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### Effectiveness of 3, 4 and 5- Parameters Adsorption Equilibrium Isotherm Models in Describing Arsenic Removal

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#### ABSTRACT

*The presence and removal of arsenic ions and salts from the environment have become worldwide environmental issues and problems because of the harmful and toxic nature of the substance. The paper presents the effectiveness of higher adsorption parameters (3, 4 and 5) in describing arsenic removal from aqueous solutions. Raw eggshells from chickens were collected from an institutional farm in Nigeria. These collected raw eggshells were washed with distilled water to remove impurities, air dried to reduce the moisture content and powdered eggshells using a silver crest blender. Energy Dispersive Spectroscopy and scanning electron microscope images of the powdered eggshell were evaluated at selected magnifications. The powdered eggshell's adsorption rates were examined in synthetic and typical arsenic-contaminated water. Parameters of adsorption equilibrium models were determined using Microsoft Excel Solver. The performances of these adsorption equilibrium models in describing arsenic removal from these arsenic-contaminated waters were evaluated statistically using the Model of Selection Criterion (MSC) and Akaike Information Criterion (AIC). The study revealed that the elemental compositions of powdered eggshells are carbon, aluminium, iron, silicon, calcium and oxygen with traces of sodium, magnesium and manganese. The mechanism of arsenic removal by adsorption using powdered eggshell includes redox and replacement reactions. Adsorption equilibrium analysis established that adsorption models' 5 and 4 parameters described the relationship between arsenic removal and the mass of the adsorbent better than the 3 and 2 parameters of adsorption models based on the values of MSC and AIC. All the 5 and 4 parameters of the adsorption models had MSC values greater than 3.0 (equivalent to greater than 0.95 correlation coefficient, 68.75 % and 17.65 % for 3 and 2 parameters of adsorption models. It was concluded that powdered eggshells removed arsenic from aqueous solutions, the removal rate was affected by the nature of the water and 5 and 4 parameters of adsorption models were effective in the description of arsenic removal by powdered eggshell.*

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## INTRODUCTION

Arsenic is an obvious metalloid element, which has obtained much attention due to its terrific toxicity to human health (Li et al., 2012; Yin et al., 2019; He et al., 2019). At higher arsenic concentrations exceeding the limit in the environment, long-term uptake of water, air and soil contaminating arsenic could result in neurological disorders, hypertension, diabetes, bladder cancer, and lung, liver, and kidney diseases (Yazdani et al., 2014; Yin et al., 2019). Further information, documents studies and literature on the effects of arsenic on humans and relevant organs are documented in the literature such as Arun et al. (2021); Aristizaba-Henano et al. (2021); Jin et al. (2022); Karachaliou et al. (2021); Liu et al. (2023); Babaeiveli et al. (2014); Wang et al. (2022); Tseng et al. (2021); Wakeel et al. (2020); Deliyanni et al. (2015); Koohzad et al. (2019); Ro et al. (2022); Tu, et al. (2023); Wu et al. (2022); Xue et al. (2021); Yang et al. (2023); Yin et al. (2022); Zhou et al. (2022); Pierce and Moore (1982); Nakano et al. (2003); Osborne and Thompson (2005); Pierce and Moore (1980); Valdes et al. (2015); Tsai et al. (2006); Ajala et al. (2018); Guo et al. (2022); Ghosh and Sit (2015); Chen et al. (2012; 2022); Calatayud and Laparra Llopis (2015); Bailey and Fry (2015) and Calatayud et al. (2022).

Figure 1a shows the schematic representation of arsenic mechanisms of action within the cell. Figure 1b describes the schematic representation of routes for arsenic transport. Among the several treatment methods and technologies developed and established for the reduction of arsenic compounds and ions from the aqueous solutions and environment, adsorption treatment methods and technologies are receiving increasing consideration.

These treatment methods and technologies are becoming attractive, emerging, and promising technologies, based on vital operational factors such as simplicity and ease of operation of these treatment methods and technologies and cheaper pollution control methods. These treatment methods and technologies are easy to handle.

sludge-free generation operation, and adsorbent regeneration capacity. In the engineering application of adsorption treatment methods and technologies, detailed data and information on adsorption equilibrium characters and properties are required in the design (hydraulic and process) of adsorbers. The adsorption equilibrium isotherm models provide fundamental physicochemical information and data for estimating the pertinency of the adsorption processes as unit operations. An adsorption equilibrium isotherm model or equation is a mathematical expression with parameters that express the surface characters and properties of the treatment methods and technologies. These isotherm parameters explained the affinity of the adsorbent, at a fixed environmental temperature and the solution's pH. In engineering design, an accurate and exact mathematical description of the adsorption equilibrium isotherm is essential for the effective design of adsorption contact processes. Adsorption processes have been categorised based on Langmuir's classifications, types of adsorption isotherms (Al-Ghouti and Da'ana, 2020) and the number of parameters in adsorption equilibrium isotherms.

Figure 2 shows the categorisation of adsorption based on isotherm type. Figure 3 shows the categorisation of adsorption based on Langmuir's classifications. Figure 4 shows the categorisation of adsorption based on the number of parameters in adsorption equilibrium isotherms. Table 1 shows the classification of adsorption based on the number of parameters and the mathematical equations. More information and data on the adsorption treatment methods, performance and modifications, and factors that influence the performance are established in the literature such as Aber and Sheydaei (2012); Al-Ghouti and Da'ana (2020); Ayawei et al. (2017); Begun et al. (2016); Atallah et al. (2020); Dada et al. (2021); Deliyanni et al. (2015); Feng et al. (2013); Guru and Dash (2014); He et al. (2012); Hee-Jeong (2019); Hee-Jong and Seung-Mok (2015) and Okafor et al. (2012).

The most commonly utilised materials for adsorbent are carbonaceous materials such as coconut, wood, and coal. These materials are utilised for the industrial production of activated carbons. These types of adsorbents are relatively expensive and frequently imported.

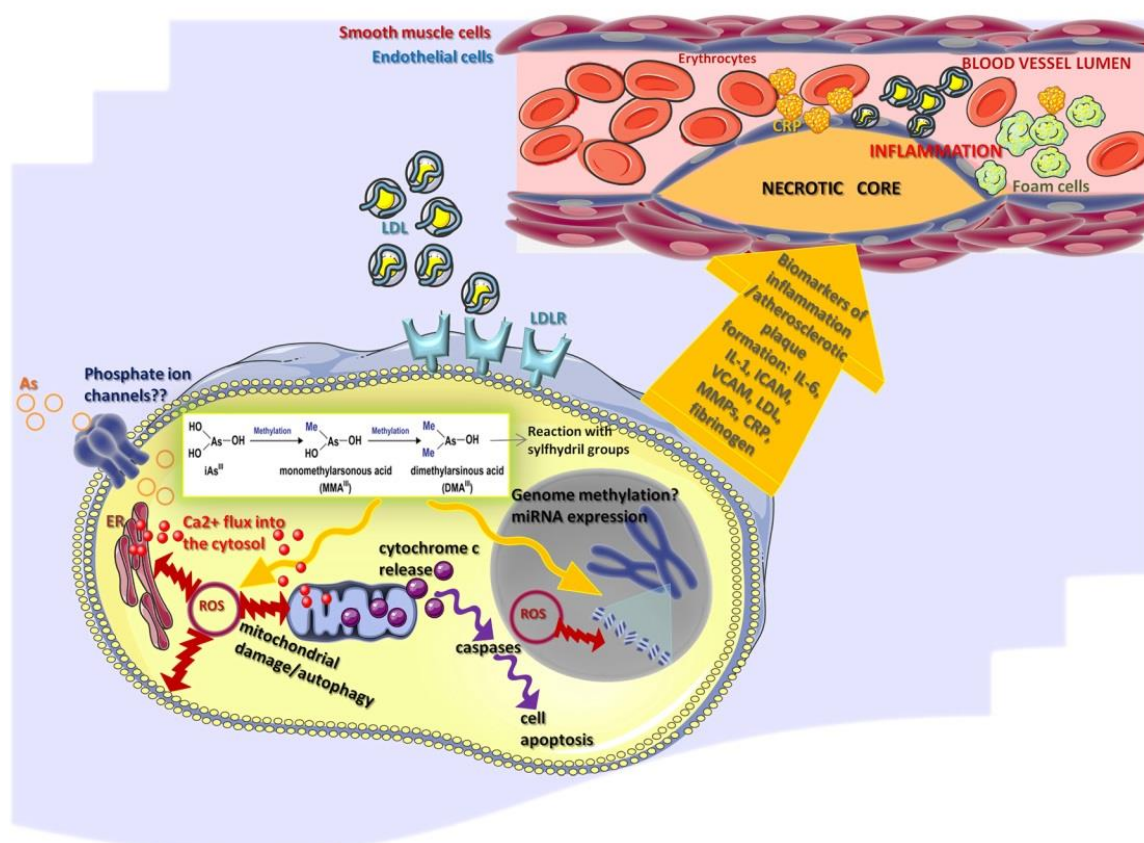


Figure 1a Schematic representation of arsenic mechanisms of action within cell (Source: Karachilou *et al.*, 2022)

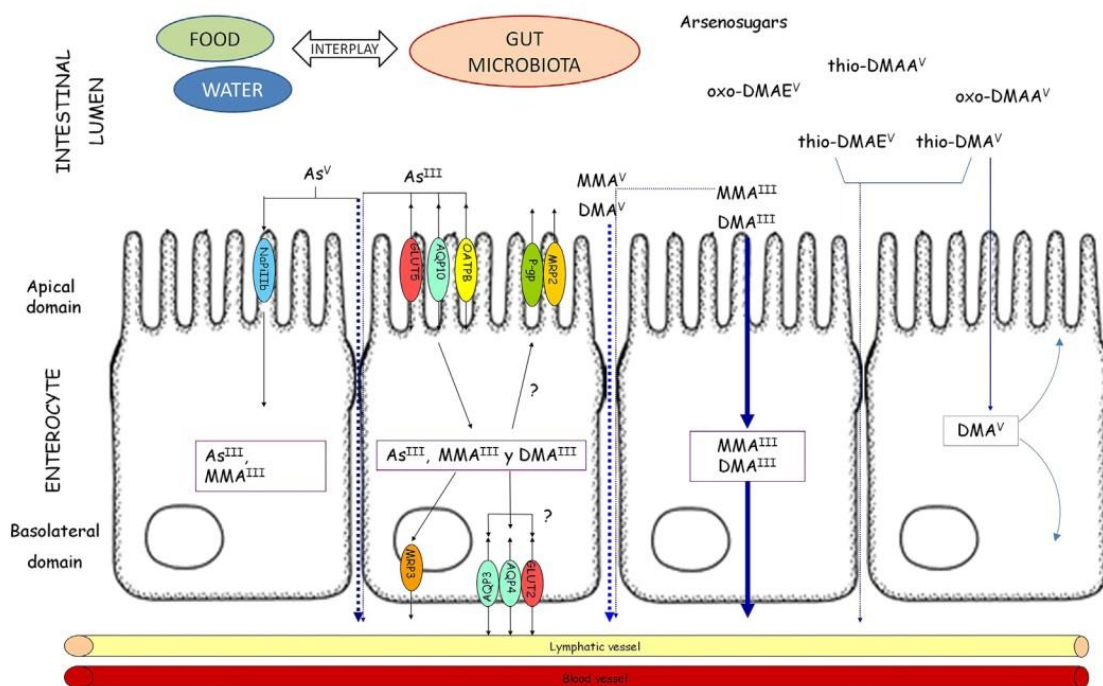


Figure 1b Schematic representation of routes for arsenic transport (Source: Calatayud and Lapara Llopis, 2015)



Isotherm type	Description	Example	Sample graph
Type I isotherms (convex upward)	Characterized by a horizontal plateau in which it maintains for very high gas pressures, and it can be described by Langmuir equation.	Adsorption of water vapor on zeolite, adsorption of hydrogen on charcoal. Iodine adsorption from potassium iodine solution on zinc chloride AC	
Type II isotherms	Describes adsorption on mesoporous monolayer materials at low pressure and on mesoporous multilayer material at high pressure near saturation with no hysteresis. It has one inflection point. Moreover, its observed in only microporous, nonporous, or disperse solids with > 50 nm pore diameter.	Adsorption of nitrogen on silica gel or iron catalyst, adsorption of water vapor on polymer based adsorbent	
Type III isotherms (concave upward)	This type occurs where the adsorbate-adsorbate interaction is big compared to adsorbate-sorbent interaction.	Adsorption of water on hydrophobic zeolites and activated carbon, adsorption of bromine and iodine on silica gel, carbon tetrachloride adsorption on mesoporous gel	
Type IV isotherms	This type describes specific mesoporous materials adsorption behavior showing the pore condensation the hysteresis which occurs between the desorption and the adsorption branch. It has 2 inflection points.	Adsorption of humid air, water vapors on specific types of activated carbon, adsorption of benzene on iron oxide and on silica gel.	
Type V isotherms	This type indicates the presence of mesopores in phase change like pore condensation could occur. It has one inflection point.	Adsorption of water on carbon molecular sieves and on activated carbon fiber.	
Type VI isotherms	At low temperatures, layers will become more pronounced and the isotherms presents stepwise multilayer adsorbates. It has several inflection points.	Adsorption of noble gases on the surfaces of planar graphite, and adsorption of butanol on aluminum silicate, adsorption of CH <sub>4</sub> on MgO	

Figure 2 the categorisation of adsorption based on isotherm type. (Source: Al-Ghouti and Da'ana, 2020)

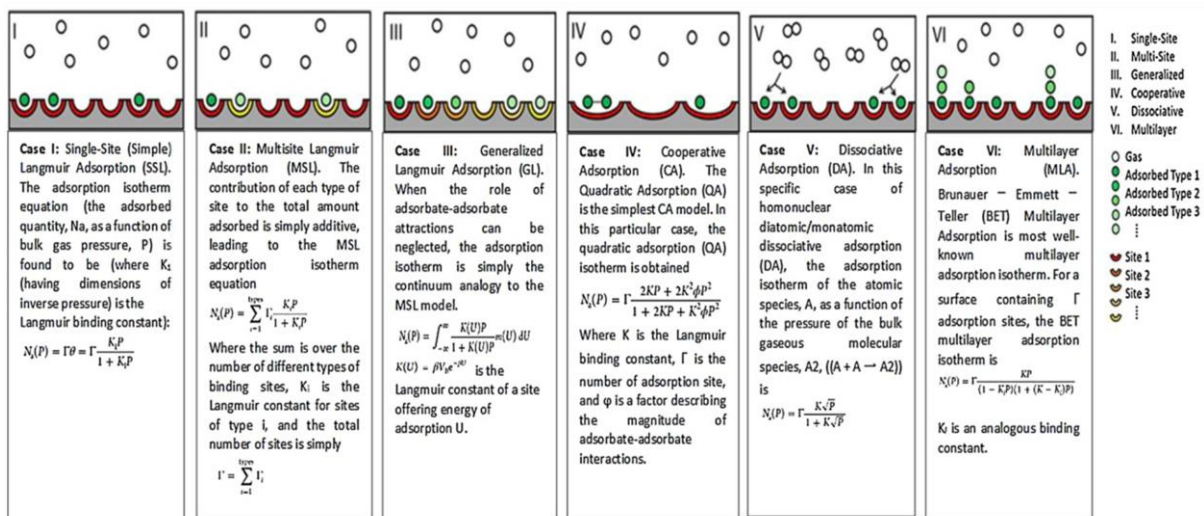


Figure 3 the categorisation of adsorption based on Langmuir's classifications. (Source: Al-Ghouti and Da'ana, 2020)

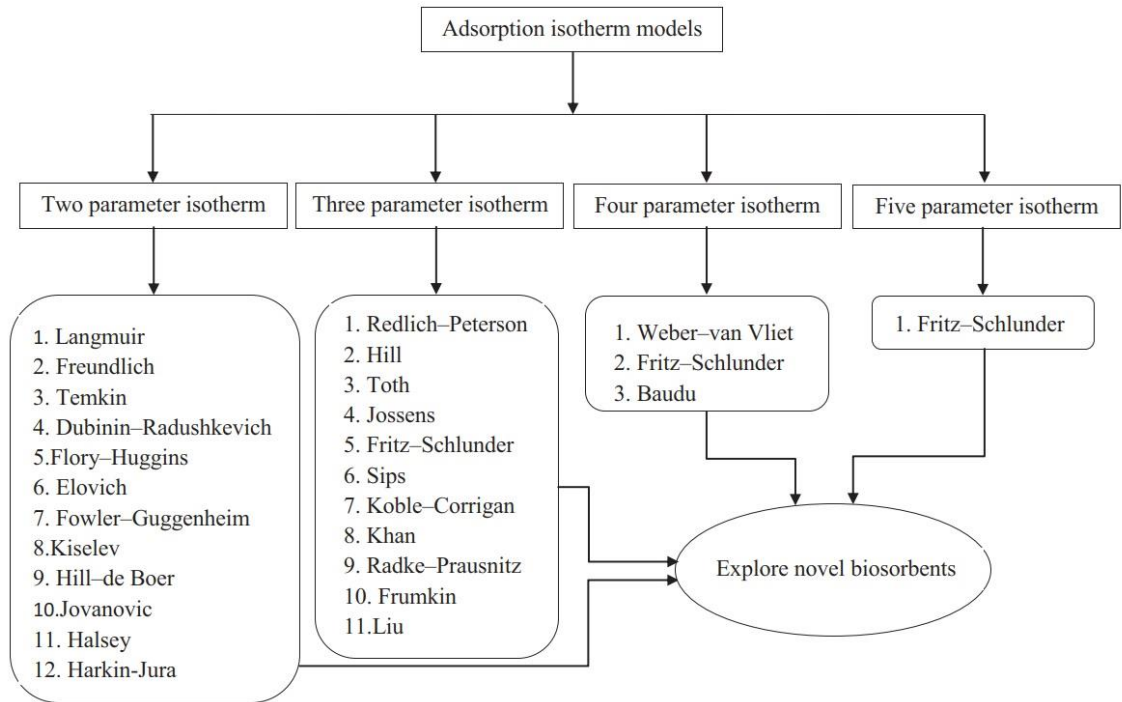


Figure 4 the categorisation of adsorption based the number of parameters in adsorption equilibrium isotherms.  
(Source: Al-Ghouti and Da'ana, 2020)

**Table 1:** the classification of adsorption based on the number of parameters and the mathematical equations for single and multi-component aqueous solutions (Sources: Hamdaoui and Naffrechoux (2007); Cano *et al.* (2007); Rangabhashiyam *et al.* (2014); Vishali and Mullai (2016); Ayawei *et al.* (2017); Al- Ghouti and Daana (2020); Outram *et al.* (2021).

Type	Name	Non- Linear Relationship	Parameters	Linear Relationship
1- Parameter	Statistical	$q_e = \frac{kC_e + (kC_e)^2 \left( \frac{\Gamma_{ii}}{2} \right)}{1 + kC_e + (kC_e)^2 \left( \frac{\Gamma_{ii}}{2} \right)}$	k	
	Linear (Henry)		$k_p$	$q_e = K_p C_e$
2- Parameters	Langmuir	$q_e = \frac{\alpha_L \beta_L C_e}{1 + \alpha_L C_e}$	$\alpha_L$ and $\beta_L$	$\left( \frac{C_e}{q_e} \right) = \frac{C_e}{\beta_L} + \frac{1}{\beta_L \alpha_L}$ $\left( \frac{1}{q_e} \right) = \frac{1}{\alpha_L \beta_L C_e} + \frac{1}{\beta_L}$ $q_e = \beta_L - \frac{\beta_L q_e}{\alpha_L C_e}$ $\left( \frac{q_e}{C_e} \right) = \beta_L \alpha_L - \alpha_L q_e$ $\left( \frac{1}{C_e} \right) = \beta_L \alpha_L \frac{1}{q_e} - \alpha_L$
	Freundlich	$q_e = K_f C_e^{\frac{1}{\alpha_f}}$	$K_f$ and $\alpha_f$	$\text{Log}(q_e) = \text{log}(K_f) + \frac{1}{\alpha_f} \text{Log}(C_e)$
	Temkin	$q_e = \frac{RT}{\beta_t} \ln(\alpha_t C_e)$	$\alpha_t$ and $\beta_t$	$q_e = \alpha_t + 2.3 \beta_t \log C_e$

Type	Name	Non- Linear Relationship	Parameters	Linear Relationship
	Dubinin–Radushkevich	$q_e = K_{dm} \text{Exp}(-\alpha_{dm} \varepsilon^2)$	$K_{dm}$ and $\alpha_{dm}$	$\ln(q_e) = \ln(K_{dm}) - \alpha_{dm} \varepsilon^2$
	Halsey A	$q_e = \left( \frac{K_H}{C_e} \right)^{\frac{1}{\alpha_H}}$	$K_H$ and $\alpha_H$	$\log(q_e) = \left( \frac{1}{N_H} \right) \log K_H - \frac{1}{N_H} \log C_e$
	Crombie-Quilty and McLoughlin (1983)	$q_e = K_m \left( \frac{C_e}{M} \right)^{\frac{1}{\alpha_m}}$	$K_m$ and $\alpha_m$	$\log(q_e) = \log K_m - \frac{1}{\alpha_m} \log \left( \frac{C_e}{M} \right)$
	Frenkel- Halsey- Hill	$q_e = \text{Exp} \left( \frac{\ln((K_{fhh}) - \ln(C_e))}{\alpha_{fhh}} \right)$	$K_{fhh}$ and $\alpha_{fhh}$	$\ln(q_e) = \left( \frac{1}{\alpha_{fhh}} \right) \ln K_{fhh} - \frac{1}{\alpha_{fhh}} \ln C_e$
	Harkin Jura A	$q_e = \left( \frac{(\alpha_{hj})}{\beta_{hj} + \log(C_e)} \right)^{0.5}$	$\alpha_{hj}$ and $\beta_{hj}$	$\log(q_e)^2 = \log(\alpha_{hj}) + \log(\beta_{hj} + \log C_e)$
	Harkin Jura B	$q_e = \left( \frac{(\alpha_{hj})}{\beta_{hj} - \log(C_e)} \right)^{0.5}$	$\alpha_{hj}$ and $\beta_{hj}$	$\log(q_e)^2 = \log(\alpha_{hj}) + \log(\beta_{hj} - \log C_e)$
	Jovanovic	$q_e = K_{jm} (1 - \exp^{-\alpha_j C_e})$	$K_{jm}$ and $\alpha_{jm}$	$\log(q_e) = \log(K_{jm}) + \log(1 - \exp^{-\alpha_j C_e})$
	Elovich	$\left( \frac{q_e}{\alpha_{mE}} \right) = K_E C_e \left( \exp^{-\frac{q_e}{\alpha_{mE}}} \right)$	$K_E$ and $\alpha_E$	$\ln \left( \frac{q_e}{C_e} \right) = \ln(K_E \alpha_{mE}) - \frac{q_e}{\alpha_{mE}}$
	Folwer –Guggenhien	$K_{FG} C_e = \frac{\theta}{1 - \theta} \exp \left( \frac{2\theta \alpha_{FG}}{RT} \right)$	$K_{FG}$ and $\alpha_{FG}$	$\ln \left( \frac{C_e (1 - \theta)}{\theta} \right) = -\ln(K_{FG}) + \frac{2\theta \alpha_{FG}}{RT}$

Type	Name	Non- Linear Relationship	Parameters	Linear Relationship
	Hill-de Boer	$K_{Hd}C_e = \frac{\theta}{(1-\theta)} \exp\left(\frac{\theta}{(1-\theta)} - \frac{\alpha_{Hd}\theta}{RT}\right)$	$K_{Hd}$ and $\alpha_{Hd}$	$\ln\left[C_e \frac{(1-\theta)}{\theta}\right] - \frac{\theta}{(1-\theta)} = -\ln(K_{Hd}) - \frac{\alpha_{Hd}\theta}{RT}$
	Kiselev	$K_{1k}C_e = \frac{\theta}{(1-\theta)(1+\alpha_{nk}\theta)}$	$K_{1k}$ and $\alpha_{1k}$	$\frac{1}{C_e(1-\theta)} = \frac{K_{1k}}{\theta} + K_{1k}\alpha_{nk}$
	Flory - Huggins	$\frac{\theta}{C_e} = K_{FH}(1-\theta)^{N_{FH}}; \theta = 1 - \frac{C_e}{C_0}$	$K_{FH}$ and $\alpha_{FH}$	$\log\left[\frac{\theta}{C_e}\right] = \log(K_{FH}) + N_{FH} \log(1-\theta)$
	Langmuir - Vageler	$q_e = \left(\frac{C_f K_{LV}}{C_f + \alpha_{LV}}\right); C_f = \frac{C_0 V}{m}$	$\alpha_{LV}$ and $K_{LV}$	$\log(q_e) = \log(C_f K_{LV}) - \log(C_f + \alpha_{LV})$
	Halsey B (Hamdaoui and Naffrechous, 2007)	$q_e = K_{Hf} \left(\frac{C_e}{C_0}\right)^{\frac{1}{\alpha_{Hf}}}$	$K_{Hf}$ and $\alpha_{Hf}$	$\log(q_e) = \log K_H - \frac{1}{\alpha_{Hf}} \log\left(\frac{C_e}{C_0}\right)$
	Halsey C(Rangabhashiyum et al., 2014)	$q_e = \exp\left(\frac{\ln(K_{Hr}) - \ln(C_e)}{\alpha_{Hr}}\right)$	$K_{Hr}$ and $\alpha_{Hr}$	$\ln(q_e) = \frac{1}{\alpha_{Hr}}(\ln(K_{Hr}) - \ln C_e)$
3- Parameters	Redlich–Peterson	$q_e = \frac{\alpha_t C_e}{1 + \beta_t C_e^\gamma}$	$\alpha_t, \gamma$ and $\beta_t$	
	Sips	$q_e = \frac{\alpha_{ts} C_e^{\gamma_{ts}}}{1 + \beta_{ts} C_e^{\gamma_{ts}}}$	$\alpha_{ts}, \gamma_{ts}$ and $\beta_{ts}$	
	Brouers-Sotolongo	$q_e = K_{BS} \left(1 - \exp(-\beta_{BS} C_e^{\alpha_{BS}})\right)$	$K_{BS}, \alpha_{BS}$ and $\beta_{BS}$	



Type	Name	Non- Linear Relationship	Parameters	Linear Relationship
	Jossens	$C_e = \frac{q_e}{\beta_{jo}} \left( \exp \left( K_{jo} q_e^{\alpha_{jo}} \right) \right)$	$\alpha_{jo}, K_{jo}, \text{ and } \beta_{jo},$	
	Hill	$q_e = \frac{K_{Hi} C_e^{\alpha_{Hi}}}{\beta_{Hi} + C_e^{\alpha_{Hi}}}$	$\alpha_{Hi}, K_{Hi}, \text{ and } \beta_{Hi},$	
	Langmuir-Freundlich	$q_e = \frac{\beta_{LF} K_{LF} C_e^{\alpha_{LF}}}{1 + K_{LF} C_e^{\alpha_{LF}}}$	$\beta_{LF}, K_{LF} \text{ and } \alpha_{LF}$	
	Toth	$q_e = \frac{K_{tt} \alpha_{tt}^{\gamma_{tt}} C_e}{\left( 1 + \alpha_{tt} C_e^{\gamma_{tt}} \right)^{\left( \frac{1}{\gamma_{tt}} \right)}}$	$K_{tt}, \alpha_{tt}, \text{ and } \gamma_{tt}$	
		$q_e = \frac{\alpha_{tt} C_e}{\left( \beta_{tt} + C_e^{\gamma_{tt}} \right)^{\left( \frac{1}{\gamma_{tt}} \right)}}$	$\alpha_{tt}, \beta_{tt} \text{ and } \gamma_{tt}$	
	Radke-Prausnitz	$\frac{1}{q_e} = \left( \frac{\alpha_{rp}}{(C_e)} \right) + \frac{\beta_{rp}}{\left( C_e^{\gamma_{rp}} \right)}$	$\alpha_{rp}, \gamma_{rp} \text{ and } \beta_{rp}$	
		$q_e = \frac{K_{rp} \alpha_{rp} C_e}{\left( 1 + \alpha_{rp} C_e^{\gamma_{rp}} \right)}$	$\alpha_{rp}, \gamma_{rp} \text{ and } K_{rp}$	

Type	Name	Non- Linear Relationship	Parameters	Linear Relationship
	Khan	$q_e = \frac{K_k \alpha_k C_e}{\left(1 + \alpha_k C_e\right)^{\gamma_k}}$	$\alpha_k, \gamma_k$ and $K_k$	
	Fritz and Schhunder	$q_e = \frac{K_{fs} \alpha_{fs} C_e^{\gamma_{fs}}}{\left(1 + \alpha_{fs} C_e^{\gamma_{fs}}\right)}$	$\alpha_{fs}, \gamma_{fs}$ and $K_{fs}$	
	Frumkin	$K_{Fm} C_e = \beta_{Fm} \left( \frac{-\alpha_{Fm} \beta_{Fm}}{1 - \beta_{Fm}} \right);$ $\beta_{Fm} = 1 - \frac{C_e}{C_0}$	$K_{Fm}, \alpha_{Fm}$ and $\beta_{Fm}$	
	Koble - Corrigan	$q_e = \frac{\alpha_{kc} C_e^{\gamma_{kc}}}{\left(1 + \beta_{kc} C_e^{\gamma_{kc}}\right)}$	$\alpha_{kc}, \beta_{kc}$ and $\gamma_{kc}$	
	Liu	$q_e = \frac{\left( K_{li} (C_e \beta_{li})^{\frac{1}{\alpha_{li}}} \right)}{1 + (C_e \beta_{li})^{\frac{1}{\alpha_{li}}}}$	$K_{li}, \beta_{li}$ and $\alpha_{li}$	
	Loading ratio	$q_e = \frac{K_{Lr} (\beta_{Lr} C_e)^{\left(\frac{1}{\alpha_{Lr}}\right)}}{1 + (\beta_{Lr} C_e)^{\left(\frac{1}{\alpha_{Lr}}\right)}}$	$K_{Lr}, \beta_{Lr}$ and $\alpha_{Lr}$	
4- Parameters	Weber-Van Vliet	$C_e = K_{wvv} Q_e^{(\alpha_{wvv} \beta_{wvv} + \gamma_{wvv})}$	$K_{wvv}, \alpha_{wvv}, \beta_{wvv}$ and $\gamma_{wvv}$	

Type	Name	Non- Linear Relationship	Parameters	Linear Relationship
	Bauder	$q_e = \left( \frac{(K_{bu})\beta_{bu}C_e^{1+\alpha_{bu}+\gamma_{bu}}}{1+(C_e^{1+\alpha_{bu}})} \right)$	$K_{bu}, \beta_{bu}, \gamma_{bu}$ and $\alpha_{bu}$ $1+\beta_{bu}, + \alpha_{bu}$ $<1$ And $1 + \beta_{bu}, < 1$	
	Marczewsk-Jaroniec	$q_e = K_{msj} \left( \frac{(C_e\gamma_{msj})^{\alpha_{msj}}}{1+(C_e\gamma_{msj})^{\alpha_{msj}}} \right)^{\left( \frac{\beta_{msj}}{\alpha_{msj}} \right)}$	$K_{msj}, \gamma_{msj},$ $\alpha_{msj}$ and $\beta_{msj}$	
	Fritz and Schhunder	$q_e = \left( \frac{K_{FS4}(C_e)^{\alpha_{FS4}}}{1+\gamma_{FS4}(C_e)^{\beta_{FS4}}} \right)$	$K_{FS4} \gamma_{FS4},$ $\alpha_{FS4}$ and $\beta_{FS4}$	
5 parameters	Fritz- Schhunder	$q_e = \left( \frac{q_{fs5}\gamma_{fs5}(C_e)^{\alpha_{fs5}}}{1+K_{fs5}(C_e)^{\beta_{fs5}}} \right)$	$q_{fs5}, K_{fs5}, \alpha_{fs5}, \gamma_{fs5}$ and $\beta_{fs5}$	
Multi Component adsorption equilibrium isotherm	Langmuir, Bulter and Ockrent, Schwlb, Markham and Benton, Moriguch and Kaneniwa	$q_e = \frac{\alpha_{mLB}C_e}{1+\sum_{i=1}^n \beta_{mLB}C_{ei}}$	$\alpha_{mLB}$ and $\beta_{mLB}$	
	Fritz and Schhunder	$q_e = \frac{\alpha_{mFS}C_e^{\gamma_{mFS}}}{\left( \beta_{mFS} + \sum_{i=1}^n \alpha_{mFS}C_{ei}^{\gamma_{mFS}} \right)}$	$\alpha_{mFS}; \beta_{mFS}$ and $\gamma_{mFS}$	
	Yon and Turnock	$q_e = \frac{\alpha_{mTY}(C_e)^{\gamma_{mTY}}}{1+\sum_{i=1}^n \beta_{mTY_i}(C_e)^{\gamma_{mTY}}}$	$\alpha_{mFS}; \beta_{mFS}$ and $\gamma_{mFS}$	

Type	Name	Non- Linear Relationship	Parameters	Linear Relationship
Multi Component adsorption equilibrium isotherm	Redlich–Peterson	$q_e = \frac{\alpha_{mLRP} C_{ei}}{1 + \sum_{i=1}^n \beta_{mLRP} C_{ei}}$	$\alpha_{mLRP}$ and $\beta_{mLRP}$	
	Ruthven	$q_e = \left( \frac{K_{mRu} (C_e)^{\alpha_{mRu}}}{1 + \sum_{j=1}^n K_{mRuj} (C_e)^{\gamma_{mRuj}}} \right)$	$K_{mRu}$ ; $\alpha_{mRu}$ and $\gamma_{mRu}$	
	Sheindorf et al. (1983),	$q_e = K_{si} (C_{ei}) \left( \sum_{j=1}^n K_{sij} C_{ej} \right)^{(\alpha_{si}-1)}$	$K_{si}$ and $\alpha_{si}$	
Multi Component adsorption equilibrium isotherm	Ruthven and Wong	$q_e = \frac{K_{RWi} C_{ei} \left( 1 + \sum_{j=1}^n K_{RWj} C_{ej} \Gamma_j \right)}{1 + \sum_{k=1}^n K_{RWk} C_{ek} \left( 1 + \sum_{j=1}^n K_{RWj} C_{ej} \frac{\Gamma_j}{2} \right)}$	$K_{si}$ and $\alpha_{si}$	
	Jain and Snoeyink	$q_{e2} = \left( \frac{(K_{mjs2}) \beta_{mjs2} C_{e2}}{1 + \beta_{mjs1} C_{e1} + \beta_{mjs2} C_{e2}} \right)$ $q_{e1} = \left( \left( \frac{(K_{mjs1} - K_{mjs2}) \beta_{mjs1} C_{e1}}{1 + \beta_{mjs1} C_{e1}} \right) - \left( \frac{(K_{mjs2}) \beta_{mjs2} C_{e2}}{1 + \beta_{mjs1} C_{e1} + \beta_{mjs2} C_{e2}} \right) \right)$	$K_{mjs2}$ ; $K_{mjs1}$ ; $\beta_{mjs1}$ and $\beta_{mjs2}$	

Type	Name	Non- Linear Relationship	Parameters	Linear Relationship
Multi Component adsorption equilibrium isotherm	Extended Langmuir	$q_{e2} = \left( \frac{(K_{mel2})\beta_{mel2}C_{e2}}{1 + \beta_{mel1}C_{e1} + \beta_{mel2}C_{e2}} \right)$ $q_{e1} = \left( \left( \frac{(K_{mel1})\beta_{mel1}C_{e1}}{1 + \beta_{mel1}C_{e1} + \beta_{mel2}C_{e2}} \right) \right)$	$K_{mel2}; K_{mel1}; \beta_{mel1} \text{ and } \beta_{mel2}$	
	Extended Langmuir - Freundlich	$q_{e2} = \left( \frac{(K_{melf2})(\beta_{melf2}C_{e2})^{\gamma_{melf2}}}{1 + (\beta_{mel1}C_{e1})^{\gamma_{melf1}} + (\beta_{mel2}C_{e2})^{\gamma_{melf2}}} \right)$ $q_{e1} = \left( \left( \frac{(K_{melf1})(\beta_{melf1}C_{e1})^{\gamma_{melf1}}}{1 + (\beta_{melf1}C_{e1})^{\gamma_{melf1}} + (\beta_{melf2}C_{e2})^{\gamma_{melf2}}} \right) \right)$	$K_{melf2}; \gamma_{melf1}$ $K_{melf1}; \beta_{melf1}$ $\gamma_{melf2} \text{ and } \beta_{melf2}$	
	Extended Jovanovic - Freundlich	$q_{e2} = \left[ \left( \frac{(K_{mejf2})\beta_{mejf2}C_{e2}}{\beta_{mejf1}C_{e1} + \beta_{mejf2}C_{e2}} \right) \times \frac{1}{1 - \exp^{-(\beta_{mejf1}C_{e1} + \beta_{mejf2}C_{e2})^{\gamma_{mejf}}}} \right]$ $q_{e1} = \left[ \left( \frac{(K_{mejf1})\beta_{mejf1}C_{e1}}{1 + \beta_{mejf1}C_{e1} + \beta_{mejf2}C_{e2}} \right) \times \frac{1}{1 - \exp^{-(\beta_{mejf1}C_{e1} + \beta_{mejf2}C_{e2})^{\gamma_{mejf}}}} \right]$	$K_{mejf2}; \gamma_{mejf1}$ $K_{mejf1}; \beta_{mejf1}$ $\gamma_{mejf2} \text{ and } \beta_{mejf2}$	
	Single Component Jovanovic - Freundlich	$q_e = K_{scjf} \left[ 1 - \exp^{-(\beta_{scjf}C_e)^{\gamma_{scjf}}} \right]$	$K_{scjf}; \beta_{scjf}$ and $\gamma_{scjf}$	



These factors of relatively expensive and frequently imported make it important and necessary for developing and developed countries to discover cheaper, economical and available raw materials for the preparation and development of activated carbon for utilization in industries, purification of drinking water from both groundwater and surface water sources and wastewater treatment. In an attempt to produce cheaper and inexpensive activated carbon, various studies have been conducted on the biodegradable part or fraction of solid products, solid wastes, and solid residues from agricultural products (such as vegetables and animal substances), forestry, and solid wastes from related industries (such as industrial solid wastes and municipal solid waste). Bio-adsorption treatment methods and technologies are biological methods of environmental pollution control, which are alternative technologies to conventional wastewater treatment facilities. Other suitable agricultural waste products such as olive-waste cakes, cattle-manure compost, chicken eggshells; bamboo materials, coconut shells and apple pulp have been examined and evaluated as adsorbents in recent years as activated carbon precursors.

Figure 5 presents information on the performance of adsorption in terms of pollutants, adsorbents relevant adsorption equilibrium isotherms and sources. More information on the techniques and methods for arsenic reduction removal are well documented in the literature such as Alka *et al.* (2020); Amen *et al.* (2020); An *et al.* (2011); Analia *et al.* (2019); Babaeiveli *et al.* (2014); Bentahar *et al.* (2016); Daus *et al.* (2004); Hamayun *et al.* (2014); He *et al.* (2012); Koohzad *et al.* (2019); Kumar *et al.* (2004); Kundu and Gupta (2006); Li *et al.* (2014); Lin *et al.* (2006); Lopez-Luna *et al.* (2019); Manna and Ghosh (2007); Matusik (2014); Min *et al.* (2015); Mukhopaahyay *et al.* (2017); Namasivayam and Sendthikumar (1998); Obijole *et al.* (2022); Oke *et al.* (2022a and b); Oke *et al.* (2008); Ramesh *et al.* (2007); Sahabi *et al.* (2009); Shakoob *et al.* (2018); Shih (2005); Singh and Pant (2004) and Khanam *et al.* (2019). In addition, information and established

mechanisms of arsenic adsorption for the environment can be established in relevant and recent literature such as Zubair *et al.* (2020); Pandi *et al.* (2020); He *et al.* (2019); Yin *et al.* (2019); Zhou *et al.* (2019); Fan *et al.* (2020); Zhu and Yan (2016); Zhu *et al.* (2018); Hu *et al.* (2017); Park *et al.* (2016); Santra and Sarkar (2016); Zhu *et al.* (2016); Zhu *et al.* (2015); Wang *et al.* (2016); Liu *et al.* (2015); Zhang *et al.* (2017); Lorenzen *et al.* (2018); Li *et al.* (2012) and Malana *et al.* (2011). Atallah *et al.* (2020) reported that the comparison between 2-parameters, 3- parameters, and 5-parameters of adsorption models revealed that the models with higher parameters were more suitable to define the equilibrium data than the adsorption models with lower parameters, but utilizations of these higher parameters' models are rare or not available in the literature. The main objectives of this research work are to utilise higher parameters (3, 4 and 5 parameters) adsorption models to explain adsorption equilibrium data of arsenic reduction and removal from both synthetic and natural water and evaluate the accuracy of selected models statistically.

## MATERIALS AND METHODS

Powdered eggshell was prepared from raw and unprocessed chicken eggshells collected from an institutional agricultural farm at Obafemi Awolowo University. The preparation processes are as detailed in previous studies such as Obijole *et al.* (2022); Oke *et al.* (2022a; 2022b, 2008); Adekunbi *et al.* (2019; 2023); and Babajide *et al.* (2022). Figure 6 presents a summary of the powdered eggshell preparation processes. The structural characteristics of the powdered eggshells were investigated by characterization with a Scanning Electron Microscope (model Carl Zeiss Smart Evo 10) with the aid of Energy Dispersive Spectroscopy. These prepared powdered eggshells of different sizes were utilised as adsorbents for arsenic removal or reduction from both typical and synthetic wastewater.

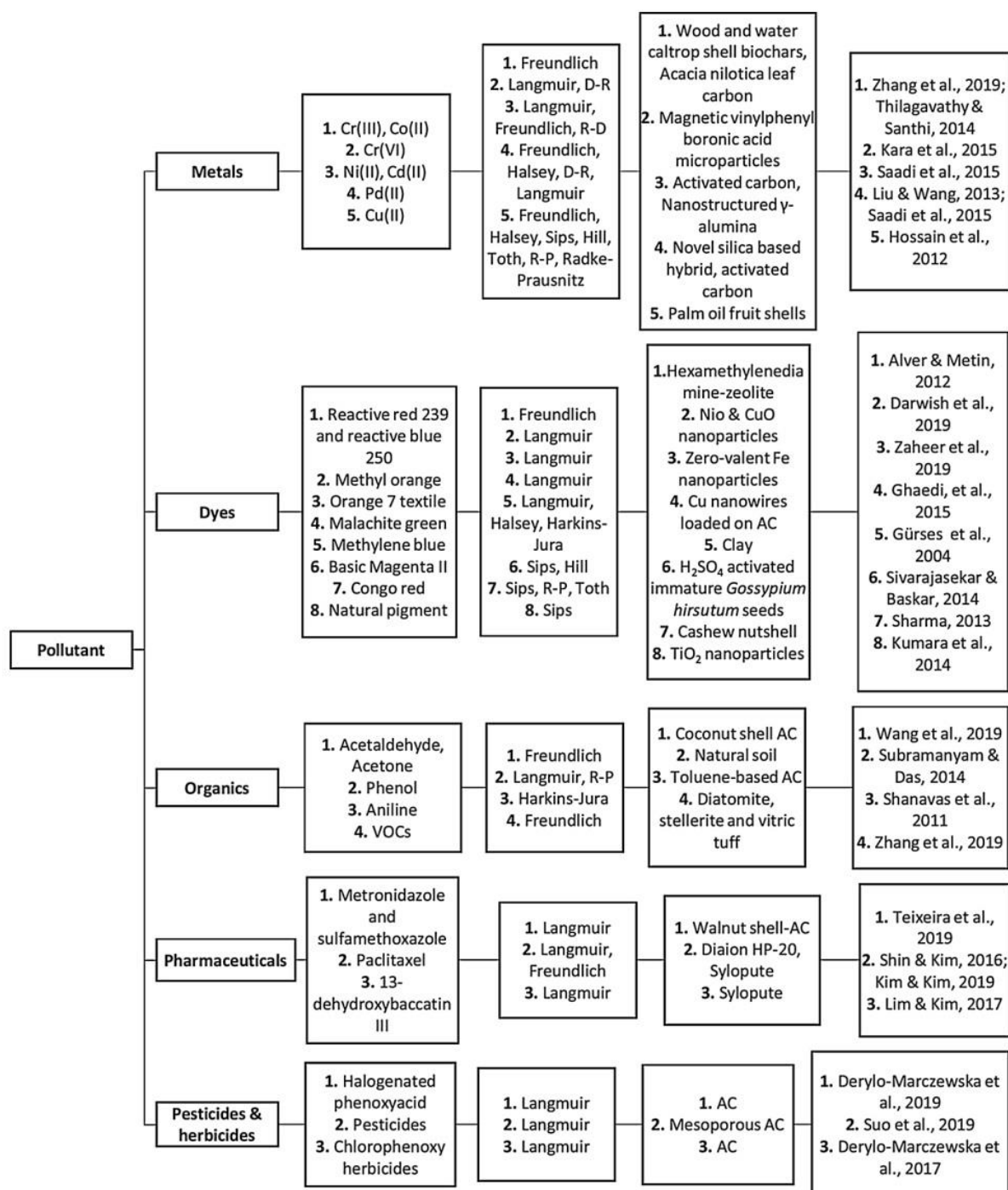


Figure 5: Information on the performance of adsorption in terms of pollutants, adsorbents relevant adsorption equilibrium isotherms and sources (Source: Al-Ghouti and Da'ana, 2020)

Evaluation of adsorption performances of the powdered eggshell was conducted utilising procedures and steps highlighted in the literature such as Obijole *et al.* (2022); Oke *et al.* (2022a; 2022b, 2008); Adekunbi *et al.* (2019; 2023); and Babajide *et al.* (2022). In the case of adsorptive rates of powdered eggshell for natural and typical water samples, raw water samples from Aponmu River, which is an

artificial lake in Elizade University, Ilara – Mokin were utilised. Raw water samples were collected weekly for four months, a specific mass (10 grams of Sodium arsenate ( $Na_2HASO_4 \cdot 7H_2O$ , 99% purity) of arsenic from the stock solution was introduced (added) and the working concentrations were subjected to similar treatments as the synthetic wastewaters. The adsorption equilibrium

isotherms were calculated as follows (equation 1):

$$q_e = \left( \frac{C_0 - C_e}{M} \right) V \quad (1)$$

Where:  $q_e$  is the adsorption capacity of the powdered eggshell at equilibrium (mg/g),  $C_0$  is initial the concentration of arsenic in the solution (mg/l),  $C_e$  is the experimental concentration of arsenic in the solution at equilibrium (mg/l),  $M$  is the mass or weight of adsorbent used (g) and  $V$  is the volume of an aqueous solution of arsenic used. The initial and final concentrations of arsenic in both untreated and treated water of both synthetic and typical water samples were determined using procedures as stated in Standard Methods (APHA, 2012; van Loosdrecht *et al.*, 2016). The adsorption equilibrium isotherm parameters in the higher parameter's models (mainly 3, 4 and 5–parameters) were calculated utilising iteration technique through Microsoft Excel Solver. Microsoft Excel Solver was utilised for the calculation of the standard adsorption equilibrium isotherm's variables based on accessibility and accuracy at no additional installation and operational costs. Figure 7 shows the Flowchart of the methodology used in the evaluation of the adsorption capacities of powdered eggshells. Figure 8 presents the flowchart of utilising Microsoft Excel Solver in the computation of the adsorption equilibrium isotherm's parameters. These calculated

adsorption equilibrium parameters were utilised to compute adsorption capacity and the calculated adsorption capacities were evaluated using standard statistical methods (Analysis of Variation, Model of Selection Criterion, and Akaike Information Criterion). Information and techniques on the computations of standard statistical methods are documented in the literature such as Ojo *et al.* (2023); Obijole *et al.* (2022); Oke *et al.* (2022a; 2022b, 2008); Adekunbi *et al.* (2019; 2023); Babajide *et al.* (2022); and Fajobi *et al.* (2023).

## RESULTS AND DISCUSSION

Figures 9a, 9b and 9c present the scanning electron microscope views and micrographs of the pore variations and surface morphology of the powdered eggshell as an adsorbent before the adsorption process. These figures revealed that the surface of the applied powdered eggshell was porous with a large number of continuous and discontinuous pores as functions or forms of megapores and micropores, which makes it appropriate for the adsorption of arsenic from the aqueous solutions

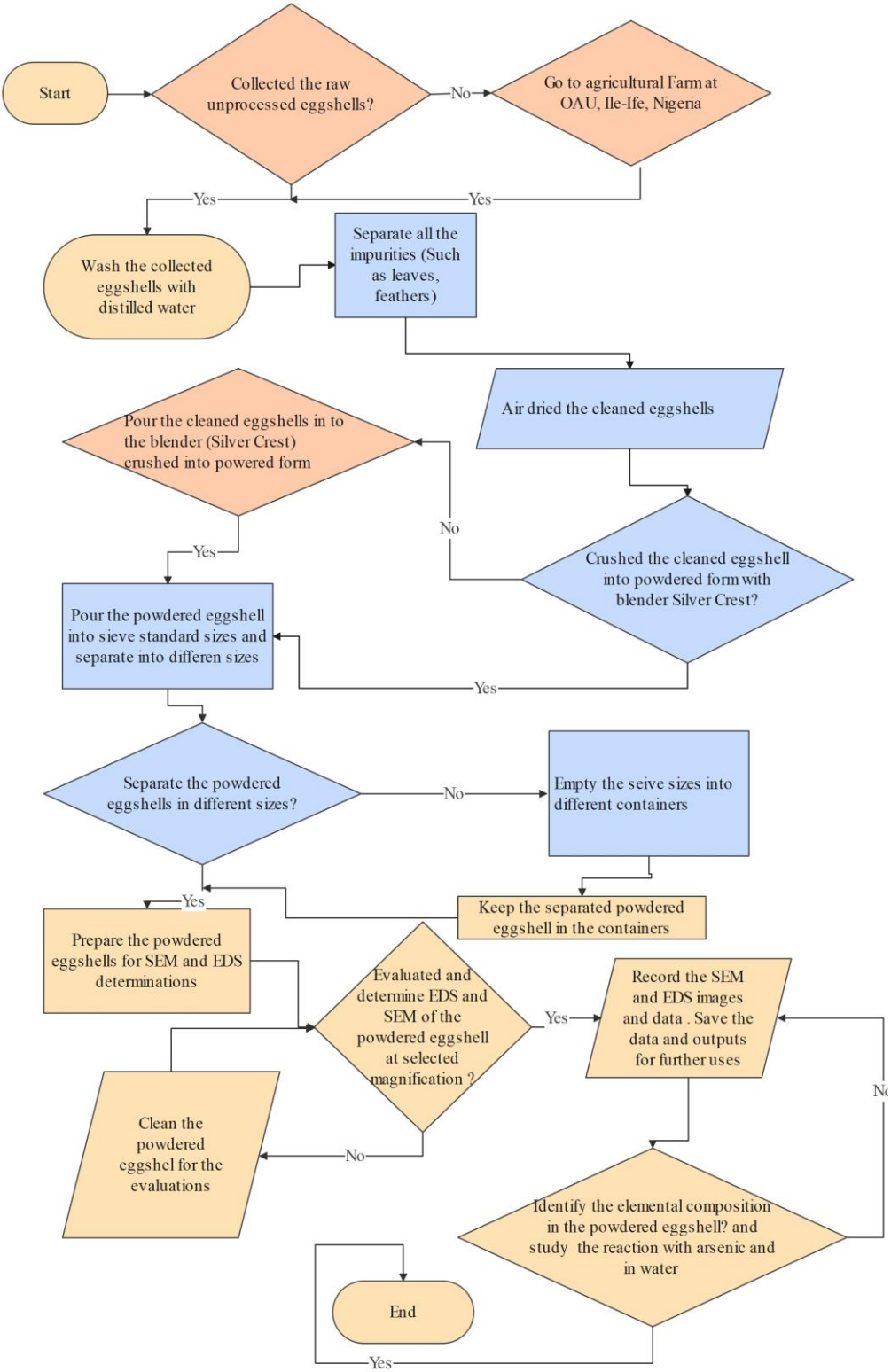


Figure 6 the summary of the powdered eggshell preparation processes and a flowchart of the methodology utilised in this study

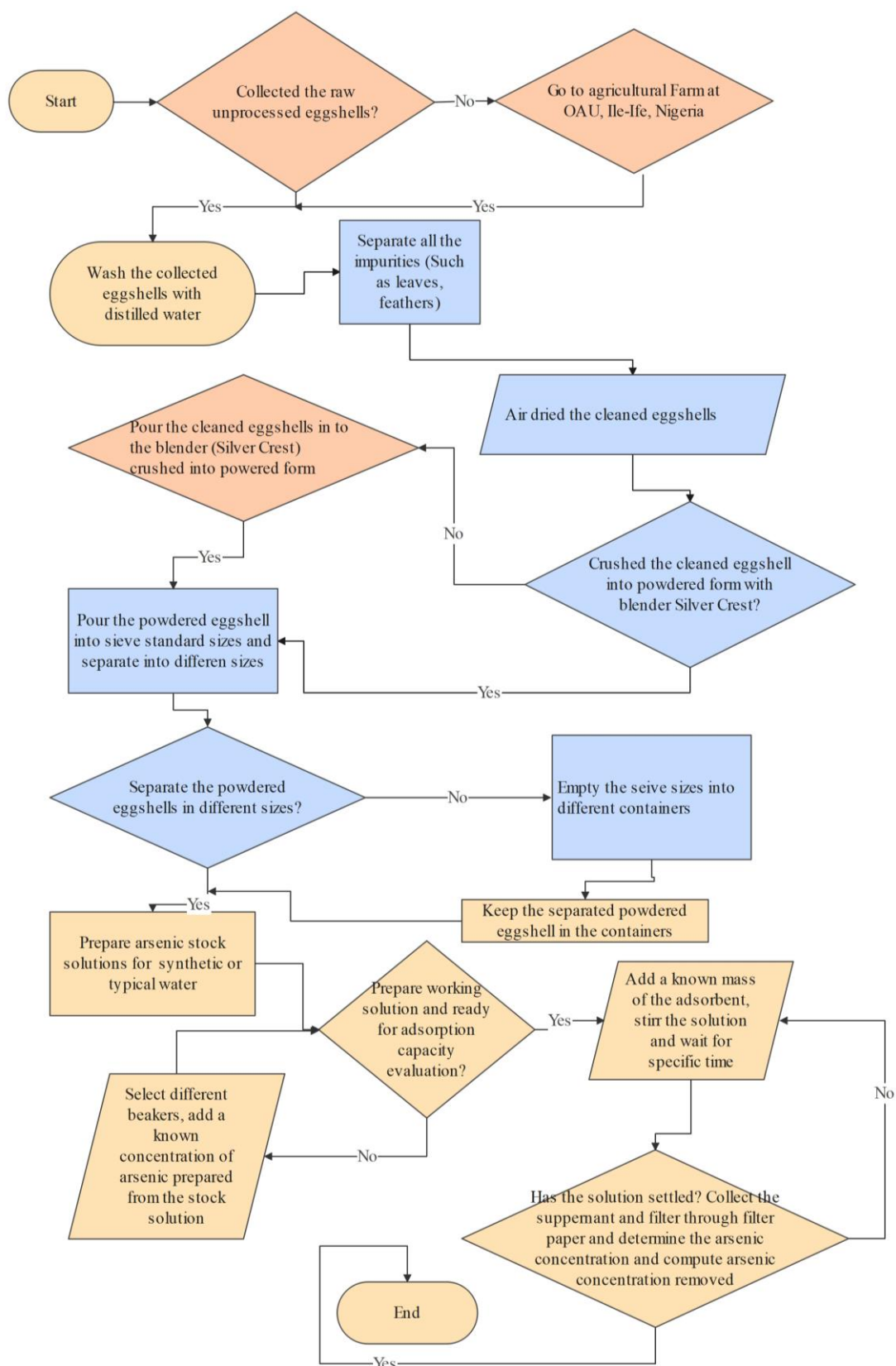


Figure 7 Flowchart of the methodology used in the evaluation of the adsorption capacities of powdered eggshell



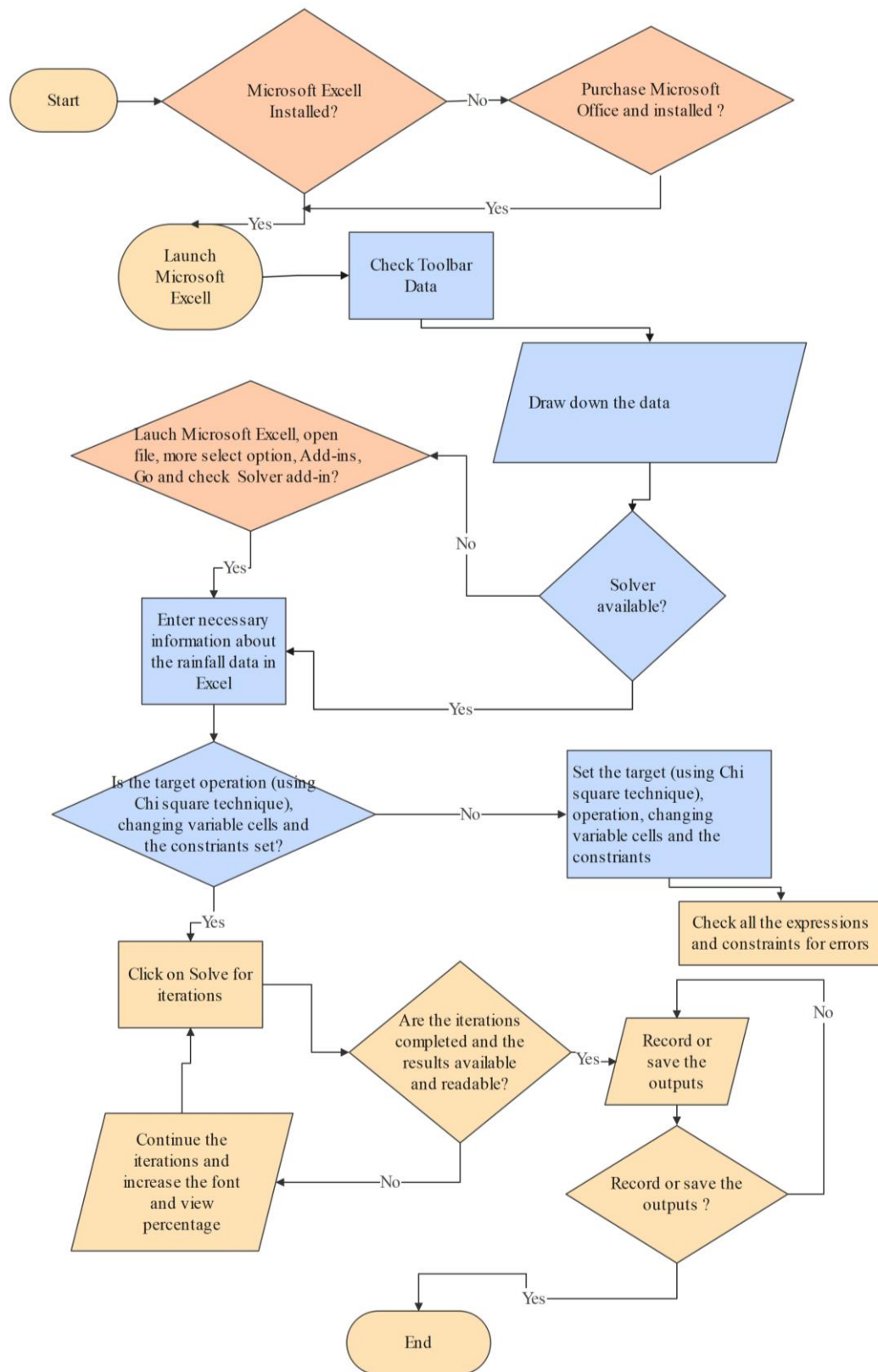


Figure 8 Flowchart of the methodology of utilizing Microsoft Excel Solver

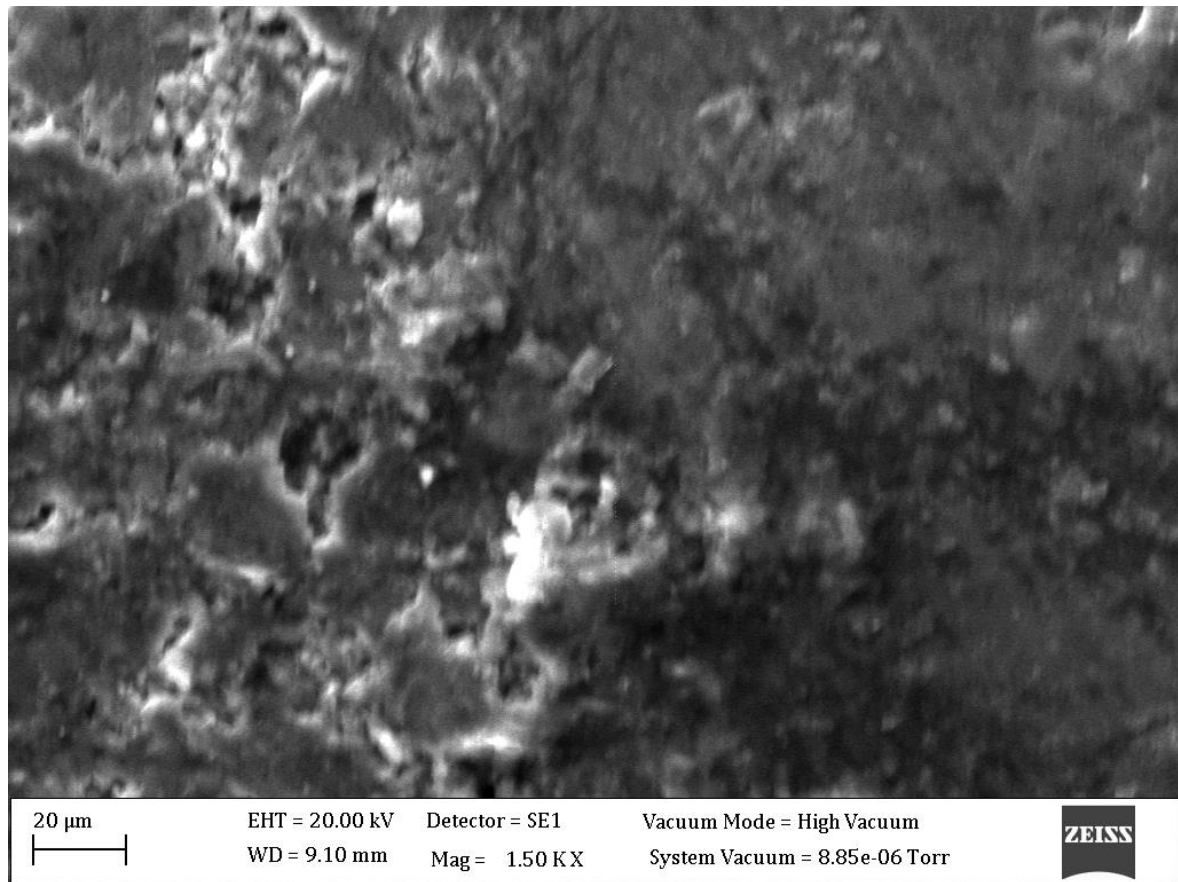


Figure 9a Surface morphology of the powdered eggshell at system vacuum of  $8.85 \times 10^{-6}$  Torr and 1500 X magnification

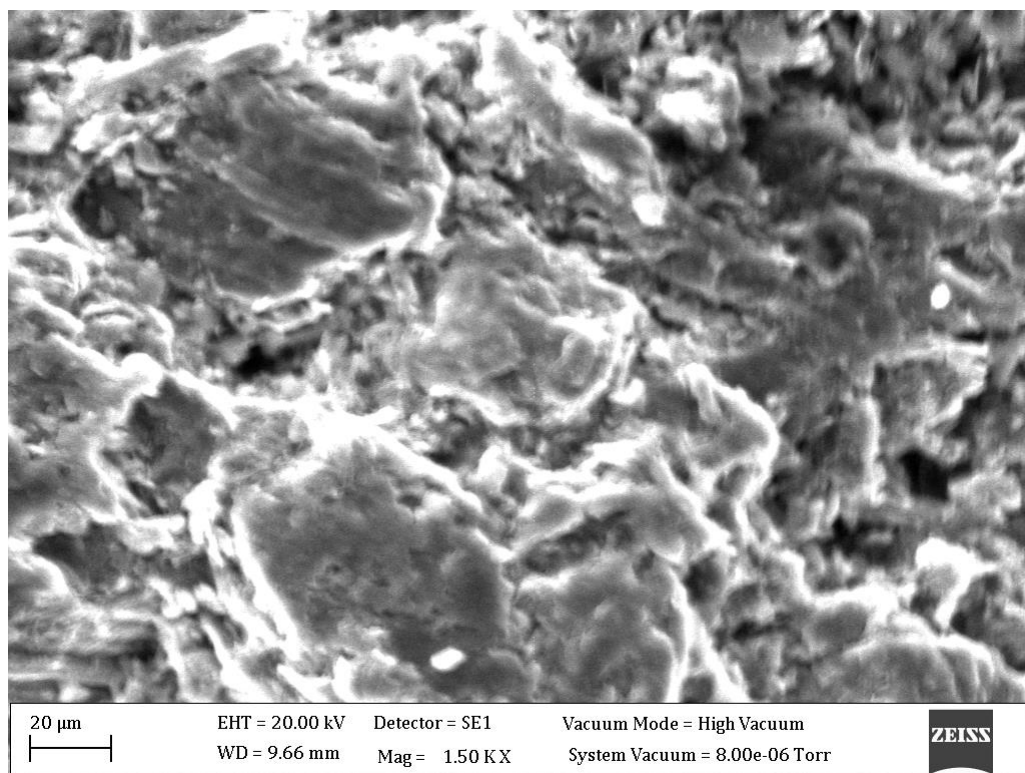


Figure 9b Surface morphology of the powdered eggshell at system vacuum of  $8.00 \times 10^{-6}$  Torr and 1500 X magnification

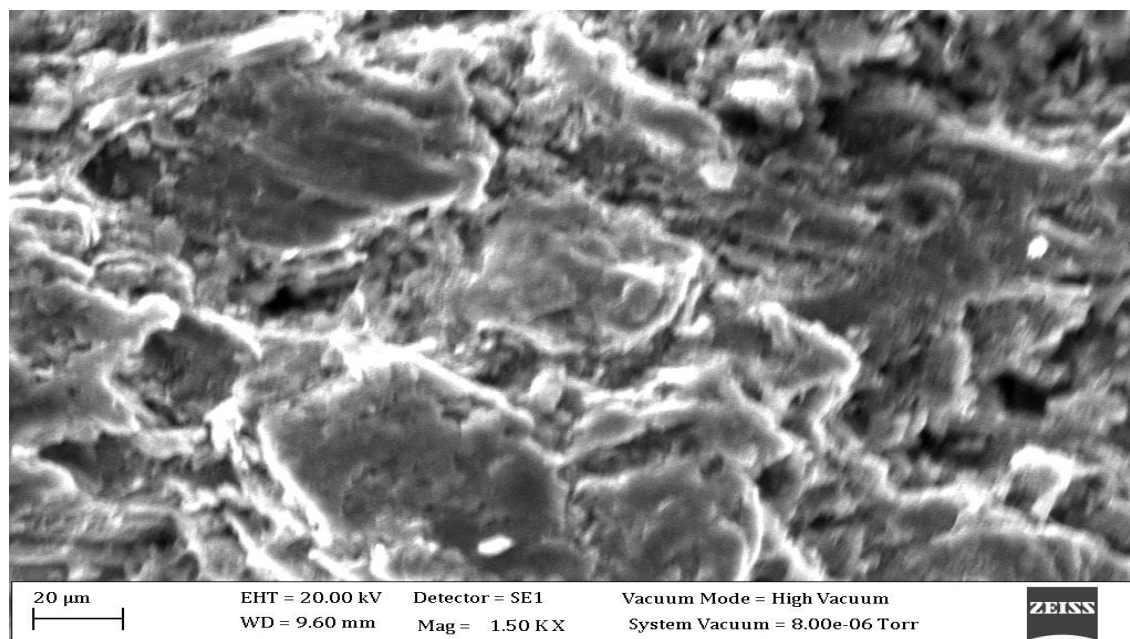


Figure 9c Surface morphology of the powdered eggshell at system vacuum of  $8.85 \times 10^{-6}$  Torr and 1500 X magnification

Figures 9a, 9b and 9c provide an outline of the microstructural geomorphology of the powdered eggshell. These four figures at different magnifications provide information and data on the mixed segregation and homogeneity of the micro compositions and constituents. In these figures, there is a fair distribution of constituents with a marked absence of several segregation. In the case of the higher magnification micrograph there are smaller regions of accumulation. These regions were tended to form clumps with the border and the pore structure is apparent.

The pores are permeate and evenly sized throughout the entire structure. In addition, these pores serve to encompass the surface area of the powdered eggshell and aid in the adsorption of impurities. Figure 10 exhibits the Scanning Electron Microscope pictures of the eggshell with other materials. These figures showed the presence of particles agglomerates with irregular shapes. In addition, these particles present clearly higher surface and certainly higher porosity than eggshell particles in accordance with the results literature. From previous studies such as Elkady et al. (2011); Köse and Kıvanç (2011); Cheng et al. (2011); Chen et al. (2012); Polat and Aslan (2014); Guru and Dash

(2014); Aslan et al. (2015); . Hee-Jeong and Seung-Mok (2015), Elabbas et al. (2016); Zhang et al. (2017); Choi (2019a and b); Yusuf (2019); Candido et al. (2019); Hee-Jong (2019); Kohzad *et al.* (2019) and Rápó et al. (2020) reported some similar observations of pores for selected adsorbents in the removal of arsenic. These results of microstructural geomorphology agreed with previous studies and research works.

Figures 10a, 10b, and 10c present the scanning electron microscope images and micrographs, and Energy Dispersive Spectroscopy results of selected adsorbents used for arsenic reductions and removal from previous studies. Figure 11 presents the results of the Energy Dispersive Spectroscopy. These figures (Figures 11a, and 11b) revealed the major composition of the powdered eggshells. The major elemental components of the powdered eggshells are aluminium (between 1.25 and 7.58 % of the adsorbent as aluminium), Calcium (between 3.7 and 10.12% of the adsorbent as calcium), Silicon (between 11.15 and 25.62 % of the adsorbent as silicon), Carbon (between 0.00 and 27.75% of the adsorbent as carbon) and oxygen (between 48.75 and 58.13% of the adsorbent as oxygen) had the highest weight percentages (Figure 10a, and 10b).



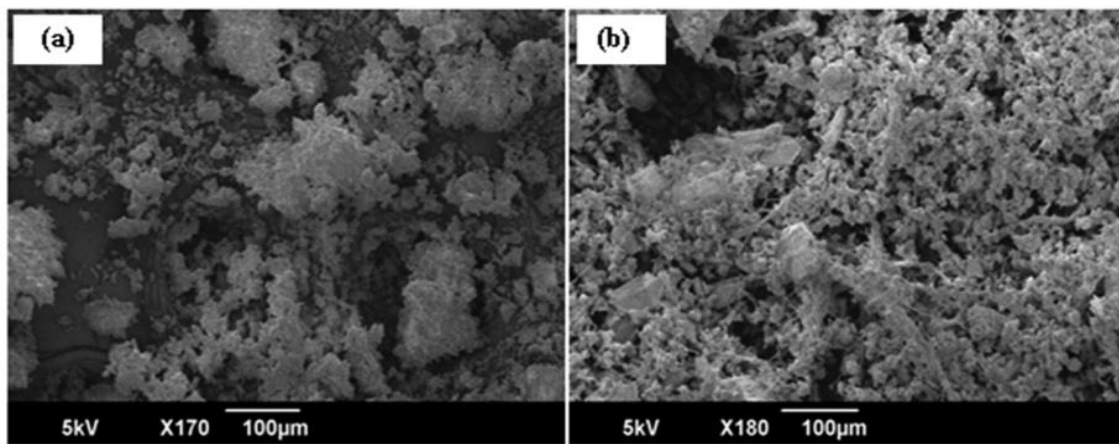


Figure 10a: scanning electron microscope images of eggshell (a) and powdered marble (b) at  $100 \times 10^{-6}$  m (Source: Elabbas et al., 2015)

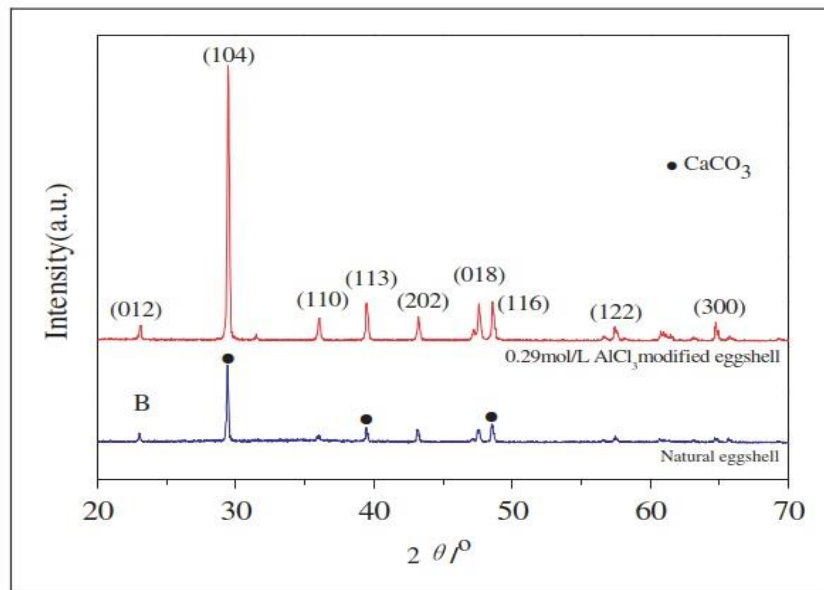


Figure 10b X-ray diffraction spectra of natural eggshell and Al-eggshell (Source: Zhang et al 2017)

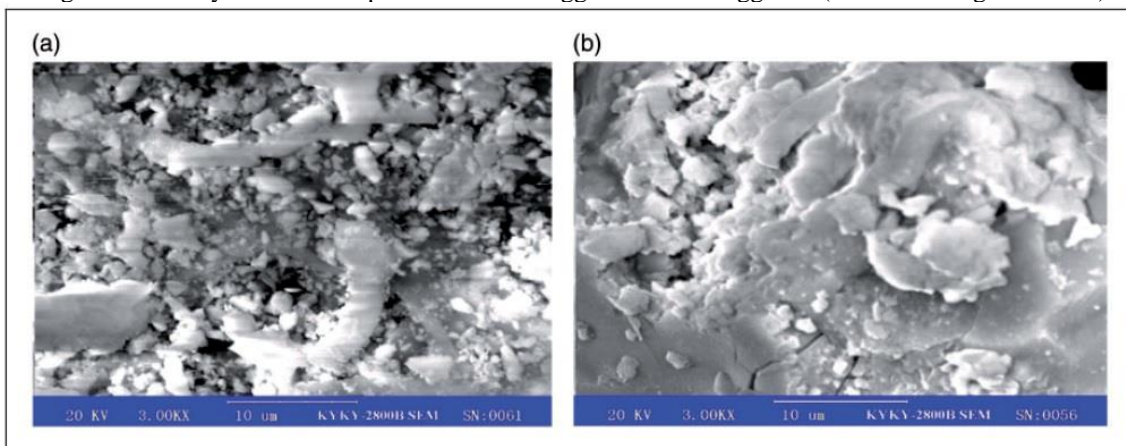


Figure 10c Scanning Electron Microscope images of natural eggshell (Label (a)) and Al-eggshell (Label (b)). (Source: Zhang et al., 2017)

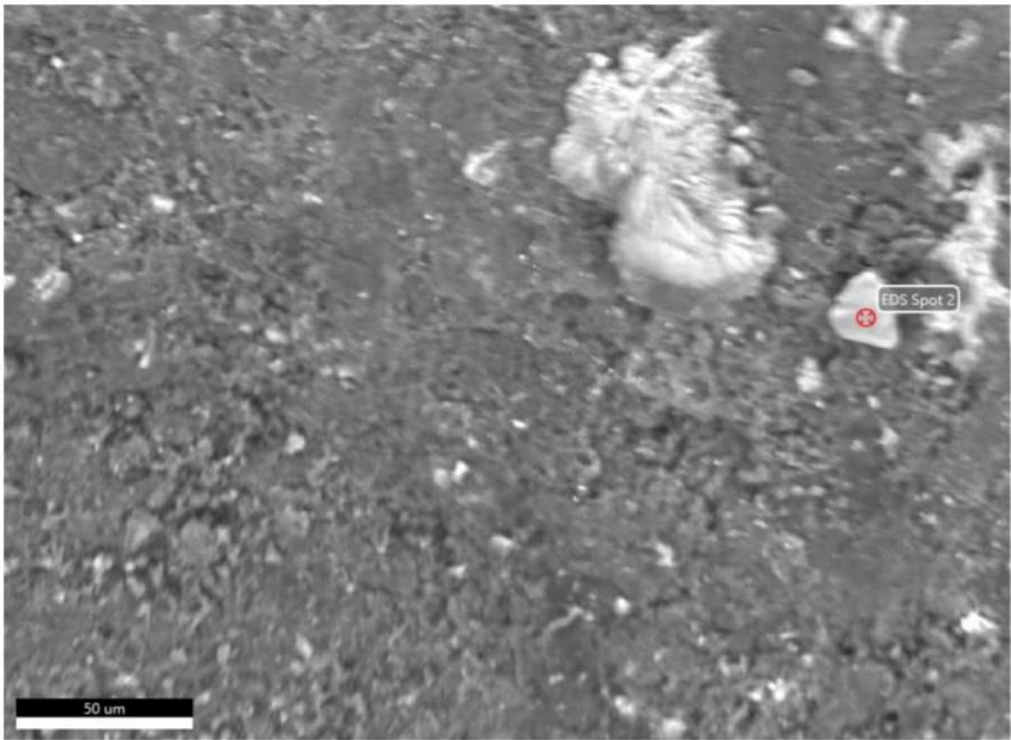


Figure 11ai: Energy Dispersive Spectroscopy view of Spot 2



Figure 11aii: Energy Dispersive Spectroscopy results of Spot 2



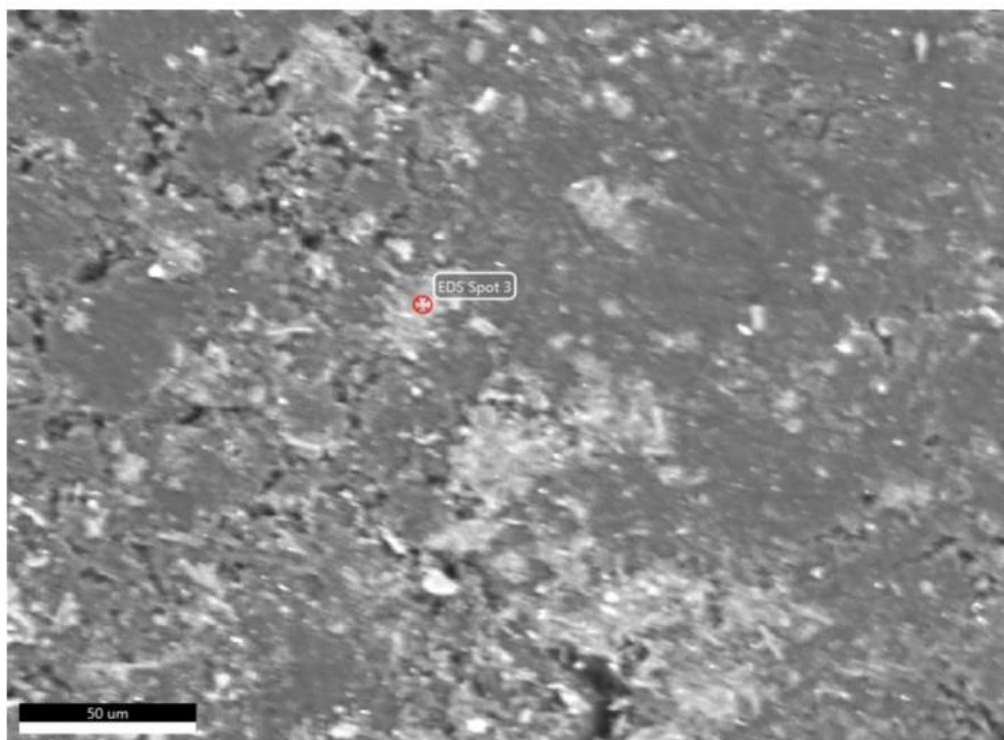


Figure 11bi: Energy Dispersive Spectroscopy view of Spot 3

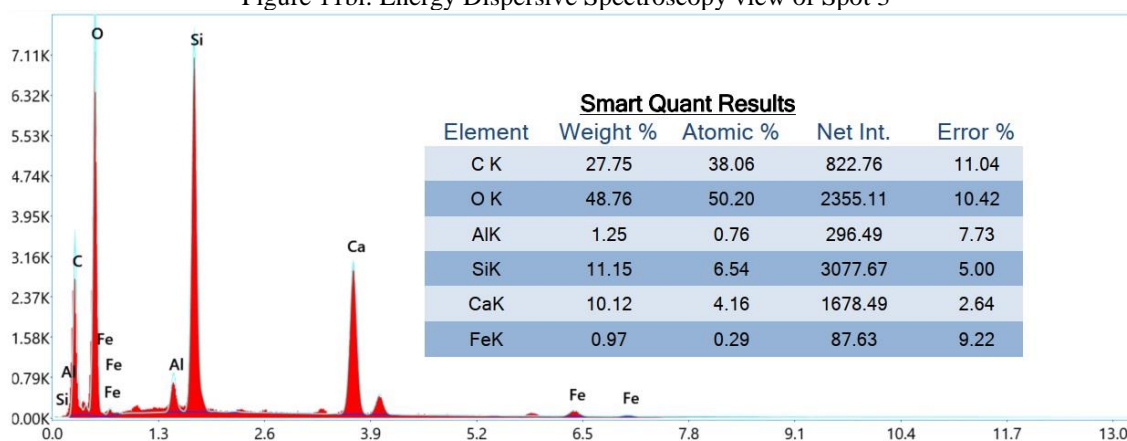


Figure 11bii Energy Dispersive Spectroscopy results of Spot 3

The other elements present in the adsorbent structure were Na, Mg, K, and Fe and their corresponding weight and atomic percentages are presented in the figures. The figures revealed that elemental compositions of eggshells are similar but with different proportions. These results of elemental compositions, agreed with Guru and Dash (2014) statement and composition which stated that the eggshells are composed of nearly 95% of calcium carbonate (Calcium, Carbon and Oxygen) in the form of calcite and almost 3.5 % of proteins, proteoglycans and glycoproteins. The exact and main role played by the organic components of the eggshell in the adsorption is

fairly understood as in the formation of functional groups. In addition, Ajala et al. (2018) reported that elemental concentrations obtained from eggshells were: calcium 2300.33 mg/L as calcium, magnesium 850.00 mg/L as magnesium, sodium 33.83 mg/L of sodium, potassium 17.06 mg/L as potassium; iron 1.4 mg/L of iron, zinc 0.99 mg/L as zinc and copper 0.063 mg/L as copper. The proximate showed that the other components of powdered eggshells are as follows moisture content 0.95 %, ash content 45.29 % , crude protein 1.40 %, lipid content 0.37 %, lipid; 4.38 % and crude fibre 0.32 %.

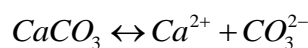
Rapo et al. (2020) Due to their porous structure, eggshells have large specific surface areas; therefore, they are excellent bio sorbents. The eggshell structure is uneven and granulated. One eggshell, which consists of 95 % to 97% calcite ( $\text{CaCO}_3$ ) crystals, contains approximately 17000 pores. The complex structure of chicken eggshell contains various organic molecules and mineralized components such as calcite (mainly in palisade and mammillary layers), which are combined in several layers. Instead of the simple  $\text{CaCO}_3$  crystal layers, the shell consists of very complex mineral formations in a protein matrix. Five different organic and calcite layers build up chicken eggshell. The eggshell thickness is between  $280 \times 10^{-6}$  m and  $400 \times 10^{-6}$  m and is composed of the inner and outer membrane ( $70.0 \times 10^{-6}$  m), mammillary layer ( $100.0 \times 10^{-6}$  m), palisade layer ( $200.0 \times 10^{-6}$  m), prismatic layer ( $8.0 \times 10^{-6}$  m) and thin cuticle ( $10.0 \times 10^{-6}$  m).

Park et al. (2007) documented that several eggshells have similar or the same major chemical components. These major components include  $\text{CaCO}_3$  and a few or some of these elements (namely, Si, Mg, P, S, Al, Na, Sr, K, and Sr. It was reported that eggshell contained  $\text{CaCO}_3$  as limestone with a total of 97.025% and MgO with a total of 0.842%. The materials are the important inorganic compositions of eggshells.

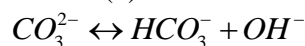
Zhang et al. (2017), stated that the chemical components of raw or natural eggshell are  $\text{Na}_2\text{O}$  (0.492 %);  $\text{MgO}$  (0.842 %);  $\text{Al}_2\text{O}_3$  (0.054%);  $\text{SiO}_2$  (0.011%);  $\text{P}_2\text{O}_5$  (0.183%);  $\text{SO}_3$  (0.745%);  $\text{CaCO}_3$  (97.025 %);  $\text{K}_2\text{O}$  (0.051%);  $\text{Fe}_2\text{O}_3$  (0.028 %);  $\text{SrO}$  (0.141%);  $\text{Cl}$  (0.127 %) and Volatile matter (0.301 %). Köse and Kivanc (2011) ; Zhang et al. (2017) reported that Brunauer, Emmett and Teller (BET), a surface area was  $6.012 \text{ m}^2/\text{g}$ ; micropore volume ( $0.093 \times 10^{-3} \text{ cm}^3/\text{g}$ ); mesopore volume ( $1.46 \times 10^{-2} \text{ cm}^3/\text{g}$ ) and total pore volume ( $1.47 \times 10^{-2} \text{ cm}^3/\text{g}$ ). It was stated that the natural eggshell has irregular granular crystal with 0.5 to  $18 \times 10^{-6}$  m. The comparison of the peak information of the natural eggshell implied that the main peak intensity increased; however, no aluminum hydroxide or oxide peak information was found. The reasons for this phenomenon maybe include (a) the mass of Al was too small and (b) aluminum hydroxide and oxide X-ray diffraction peak is wide. The natural eggshell exhibit one peak around  $2.0$  to  $10 \times 10^{-9}$  m. The X-ray diffraction patterns of the natural eggshell. The main peak appeared

at  $2\theta$  is equal to  $29.5^\circ$  several other small peaks at  $2\theta$  equal to  $23.2^\circ$ ,  $39.5^\circ$ ,  $47.3^\circ$ ,  $48.7^\circ$ , and  $57.6^\circ$  in adsorbent. This outcome also confirms that calcium carbonate is the main constituent in the eggshell powder (Zhang et al., 2017).

Polat and Aslan (2014) stated that the key chemical compositions of by-products of eggshell are as indicated  $\text{CaCO}_3$  as limestone by weight (94%), magnesium carbonate by weight is equivalent to 1% of the total weight, calcium phosphate by weight is equivalent to 1% of the total weight, and organic matter by weight is equivalent to 4% of the total weight. It was highlighted that the primary components of eggshells are in the form of  $\text{CaCO}_3$  and  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{CaHCO}_3^+$ , and  $\text{CaHO}^+$ . These complex ions are formed in the solution and their proportion is a function of pH or is dependent on the pH value of the medium. It was expected that any water equilibrated with the eggshell became basic confirmed with the following mechanisms (Arunlertaree et al. 2007):



(1)



(2)

As can be illustrated and seen in equation (2), the solution has become more basic due to the hydrolysis reaction of  $\text{CaCO}_3$  which gives  $\text{OH}^-$  and  $\text{Ca}^{2+}$  content of the solution is also increased. In general, sorption of divalent metal cations on metal oxides, hydroxides and oxyhydroxides is known to be promoted by increasing pH. When divalent metal cations adsorb on these materials, the cations undergo a reaction with a surface hydroxyl group. Adsorption or precipitation mechanisms involve characteristic reactions of some metals with  $\text{CaO}$  and  $\text{MgO}$  surfaces, with adsorption occurring at low concentration of metals solution, and precipitation dominating at high concentrations. Carbonates formed by  $\text{CaCO}_3$  dissolution increase the pH values in the solution and therefore may be formation of precipitate form of copper precipitate near the surface of eggshell and then these forms adsorb on the eggshell.

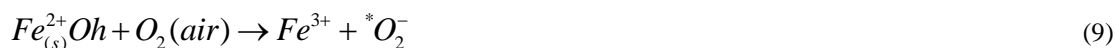
In addition, Yusuff (2019) reported the chemical composition of eggshell as follows: Silicon oxide ( $\text{SiO}_2$ ; 0.79 %); aluminium oxide ( $\text{Al}_2\text{O}_3$  ; 0.12%); total iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  ; 2.68%); magnesium oxide ( $\text{MgO}$ , 1.78 %); Calcium oxide ( $\text{CaO}$ , 86.74%), alkali oxide

(potassium oxide,  $K_2O$ , 0.09 %); phosphate ( $P_2O_5$ ; 1.21% ); sulphite ( $SO_3$  ; 0.12 %) and local organic ignition (LOI, 6.47%). Further reported in the literature such as Guru and Dash (2014) documented that eggshell is a highly well-organized structure, which comprises five structurally dissimilar layers. From the inside to the outwards, the structures include the shell membranes (inner and outer), palisade layer, mammillary layer, vertical crystal layer and cuticle. The arrangement from the inner membranes are the mineralized layer is the mammillary layer (which contain randomly orientated calcite (as  $CaCO_3$ ) crystals). These calcite crystals layers are large with a size of greater than 1 millimetres. The palisade layer makes up the majority of the calcified portion of the shell. The palisade layer is continued as the vertical crystal layer, which is a small layer immediately underneath the cuticle. The loose and viscous–elastic porous structures provide eggshell more flexibility, and improved

chemical adsorption performance. Figures 12 and 13 present scanning electron microscope and Fourier transform infrared spectra of eggshell and egg membrane. Tsai et al. (2006) reported that the results of ultimate analysis of eggshell and eggshell membrane particles revealed that the elemental contents eggshell and egg membrane are Calcium, Carbon, Hydrogen, Oxygen, Nitrogen and Sulphur. Figure 12 shows the most significant peak of intensity of eggshell particles at  $1417\text{ cm}^{-1}$ , Which is strongly associated with the presence of carbonate minerals within the eggshell matrix (Tsai et al., 2006). There are also Mo observable peaks at about  $875\text{ cm}^{-1}$  and  $712\text{ cm}^{-1}$ , these two peaks should be associated with the outplane deformation and in-plane deformation modes in the presence of calcium carbonate. The EDS results revealed that powdered eggshell contains Fe, which can be in the form of Fe,  $Fe^{2+}$  or  $Fe^{3+}$ . The composition indicated that the possible redox reactions can be summarised as follows (Zubair et al., 2020):



In the aqueous solution oxidative radicals (superoxide anions) could be created or generated through electron transfer from Fe component pf powdered eggshell to dissolved oxygen, as follows (Zubair et al., 2020):



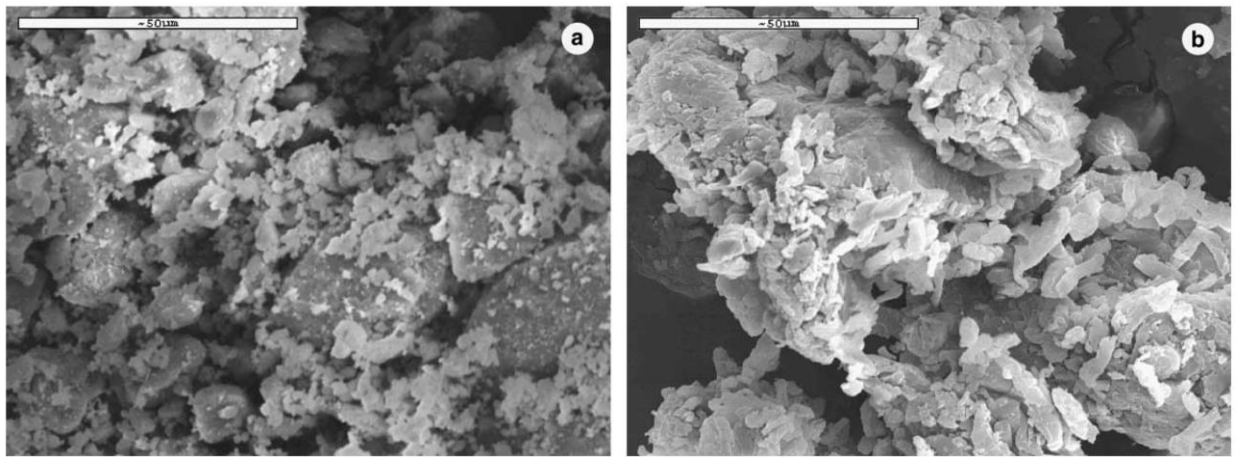


Figure 12 Scanning Electron Microscope pictures (X 1000) of eggshell, and eggshell membrane particles (Source: Tsai et al., 2006)

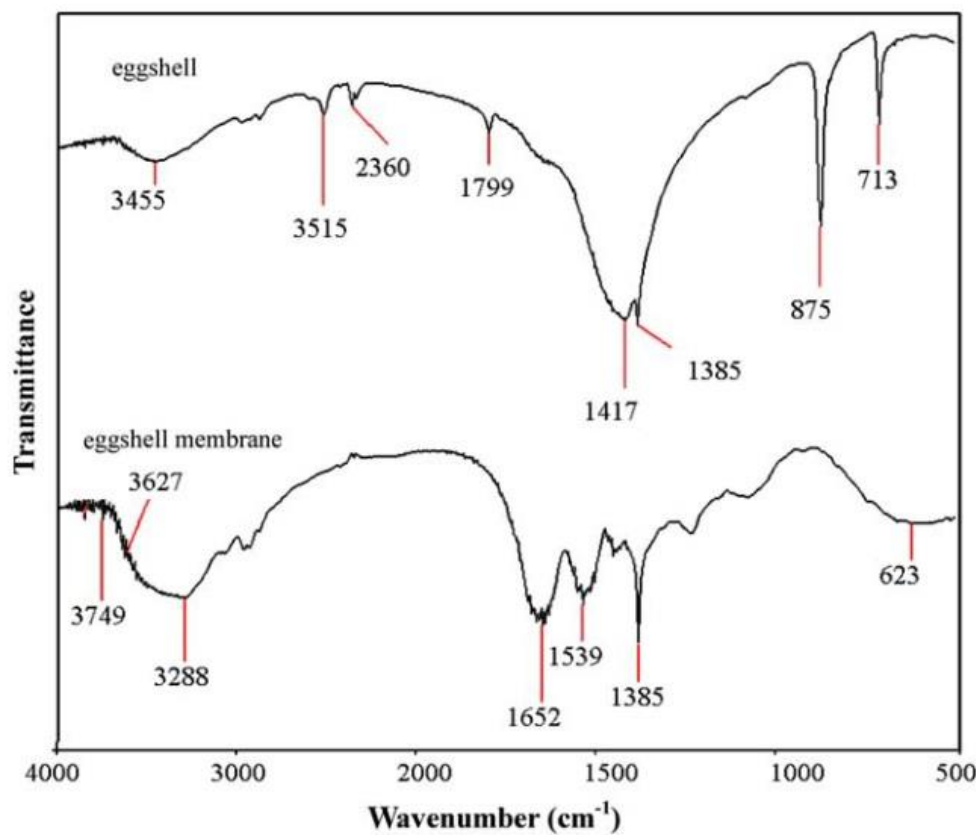


Figure 13. Fourier transform infrared spectra of eggshell and eggshell membrane particles. (Source: Tsai et al., 2006)

In conclusion, the surface redox reactions and mechanism contributed partially to arsenic reduction or removal, based on the composition of powdered eggshell can be summarized as follows (Zubair et al., 2020):





**Arsenic Adsorption Uptake Isotherm models:** The adsorption equilibrium isotherm model data were fitted to three (16 isotherm models), four (4 isotherm models) and five (1 isotherm model) parameters adsorption equilibrium isotherm models. The description of these adsorption isotherm data with these twenty-one adsorption isotherm models provides insight into the relationship between the arsenic removal and the adsorbent with the adsorption type. An adsorption equilibrium model fitting with an Model Selection criterion greater than 3.00 is considered strong, which indicates possible multilayer formation and monolayer by chemical or physical adsorption. In addition, adsorbate adsorption is more favourable for multilayer adsorption than for single-layer adsorption because of the better utilization of the heterogeneous nature of the adsorbent.

The adsorption isotherm experimental data were fitted with Redlich–Peterson, Sips, Jossens, Hill, Langmuir- Freundlich, Toth, Radke-Prausnitz, Khan, Fritz and Schhunder, Koble – Corrigan, Liu, Weber-Van Vliet, Bauder and Marczewsk-Jaroniec models with MSC greater than 3.0 ( $R^2$  greater than 0.971, Amoko et al., 2023) to establish the heterogeneity of the adsorption and to avoid limitations of an increase in adsorbate concentration that is associated with the Freundlich model (Amoko et al., 2023). The heterogeneity factors ( $\gamma$ ) for arsenic removal exceeds 1, which indicates that there is an heterogeneous interaction between the arsenic and the adsorbent (powdered eggshell). Figure 13 demonstrates the amount of arsenic adsorbed by powdered eggshell at equilibrium arsenic concentration for both synthetic and typical water. From the figure adsorption equilibrium and equilibrium concentrations for typical water were higher than adsorption equilibrium and equilibrium concentrations for synthetic water, which indicates more pollutants were removed in synthetic water than typical water.

These lower adsorption equilibrium and equilibrium concentrations for typical water can be attributed to the presence other pollutants. Lower adsorption performance in natural and typical surface water can be attributed to multicomponent nature of the water samples. These results and observation agreed with literature such as Cassol *et al.* (2014); Prosser and Franses (2001); Yu *et al.*

(1988); Simsek and Beker (2014); Cano *et al.* (2007); Hu and Do (1995); Rudisill *et al.* (1988); Oskuli *et al.* (2019); Vilardi *et al.* (2018); Gomez-Gonzalez *et al.* (2016); Largitte and Pasquier (2016); Othman *et al.* (2019); Koopal *et al.* (2020); Hu *et al.* (2020 and 2021); Chen *et al.* (2021); Yang *et al.* (2023); Zhang *et al.* (2003); Khademi *et al.* (2018) and Thirunavukkarasu and Nithya (2020). Literature reported that the presence of other pollutants influence on As(III) adsorption onto adsorbents, which may follow the order of  $\text{H}_2\text{PO}_4^-$  greater than  $\text{SO}_4^{2-}$  greater than  $\text{F}^-$  greater than  $\text{HCO}_3^{2-}$  greater than  $\text{NO}_3^-$  greater than  $\text{Cl}^-$ , and that for As(V) followed the order of  $\text{H}_2\text{PO}_4^-$  greater than  $\text{HCO}_3^{2-}$  greater than  $\text{F}^-$  greater than  $\text{SO}_4^{2-}$  greater than  $\text{NO}_3^-$  greater than  $\text{Cl}^-$ .

The high adsorption capacity of the optimal adsorbents (anthill with eggshell) in the adsorption of dye from an aqueous solution may be due to the presence of the surface functional groups, among which carboxylic (C-O and C=O) and hydroxyl (OH) groups play the main role. The major compositions in the anthill sample as an adsorbent were determined to be silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and zirconia ( $\text{ZrO}_2$ ), while the main mineral composition in eggshells was found to be calcium oxide (CaO). The high Local Organic Ignition in the raw anthill and eggshell samples is due to the presence of organic matters and moisture content. However, CaO constitutes the larger amount in an optimal adsorbent sample, followed by  $\text{SiO}_2$ . It was observed that the calcination at 823.45 °C for 3.54 h was able to transform the mixed eggshell-anthill clay into a synergetic mixed oxide structure.

Thus, the result obtained indicates that not only CaO plays a significant role in the adsorbent performance but also the other metal oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{Fe}_2\text{O}_3$ ) contained in the optimal adsorbent sample can determine the form of the molecular adsorption sites and their level of capacity. The presence of  $\text{SiO}_2$  in the composite adsorbent plays a key role in the adsorption.  $\text{SiO}_2$  is known as an inorganic adsorbent and could adsorb either positive or negative contaminant depending on the pH of the solution. Its surface contains silinol (-OH group), which can act as the centre of a



molecular adsorption during their specific interaction with adsorbates. Other mineral oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{ZrO}_2$ , also exhibit the phenomenon of electrostatic interaction. This indicates that the maximum dye adsorption capacity of the adsorbent can be attributed to the electrostatic interaction of the adsorbate with the surface  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  sites. This observation could be the reason that the adsorbent adsorbent had an improved performance in the adsorption of the Methly Blue dye compared to the adsorbent prepared only from eggshells, which has a single adsorption site ( $\text{CaO}$ ). The results and the figure established that initial concentration of arsenic and type of aqueous solution had effect on the adsorption of arsenic

#### Analysis of Effects of Selected factors on Arsenic Adsorption:

Tables 4 and 5 present effects of adsorption of nature of the solution on adsorption equilibrium and arsenic equilibrium concentration. These Table 4 revealed that adsorption equilibrium concentration and nature of the aqueous solution has significant effects on arsenic adsorption at a 95 % confidence level ( $F_{5,5} = 1.476$  and p- value of 0.3397 for adsorption equilibrium and  $F_{1,5} = 16.569$  with p-value of 0.010). These Table 5 revealed that arsenic equilibrium concentration and nature of the aqueous solution has significant effects on arsenic adsorption at a 95 % confidence level ( $F_{5,5} = 2.546$  and p- value of 0.1641 for adsorption equilibrium and  $F_{1,5} = 1865.03$  with p-value of  $1.26 \times 10^{-7}$ ).

#### Performance Evaluation of Adsorption Equilibrium Models:

The parameters (3, 4 and 5 parameters) obtained in fitting the field data in adsorption equilibrium were summarized in Tables 6 and 7. Figure 14 presents correlation between equilibrium concentrations and equilibrium properties for both synthetic wastewaters and typical water. It (Table 7) was clear that the adsorption data of Arsenic could

be best fitted with all the adsorption equilibrium models with 4-parameters (Weber-Van Vliet, Bauder, Marczewsk- Jaroniec, and Fritz and Schhunder), 5- parameters (Fritz and Schhunder) and some of the 3 parameters (Sips, Brouers- Sotolongo, Jossens, Hill, Langmuir- Freundlich, Radke-Prausnitz, Khan, Fritz and Schhunder, Koble – Corrigan, Liu and Loading ratio) isotherm based on the values of MSC of greater than 3.0 which is greater that correlation coefficient greater than 0.95 (Amoko et al., 2023) compared with that produced by the other isotherms. Tables 6 and 7 present the detail information on these adsorption isotherms performance.

With reference to the values of MSC and AIC, it was observed the adsorption equilibrium isotherm models with MSC value greater than 3.0 are as follows: 2-parameters adsorption equilibrium isotherm models are 3 out of 17 (17.65 %); 3-parameters adsorption equilibrium isotherm models are 11 out of 16 (68.75 %); 4-parameters adsorption equilibrium isotherm models are 4 out of 4 (100 %); and 5-parameters adsorption equilibrium isotherm models are 1 out of 1 (100 %). The adsorption equilibrium isotherm models with MSC value greater than 1.0 but less than 3.0 ( $3.0 < x < 1.0$ ) are as follows: 2-parameters adsorption equilibrium isotherm models are 6 out of 17 (35.29 %); 3-parameters adsorption equilibrium isotherm models are 1 out of 16 (6.25 %). The adsorption equilibrium isotherm models with MSC value less than 1.0 are as follows: 2-parameters adsorption equilibrium isotherm models are 8 out of 17 (47.06 %); 3-parameters adsorption equilibrium isotherm models are 4 out of 16 (25.00 %).

Table 4: Effects of arsenic adsorption equilibrium and Nature of Solution on arsenic adsorption

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	Statistical F-Value	Probability value	Statistical F critical at 95 % confidence level
Experiments of adsorption equilibrium	24.16338	5	4.832677	1.476454	0.339697	5.050329
Nature of Solution	54.23305	1	54.23305	16.56899	0.009629	6.607891
Error	16.36582	5	3.273165			
Total	94.76226	11				

Table 5: Effects of arsenic equilibrium concentration and Nature of Solution on arsenic adsorption

Source of Variation	Sum of Square	Degree of freedom	Mean Sum of Square	Statistical F-Value	Probability value	Statistical F critical at 95 % confidence level
Experiments of arsenic equilibrium concentration	0.04165	5	0.008329919	2.545815	0.164089	5.050329
Nature of aqueous solution	6.102373	1	6.102372773	1865.025	$1.26 \times 10^{-07}$	6.607891
Error	0.01636	5	0.003272005			
Total	6.160382	11				

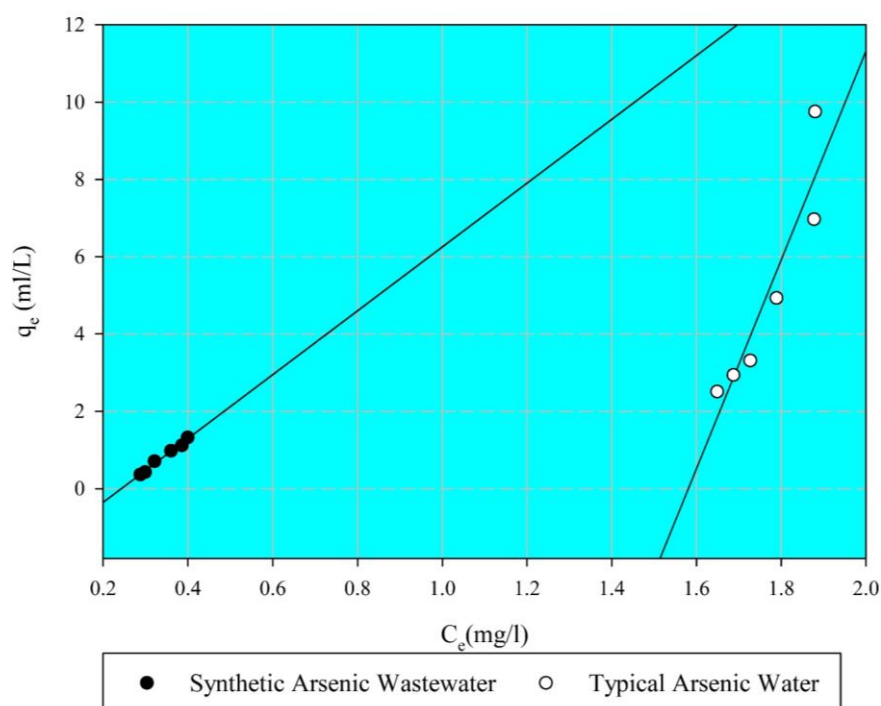


Figure 14: Correlation between adsorption equilibrium and arsenic equilibrium concentration

**Table 6:** the adsorption equilibrium properties and parameters of arsenic adsorption by powdered eggshell in typical water

Type	Name	Non- Linear Relationship	Parameters	K	$\alpha$	$\beta$	$\gamma$	q	MSC	AIC
3- Parameters	Redlich–Peterson	$q_e = \frac{\alpha_t C_e}{1 + \beta_t C_e^\gamma}$	$\alpha_t, \gamma$ and $\beta_t$	-	$6.03 \times 10^5$	$6.03 \times 10^6$	-5.89	-	1.43	15.35
	Sips	$q_e = \frac{\alpha_{ts} C_e^{\gamma_{ts}}}{1 + \beta_{ts} C_e^{\gamma_{ts}}}$	$\alpha_{ts}, \gamma_{ts}$ and $\beta_{ts}$	-	0.034	0.0002	8.23	-	2.05	11.78
	Brouers- Sotolongo	$q_e = K_{BS} \left( 1 - \exp \left( -\beta_{BS} C_e^{\alpha_{BS}} \right) \right)$	$K_{BS}, \alpha_{BS}$ and $\beta_{BS}$	3.35	2.46	3.46	-	-	-0.70	28.83
	Jossens	$C_e = \frac{q_e}{\beta_{jo}} \left( \exp \left( K_{jo} q_e^{\alpha_{jo}} \right) \right)$	$\alpha_{jo}, K_{jo},$ and $\beta_{jo},$	$-1.46 \times 10^4$	-41.68	3.52	-	-	2.194	10.94
	Hill	$q_e = \frac{K_{Hi} C_e^{\alpha_{Hi}}}{\beta_{Hi} + C_e^{\alpha_{Hi}}}$	$\alpha_{Hi}, K_{Hi},$ and $\beta_{Hi},$	$2.00 \times 10^5$	1.58	$9.13 \times 10^4$	-	-	-0.02	24.24
	Langmuir- Freundlich	$q_e = \frac{\beta_{LF} K_{LF} C_e^{\alpha_{LF}}}{1 + K_{LF} C_e^{\alpha_{LF}}}$	$\beta_{LF}, K_{LF}$ and $\alpha_{LF}$	0.008	7.24	14.89	-	-	0.66	20.15
	Toth	$q_e = \frac{K_{tt} \alpha_{tt}^{\gamma_{tt}} C_e}{\left( 1 + \alpha_{tt} C_e^{\gamma_{tt}} \right)^{\left( \frac{1}{\gamma_{tt}} \right)}}$	$K_{tt}, \alpha_{tt},$ and $\gamma_{tt}$	11.94	$1.0 \times 10^{-4}$	-	0.167	-	-0.14	<b>24.94</b>

Type	Name	Non- Linear Relationship	Parameters	K	$\alpha$	$\beta$	$\gamma$	q	MSC	AIC
		$q_e = \frac{\alpha_{tt} C_e}{\left( \beta_{tt} + C_e^{\gamma_{tt}} \right)^{\left( \frac{1}{\gamma_{tt}} \right)}}$	$\alpha_{tt}, \beta_{tt}$ and $\gamma_{tt}$	-	$4.36 \times 10^4$	$1.30 \times 10^4$	0.986	-	-0.14	24.94
	Radke-Prausnitz	$\frac{1}{q_e} = \left( \frac{\alpha_{rp}}{(C_e)} \right) + \frac{\beta_{rp}}{\left( C_e^{\gamma_{rp}} \right)}$	$\alpha_{rp}, \gamma_{rp}$ and $\beta_{rp}$	-	0.001	31.30	8.66	-	3.268	-33.71
		$q_e = \frac{K_{rp} \alpha_{rp} C_e}{\left( 1 + \alpha_{rp} C_e^{\gamma_{rp}} \right)}$	$\alpha_{rp}, \gamma_{rp}$ and $q_{rp}$	$1.41 \times 10^{-2}$	$1.4 \times 10^3$	-	-9.46	-	1.92	12.58
	Khan	$q_e = \frac{K_k \alpha_k C_e}{\left( 1 + \alpha_k C_e \right)^{\gamma_k}}$	$\alpha_k, \gamma_k$ and $K_k$	0.003	0.131	-	-42.6	-	1.96	12.34
	Fritz and Schhunder	$q_e = \frac{K_{fs} \alpha_{fs} C_e^{\gamma_{fs}}}{\left( 1 + \alpha_{fs} C_e^{\gamma_{fs}} \right)}$	$\alpha_{fs}, \gamma_{fs}$ and $K_{fs}$	26.58	$1.0 \times 10^{-3}$	-	12.37	-	1.97	1.23
	Frumkin	$K_{Fm} C_e = \beta_{Fm} \left( \frac{-\alpha_{Fm} \beta_{Fm}}{1 - \beta_{Fm}} \right);$ $\beta_{Fm} = 1 - \frac{C_e}{C_0}$	$K_{Fm}, \alpha_{Fm}$ and $\beta_{Fm}$	0.208	-1.666	0.372	-	-	-2.06	31.93

Type	Name	Non- Linear Relationship	Parameters	K	$\alpha$	$\beta$	$\gamma$	q	MSC	AIC
	Koble - Corrigan	$q_e = \frac{\alpha_{kc} C_e^{\gamma_{kc}}}{\left(1 + \beta_{kc} C_e^{\gamma_{kc}}\right)}$	$\alpha_{kc}, \beta_{kc} \text{ and } \gamma_{kc}$	-	0.211	-0.072	3.69	-	2.09	11.58
	Liu	$q_e = \frac{\left(K_{li} (C_e \beta_{li})^{\frac{1}{\alpha_{li}}}\right)}{\left(1 + (C_e \beta_{li})^{\frac{1}{\alpha_{li}}}\right)}$	$K_{li}, \beta_{li} \text{ and } \alpha_{li}$	558.12	10.22	0.353	-	-	2.022	11.97
	Loading ratio	$q_e = \frac{K_{Lr} (\beta_{Lr} C_e)^{\left(\frac{1}{\alpha_{Lr}}\right)}}{1 + (\beta_{Lr} C_e)^{\left(\frac{1}{\alpha_{Lr}}\right)}}$	$K_{Lr}, \beta_{Lr} \text{ and } \alpha_{Lr}$	695.3	0.098	0.395	-	-	2.022	11.97
4- Parameters	Weber-Van Vliet	$C_e = K_{wvv} Q_e^{(\alpha_{wvv} \beta_{wvv} + \gamma_{wvv})}$	$K_{wvv}, \alpha_{wvv}, \beta_{wvv} \text{ and } \gamma_{wvv}$	1.521	3.86	0.11	-0.33	-	8.63	-32.22
	Bauder	$q_e = \left( \frac{(K_{bu}) \beta_{bu} C_e^{1+\alpha_{bu}+\gamma_{bu}}}{1 + (C_e^{1+\alpha_{bu}})} \right)$	$K_{bu}, \beta_{bu}, \gamma_{bu} \text{ and } \alpha_{bu}$ $1 + \beta_{bu} + \alpha_{bu} < 1$ And $1 + \beta_{bu} < 1$	$8.9 \times 10^5$	10.16	9.87	0.010	-	2.02	11.961
	Marczewsk- Jaroniec	$q_e = K_{msj} \left( \frac{(C_e \gamma_{msj})^{\alpha_{msj}}}{1 + (C_e \gamma_{msj})^{\alpha_{msj}}} \right)^{\left( \frac{\beta_{msj}}{\alpha_{msj}} \right)}$	$K_{msj}, \gamma_{msj}, \alpha_{msj} \text{ and } \beta_{msj}$	$9.51 \times 10^2$	1.95	$5.75 \times 10^2$	4.41	-	1.98	12.21
	Fritz and Schhunder	$q_e = \left( \frac{K_{FS4} (C_e)^{\alpha_{FS4}}}{1 + \gamma_{FS4} (C_e)^{\beta_{FS4}}} \right)$	$K_{FS4}, \gamma_{FS4}, \alpha_{FS4} \text{ and } \beta_{FS4}$	1.05	10.96	0.83	74.0	-	1.98	12.21
5 parameters	Fritz- Schhunder	$q_e = \left( \frac{q_{fs5} \gamma_{fs5} (C_e)^{\alpha_{fs5}}}{1 + K_{fs5} (C_e)^{\beta_{fs5}}} \right)$	$q_{fs5}, K_{fs5}, \alpha_{fs5}, \gamma_{fs5} \text{ and } \beta_{fs5}$	4.61	10.34	0.23	0.723	0.11	2.02	11.96



**Table 7:** the adsorption equilibrium properties and parameters of arsenic adsorption by powdered eggshell in synthetic water

Type	Name	Non- Linear Relationship	Parameters	K	$\alpha$	$\beta$	$\gamma$	q	MSC	AIC
3- Parameters	Redlich–Peterson	$q_e = \frac{\alpha_t C_e}{1 + \beta_t C_e^\gamma}$	$\alpha_t, \gamma$ and $\beta_t$	-	2.48	0.44	20.94	-	0.35	-1.92
	Sips	$q_e = \frac{\alpha_{ts} C_e^{\gamma_{ts}}}{1 + \beta_{ts} C_e^{\gamma_{ts}}}$	$\alpha_{ts}, \gamma_{ts}$ and $\beta_{ts}$	-	32.5	-0.04	3.49	-	3.24	-19.2
	Brouers- Sotolongo	$q_e = K_{BS} \left( 1 - \exp(-\beta_{BS} C_e^{\alpha_{BS}}) \right)$	$K_{BS}, \alpha_{BS}$ and $\beta_{BS}$	1.50	339.97	5.659	-	-	3.66	-21.73
	Jossens	$C_e = \frac{q_e}{\beta_{jo}} \left( \exp(K_{jo} q_e^{\alpha_{jo}}) \right)$	$\alpha_{jo}, K_{jo}$ , and $\beta_{jo}$ ,	-5.926	0.130	0.007	-	-	6.793	-40.56
	Hill	$q_e = \frac{K_{Hi} C_e^{\alpha_{Hi}}}{\beta_{Hi} + C_e^{\alpha_{Hi}}}$	$\alpha_{Hi}, K_{Hi}$ , and $\beta_{Hi}$ ,	18.57	3.661	0.454	-	-	3.280	-19.49
	Langmuir- Freundlich	$q_e = \frac{\beta_{LF} K_{LF} C_e^{\alpha_{LF}}}{1 + K_{LF} C_e^{\alpha_{LF}}}$	$\beta_{LF}, K_{LF}$ and $\alpha_{LF}$	1581.0	6.96	1.75	-	-	3.77	-22.4
	Toth	$q_e = \frac{K_{tt} \alpha_{tt}^{\gamma_{tt}} C_e}{\left( 1 + \alpha_{tt} C_e^{\gamma_{tt}} \right)^{\left( \frac{1}{\gamma_{tt}} \right)}}$	$K_{tt}, \alpha_{tt}$ , and $\gamma_{tt}$	1.48	1.05	-	10.47	-	0.35	-1.92

Type	Name	Non- Linear Relationship	Parameters	K	$\alpha$	$\beta$	$\gamma$	q	MSC	AIC
		$q_e = \frac{\alpha_{tt} C_e}{\left(\beta_{tt} + C_e^{\gamma_{tt}}\right)^{\left(\frac{1}{\gamma_{tt}}\right)}}$	$\alpha_{tt}, \beta_{tt}$ and $\gamma_{tt}$	-	2.48	0.995	14.94	-	0.352	-1.92
	Radke-Prausnitz	$\frac{1}{q_e} = \left(\frac{\alpha_{rp}}{(C_e)}\right) + \frac{\beta_{rp}}{\left(C_e^{\gamma_{rp}}\right)}$	$\alpha_{rp}, \gamma_{rp}$ and $\beta_{rp}$	-	18.17	-19.47	0.916	-	3.24	-19.2
		$q_e = \frac{K_{rp} \alpha_{rp} C_e}{\left(1 + \alpha_{rp} C_e^{\gamma_{tt}}\right)}$	$\alpha_{rp}, \gamma_{rp}$ and $q_{rp}$	32.68	1413.8	-	-2.5	-	1.06	3.09
	Khan	$q_e = \frac{K_k \alpha_k C_e}{\left(1 + \alpha_k C_e\right)^{\gamma_k}}$	$\alpha_k, \gamma_k$ and $K_k$	0.004	7.11	-	-3.52	-	3.18	-18.9
	Fritz and Schhunder	$q_e = \frac{K_{fs} \alpha_{fs} C_e^{\gamma_{fs}}}{\left(1 + \alpha_{fs} C_e^{\gamma_{fs}}\right)}$	$\alpha_{fs}, \gamma_{fs}$ and $K_{fs}$	15.458	2.772		3.696		3.289	-19.54
	Frumkin	$K_{Fm} C_e = \beta_{Fm} \left(\frac{-\alpha_{Fm} \beta_{Fm}}{1 - \beta_{Fm}}\right);$ $\beta_{Fm} = 1 - \frac{C_e}{C_0}$	$K_{Fm}, \alpha_{Fm}$ and $\beta_{Fm}$	0.238	-1.331	0.236			-5.61	8.450

Type	Name	Non- Linear Relationship	Parameters	K	$\alpha$	$\beta$	$\gamma$	q	MSC	AIC
	Koble - Corrigan	$q_e = \frac{\alpha_{kc} C_e^{\gamma_{kc}}}{\left(1 + \beta_{kc} C_e^{\gamma_{kc}}\right)}$	$\alpha_{kc}, \beta_{kc}$ and $\gamma_{kc}$	-	2743.3	1567.9	6.95	-	3.77	-22.42
	Liu	$q_e = \frac{\left(K_{li} (C_e \beta_{li})^{\frac{1}{\alpha_{li}}}\right)}{\left(1 + (C_e \beta_{li})^{\frac{1}{\alpha_{li}}}\right)}$	$K_{li}, \beta_{li}$ and $\alpha_{li}$	1.747	6.963	2.833	-	-	3.770	-22.42
	Loading ratio	$q_e = \frac{K_{Lr} (\beta_{Lr} C_e)^{\left(\frac{1}{\alpha_{Lr}}\right)}}{1 + (\beta_{Lr} C_e)^{\left(\frac{1}{\alpha_{Lr}}\right)}}$	$K_{Lr}, \beta_{Lr}$ and $\alpha_{Lr}$	1.75	0.144	2.88	-	-	3.77	-22.4
4- Parameters	Weber-Van Vliet	$C_e = K_{wvv} Q_e^{(\alpha_{wvv} \beta_{wvv} + \gamma_{wvv})}$	$K_{wvv}, \alpha_{wvv}, \beta_{wvv}$ and $\gamma_{wvv}$	0.368	4.391	0.125	-0.29	-	3.033	-23.42
	Bauder	$q_e = \left( \frac{(K_{bu}) \beta_{bu} C_e^{1+\alpha_{bu}+\gamma_{bu}}}{1 + (C_e^{1+\alpha_{bu}})} \right)$	$K_{bu}, \beta_{bu}, \gamma_{bu}$ and $\alpha_{bu}$ $1 + \beta_{bu} + \alpha_{bu} < 1$ And $1 + \beta_{bu} < 1$	890178.2	2.069	9.872	8.774	-	4.092	-24.36
	Marczewsk- Jaroniec	$q_e = K_{msj} \left( \frac{(C_e \gamma_{msj})^{\alpha_{msj}}}{1 + (C_e \gamma_{msj})^{\alpha_{msj}}} \right)^{\left( \frac{\beta_{msj}}{\alpha_{msj}} \right)}$	$K_{msj}, \gamma_{msj}, \alpha_{msj}$ and $\beta_{msj}$	0.528	18.5	15.91	3.52	-	4.25	-25.28
	Fritz and Schhunder	$q_e = \left( \frac{K_{FS4} (C_e)^{\alpha_{FS4}}}{1 + \gamma_{FS4} (C_e)^{\beta_{FS4}}} \right)$	$K_{FS4}, \gamma_{FS4}, \alpha_{FS4}$ and $\beta_{FS4}$	389.72	5.12	3.123	29.94	-	3.43	-20.36
5 parameters	Fritz- Schhunder	$q_e = \left( \frac{q_{fs5} \gamma_{fs5} (C_e)^{\alpha_{fs5}}}{1 + K_{fs5} (C_e)^{\beta_{fs5}}} \right)$	$q_{fs5}, K_{fs5}, \alpha_{fs5},$ $\gamma_{fs5}$ and $\beta_{fs5}$	0.877	3.50	15.91	14.79	2.21	3.24	-19.24

## Conclusion

With reference to the findings it can be concluded that major elemental components of the powdered eggshells are aluminium (between 1.25 and 7.58 % of the adsorbent as aluminium), Calcium (between 3.7 and 10.12% of the adsorbent as calcium), Silicon (between 11.15 and 25.62 % of the adsorbent as silicon), Carbon (between 0.00 and 27.75% of the adsorbent as carbon) and oxygen (between 48.75 and 58.13% of the adsorbent as oxygen) had the highest weight percentages. There is a fair distribution of constituents of eggshell with a marked absence of several segregation in the SEM pictures. powdered eggshells removed arsenic from aqueous solutions, the removal rate was affected by the nature of the water and 5 and 4 parameters of adsorption models were effective in the description of arsenic removal by powdered eggshell. the adsorption data of Arsenic could be best fitted with all the adsorption equilibrium models with 4-parameters (Weber-Van Vliet, Bauder, Marczewsk- Jaroniec, and Fritz and Schhunder), 5- parameters (Fritz and Schhunder) and some of the 3 parameters (Sips, Brouers- Sotolongo, Jossens, Hill, Langmuir- Freundlich, Radke-Prausnitz, Khan, Fritz and Schhunder, Koble – Corrigan, Liu and Loading ratio) isotherm based on the values of MSC of greater than 3.0 which is greater that correlation coefficient greater than 0.95.

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## Abbreviations and Symbols

R is the gas constant ( $8.31 \text{ mol}^{-1} \text{ K}^{-1}$ ); T is the absolute temperature (K);  $q_e$  is the adsorption capacity of the adsorbent at equilibrium (mg/g);  $C_0$  is the initial concentration of arsenic in the aqueous solution (mg/l);  $C_e$  is the final concentration of arsenic in the aqueous solution at equilibrium (mg/l); M is the mass of the adsorbent added (g);  $\Gamma$  is the Gamma function symbol; exp or Exp is the exponential and V is the volume of the water sample utilised (300ml = 0.30 litres).  
 k is the statistical isotherm parameter for the mass of the pollutant per unit mass of the adsorbent (mg/g)  
 $k_p$  is the isotherm constant for the linear model for the mass of the pollutant per unit mass of the adsorbent (mg/g)  
 $q_e$  is the equilibrium solid-phase concentration of sorbate t (mg/mg)  
 $\alpha_L$  and  $\beta_L$  are the Langmuir adsorption constant (L/mg) and Langmuir isotherm parameter (mg/g) respectively  
 $K_f$  and  $\alpha_f$  are the Freundlich isotherm exponents for pollutant mass per unit mass of the adsorbent (g/mg) and Freundlich isotherm parameter for the volume of the solution per unit mass of the pollutant (L/mg) respectively  
 $K_H$  and  $\alpha_H$  are Hasley's isotherm parameters for pollutant mass per unit mass of the adsorbent and for the volume of the solution per unit mass of the pollutant respectively  
 $K_m$  and  $\alpha_m$  are constant for activated sludge model as volume of the solution per unit mass of the pollutant) and exponential constant for activated sludge model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{Hf}$  and  $\alpha_{Hf}$  are isotherm parameters for Halsey C (Rangabhashiyum *et al.*, 2014) as volume of the solution per unit mass of the pollutant) and exponential constant for Halsey C model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{Hf}$  and  $\alpha_{Hf}$  are isotherm parameters for Halsey B (Hamdaoui and Naffrechous, 2007) as volume of the solution per unit mass of the pollutant) and exponential constant for Halsey B model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{LV}$  and  $\alpha_{LV}$  are isotherm parameters for Langmuir — Vageler as the volume of the solution per unit mass of the pollutant) and exponential constant for the Langmuir — Vagel model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{FH}$  and  $\alpha_{FH}$  are isotherm parameters for Flory — Huggins as volume of the solution per unit mass of the pollutant) and exponential constant for the Flory — Huggins model as pollutant mass per unit mass of the adsorbent respectively  
 $K_k$  and  $\alpha_k$  are isotherm parameters for Kiselev as volume of le solution per fruit mass of the pollutant) and exponential constant for Kiselev model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{Hd}$  and  $\alpha_{Hd}$  are isotherm parameters for Hill-de Boer as volume of the solution per unit mass of the pollutant) and exponential constant for Hill-de Boer model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{FG}$  and  $\alpha_{FG}$  are isotherm parameters for Folwer — Guggenhiem as volume of the solution per unit mass of the pollutant) and exponential constant for Folwer — Guggenhiem model as pollutant mass per unit mass of the adsorbent respectively  
 $K_E$  and  $\alpha_E$  are isotherm parameters for Elovich as the volume of the solution per unit mass of the pollutant) and exponential constant for Elovich model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{jn}$  and  $\alpha_{jn}$  are isotherm parameters for Jovanovic the volume of the solution per unit mass of the pollutant) and exponential constant for Jovanovic model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{fth}$  and  $\alpha_{fth}$  are isotherm parameters for Frenkel- Halsey- Hill the volume of the solution per unit mass of the pollutant) and exponential constant for Frenkel- Halsey- Hill model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{hj}$  and  $\alpha_{hj}$  are isotherm parameters for Harkin Jura A the volume of the solution per unit mass of the pollutant) and exponential constant for Harkin Jura A model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{hj}$  and  $\alpha_{hj}$  are isotherm parameters for Harkin Jura B the volume of the solution per unit mass of the pollutant) and exponential constant for Harkin Jura B model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{rw}$  and  $\alpha_{rw}$  are isotherm parameters for Ruthven and Wong the volume of the solution per unit mass of the pollutant) and exponential constant for Ruthven and Wong model as pollutant mass per unit mass of the adsorbent respectively  
 $K_{si}$  and  $\alpha_{si}$  are isotherm parameters for Sheindorf *et al.* (1983), the volume of the solution per unit mass of the pollutant) and exponential constant for Sheindorf *et al.* (1983), model as pollutant mass per unit mass of the adsorbent respectively  
 $\alpha_{mLB}$  and  $\beta_{mLB}$  are isotherm parameters for Langmuir, Bulter and Ockrent, Schwlb, Markham and Benton, Moriguch and Kaneniwa as volume of the solution per unit mass of the pollutant) and exponential constant for Langmuir, Bulter and Ockrent, Schwlb, Markham and Benton, Moriguch and Kaneniwa model as pollutant mass per unit mass of the adsorbent respectively  
 $\beta_{LF}$ ,  $K_{LF}$  and  $\alpha_{LF}$  are isotherm parameters for Langmuir- Freundlich isotherm exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the adsorbent (mg/g) and the mass of the pollutant per unit mass of the adsorbent (mg/g), respectively  
 $\alpha_t$ ,  $\beta_t$ , and  $\gamma_t$  are the Redlich–Peterson isotherm exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the adsorbent (mg/g) and the mass of the pollutant per unit mass of the adsorbent (mg/g), respectively  
 $\alpha_{fs}$ ,  $\gamma_{fst}$  and  $q_{mfs}$  are the Fritz and Schhunder's isotherm parameters for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the adsorbent (mg/g) and the mass of the pollutant per unit mass of the adsorbent (mg/g), respectively  
 $\alpha_k$ ,  $\gamma_k$  and  $q_{mk}$  are the Khan's isotherm parameters for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the adsorbent (mg/g) and the mass of the pollutant per unit mass of the adsorbent (mg/g), respectively

$\alpha_{kc}$ ,  $\beta_{kc}$  and  $\gamma_{kc}$  are the Koble-Corrigan's isotherm parameters for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$\alpha_{rp}$ ,  $\gamma_{rp}$  and  $q_{rp}$  are the Radke-Prausnitz's isotherm parameters for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$\alpha_{ts}$ ,  $\beta_{ts}$  and  $\gamma_{ts}$  are the Sips isotherm parameters for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$\alpha_{tt}$ ,  $\beta_{tt}$  and  $\gamma_{tt}$  are the Toth isotherm parameters for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$q_m$ ,  $\alpha_{tt}$  and  $\gamma_{tt}$  are the Toth isotherm parameters for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$q_m$ ,  $K_{LF}$  and  $K_i$  are the Langmuir – Freundlich isotherm constants for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$q_{mL}$ ,  $b_{L1}$  and  $k_i$  are the Loading ratio's isotherm parameter for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{md}$ ,  $\alpha_{md}$  and  $\varepsilon$  are the Dubinin-Radushkevich's isotherm parameters for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{mRu}$ ;  $\alpha_{mRu}$  and  $\gamma_{mRu}$  are the Ruthven for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$\alpha_{mLRP}$ ,  $\gamma_{mLRP}$  and  $\beta_{mLRP}$  are the Redlich–Peterson for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$\alpha_{mFS}$ ;  $\beta_{mFS}$  and  $\gamma_{mFS}$  are the Yon and Turnock for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$\alpha_{mFS}$ ;  $\beta_{mFS}$  and  $\gamma_{mFS}$  are the Fritz and Schhunder for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{scjf}$ ;  $\beta_{scjf}$  and  $\gamma_{scjf}$  are the Single Component Jovanovic -Freundlich for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{BS}$ ,  $\alpha_{BS}$  and  $\beta_{BS}$  are isotherm parameters for Brouers- Sotolongo isotherm exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{wvv}$ ,  $\alpha_{wvv}$ ,  $\beta_{wvv}$  and  $\gamma_{wvv}$  are isotherm parameters for Weber-Van Vliet isotherm exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g), exponents for the volume of the solution per unit mass of the pollutant (L/mg) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{bu}$ ,  $\beta_{bu}$ ,  $\gamma_{bu}$  and  $\alpha_{bu}$  are isotherm parameters for Bauder isotherm exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g), exponents for the volume of the solution per unit mass of the pollutant (L/mg) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{msj}$ ,  $\gamma_{msj}$ ,  $\alpha_{msj}$  and  $\beta_{msj}$  are isotherm parameters for Marczewsk- Jaroniec isotherm exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g), exponents for the volume of the solution per unit mass of the pollutant (L/mg) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{FS4}$   $\gamma_{FS4}$ ,  $\alpha_{FS4}$  and  $\beta_{FS4}$  are isotherm parameters for Fritz- Schhunder isotherm exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$q_{fs5}$ ,  $K_{fs5}$ ,  $\alpha_{fs5}$ ,  $\gamma_{fs5}$  and  $\beta_{fs5}$  are isotherm parameters for Fritz- Schhunder isotherm exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$  and  $q_m$  are isotherm parameters for Four parameters' isotherm parameter exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{mjs2}$ ;  $K_{mjs1}$ ;  $\beta_{mjs1}$  and  $\beta_{mjs2}$  are isotherm parameters for Jain and Snoeyink exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{mej2}$ ;  $\gamma_{mej1}$   $K_{mej1}$ ;  $\beta_{mej1}$   $\gamma_{mej2}$  and  $\beta_{mej2}$  are isotherm parameters for Extended Jovanovic -Freundlich exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{mf2}$ ;  $\gamma_{mf1}$   $K_{mf1}$ ;  $\beta_{mf1}$   $\gamma_{mf2}$  and  $\beta_{mf2}$  are isotherm parameters for Extended Langmuir -Freundlich exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively

$K_{me2}$ ;  $K_{me1}$ ;  $\beta_{me1}$  and  $\beta_{me2}$  are isotherm parameters for Extended Langmuir exponents for the volume of the solution per unit mass of the pollutant (L/mg); the mass of the pollutant per unit mass of the absorbent ( mg/g) and the mass of the pollutant per unit mass of the absorbent (mg/g), respectively