	0.993	19.3	1.69	0.967	46.61	0.211	0.977
4.3	0.449	0.190	0.945	3.199	0.372	0.341	0.988	17.6	1.86	0.938	51.28	0.208	0.957
6.4	0.991	0.339	0.941	1.584	0.297	0.433	0.972	13.1	1.13	0.944	53.78	0.254	0.960
7.2	1.329	0.376	0.855	2.356	0.448	0.436	0.986	16.1	3.93	0.935	65.79	0.185	0.944
8.2	0.664	0.250	0.989	1.761	0.261	0.385	0.991	13.3	0.73	0.981	44.89	0.291	0.974
9.8	0.329	0.161	0.939	3.902	0.274	0.265	0.979	22.0	1.22	0.908	39.39	0.214	0.930
11.5	0.236	0.118	0.992	7.521	0.364	0.220	0.994	36.5	7.06	0.946	38.62	0.145	0.958

Table 5 The adsorption kinetic model rate constants for the synthetic wastewater at different particle sizes

Particle sizes (μm)	Pseudo first-order			Pseudo second-order				Elovich model			Intraparticle diffusion		
	k_1 (l/h)	q_e (mg/g)	R^2	k_2 (g/mg·h)	h (mg/g·h)	q_e (mg/g)	R^2	β (g/mg)	α (mg/g·h)	R^2	k_{id} (l/h)	A (%/h)	R^2
63	0.698	0.352	0.899	0.878	0.595	0.311	0.989	7.94	0.0719	0.960	39.06	0.351	0.968
75	0.962	0.452	0.899	0.948	0.553	0.290	0.989	9.00	0.698	0.960	36.82	0.351	0.968
150	0.896	0.307	0.898	1.039	0.503	0.263	0.989	9.38	0.609	0.961	33.09	0.351	0.968

Table 6 The adsorption kinetic model rate constants for the synthetic wastewater at different initial concentrations

Initial concentration (mg/L)	Pseudo first-order			Pseudo second-order				Elovich model			Intraparticle diffusion		
	k_1 (l/h)	q_e (mg/g)	R^2	k_2 (g/mg·h)	h (mg/g·h)	q_e (mg/g)	R^2	β (g/mg)	α (mg/g·h)	R^2	k_{id} (l/h)	A (%/h)	R^2
0.5	0.717	0.030	0.944	18.47	0.198	0.724	0.999	76.34	33.10	0.902	50.86	0.098	0.933
0.7	0.570	0.164	0.925	2.58	0.334	0.287	0.996	22.42	1.35	0.902	56.65	0.213	0.934
0.8	0.625	0.173	0.947	2.58	0.334	0.287	0.996	19.08	1.59	0.963	58.38	0.209	0.970
0.9	0.861	0.379	0.871	1.38	0.396	0.217	0.997	18.32	2.13	0.930	49.72	0.293	0.971
1.0	0.660	0.211	0.928	2.09	0.372	0.289	0.992	10.26	0.68	0.928	50.86	0.212	0.954
1.3	0.612	0.350	0.923	0.93	0.499	0.232	0.979	8.15	0.75	0.954	39.99	0.297	0.962
1.5	0.917	0.315	0.967	0.97	0.582	0.327	0.991	13.37	0.81	0.971	39.81	0.33	0.957

The Elovich model equation is generally expressed as indicated in (12):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{12}$$

Erhan et al. (2004) simplifies Elovich equation as shown in (13)

$$q_t = \frac{1}{\beta}\log_e(\alpha\beta) + \frac{1}{\beta}\log_e(t) \tag{13}$$

If arsenic adsorption fits the Elovich model, a plot of q_t vs. $\log_e(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\log_e(\alpha\beta)$. Figure 7, Tables 4, 5 and 6 present more on this dynamic model.

The intraparticle diffusion model is expressed as (14)

$$R = k_{id}(t)^a \tag{14}$$

A linearised form of the equation is followed by $\log R = \log k_{id} + a \log(t)$. Erhan et al. (2004) reports that “a” depicts the adsorption mechanism and k_{id} may be taken as a rate factor (per cent pollutant adsorbed per unit time). Higher values of k_{id} illustrate an enhancement in the rate of adsorption, whereas larger k_{id} values illustrate a better adsorption mechanism, which is related to an improved bonding between pollutant and the adsorbent particles. Figure 8, Tables 4, 5 and 6 present more on this dynamic model.

Tables 4 to 6 show kinetic parameters. From Table 4 it can be seen that in all cases the values of correlation coeffi-

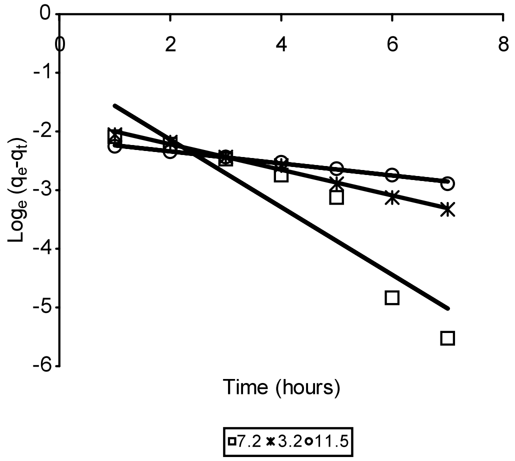

Fig. 5 Pseudo first order at variable pH

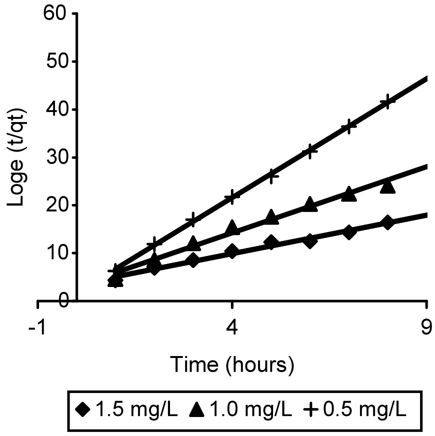

Fig. 6 Pseudo second order at variable concentration

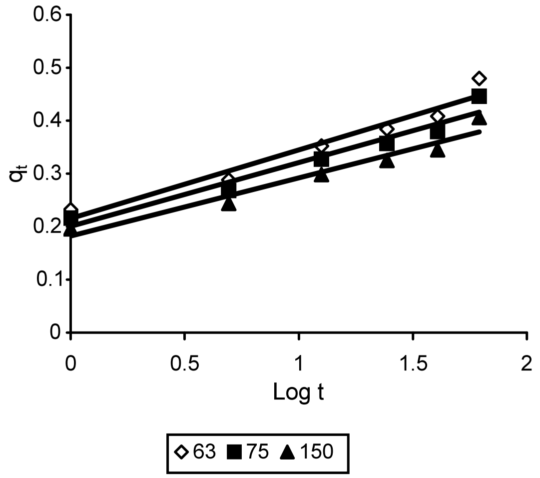

Fig. 7 Elovich model at variable particle sizes

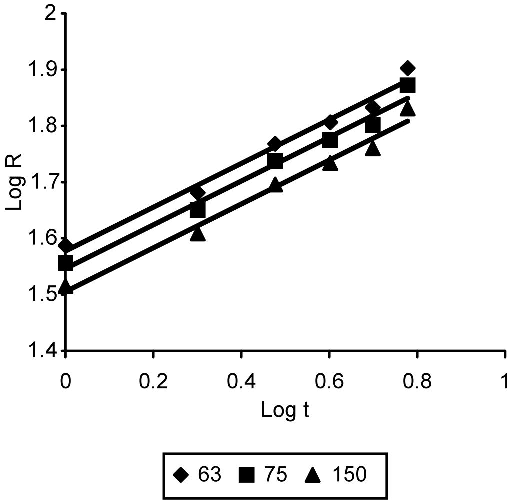

Fig. 8 Intraparticle model at variable particle sizes

cient decreases from Pseudo second-order, Intraparticle diffusion, Elovich model to Pseudo first-order. This indicates that adsorption of arsenic follows Pseudo second-order than any other model. From Tables 5 and 6, R^2 follows the same order as in the case of Table 4. The results indicate that arsenic adsorption onto PES fitted well into Pseudo second-order kinetics.

The amounts of arsenic adsorbed increase as the pH decrease toward 7.2. The variation in adsorption capacity in this pH range is largely due to the influence of pH on the adsorption characteristics of the powdered eggshell, which indicates that the adsorption capacity of the adsorbent is clearly pH dependent. The data obtained separately for each of the kinetic models from the slopes of plots showed a good compliance with the pseudo second-order equation with a correlation coefficient constant (R^2) ranging from 0.972 to 0.999 for synthetic wastewater, which indicates that the kinetic data fitted the pseudo second-order adsorption kinetic (Table 4). It was an evidence from Tables 4, 5 and 6 that the removal of arsenic from solution was dependent on the initial concentration of arsenic, pH and particle size since the adsorption dynamic kinetics increase with an increase in the arsenic ion concentration. The results also show that the adsorption reaction can be approximated with the pseudo second-order kinetic model. The smallest value of correlation coefficient is 0.972 (Table 4). The rate constants are represented also in Table 6. The values of the second-order rate constants (k_2) were found to increase (from 0.965 to 18.47 mg/L hour) with an increase in the initial arsenic ion concentration from 0.5 to 1.5 mg/L. This observation is similar to Lazaridis and Asouhidou (2003) observation of kinetic equations. Lazaridis and Asouhidou (2003) used three kinetic equations (pseudo 1st, 2nd and Elovich model equations) to describe chromium VI sorption onto hydrotalcite and their result shows that adsorption of chromium onto hydrotalcite fitted into the first pseudo model best (one model out of three).

3.2 Mechanism of adsorption

The mechanism of adsorption of arsenic onto PES as an adsorbent follows two-steps, namely pore diffusion and intraparticle transport. This result is the general observation for batch reactor, while for a continuous flow system film diffusion is likely to be included and as the limiting step. It is well known that there is a high possibility for pore diffusion to be the rate-limiting step in a batch process and that the adsorption rate parameter, which controls the batch process for most of the contact time is the intraparticle diffusion (Saswati and Ghosh 2005). In order to verify this postulation a plot of arsenic adsorbed at equilibrium (q_e, mg/g) against time (min) was drawn. Figures 7 and 8 show the two separate linear portions for different pH, initial concentration and at different particle size of PES. The first parts of the curves are attributed to mass transfer effects, which take place with boundary layer diffusion, while the final parts indicate intraparticle diffusion. The slopes indicate that the pores are micro-pores and the interparticle diffusional resistance is due to micro-pores only.

4 Conclusion

This study indicated that arsenic could be removed by an inexpensive waste product—the powdered eggshell—with the equilibrium time of 8 hours. A second-order kinetic model was found to be statistically significant at the 95% confidence level, but there are other area of PES that needs to be studied.

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