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Linear and Non-Linear of 2-Parameters Adsorption Equilibrium Isotherm Models of Synthetic Arsenic Wastewaters

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ABSTRACT

Contamination of groundwater and surface water with arsenic (Asic) has become emerging health and environmental problem around the world. This problem has received significant attention amongst scientists for the development of new adsorbents to remediate Asic -contaminated water. The ability of the immobilized powdered eggshell (Poes), as adsorbent, to remove Asic was studied under batch conditions. Equilibrium data were analysed using non-linear and linearized two-parameter adsorption isotherms models (Langmuir, Freundlich, Elovich, Flory–Huggins, Temkin, Frenkel- Hasley- Hill; Langmuir- Vageler, Hill-de Boer, Kiselev, Fowler- Guggenheim, Dubinin – Radushkevich, Jovanovic, Harkins–Jura and Halsey). The performance of adsorption equilibrium isotherm models was evaluated statistically using the following analysis of variance (ANOVA), model of' selection criterion (MSC), Coefficient of Determination (CD), Correlation coefficient (R) and Akaike Information Criterion (AIC). The study revealed that for non-linear equilibrium isotherm models, Freundlich (0.986 and 3.906) > Fowler—Guggenheim (0.996 and 5.176) and Hasley (0.986 and 3.906) performed well in predicting experimental data-based on the magnitudes of R and MSC. The linearized adsorption equilibrium isotherm models, Dubinin – Radushkevich (0.993 and 4.621) < Temkin (0.994 and 4.701) < Kiselev (0.9999 and 8.856). These three models are the best isotherm models for Asic adsorption onto Poes. It was concluded that Poes particles contain numerous materials that aid Asic adsorption. Based on the performance indicators and to ensure reliable results of adsorption equilibrium data analysis through the adsorption isotherm models, it is necessary that these data sets should be evaluated by both non-linear and linear regression analyses.

1. Introduction

Many systems have been established for the A_{sic} removal from raw water and industrial wastewater (Vishali and Mullai, 2016). The techniques include electrochemical degradation, ion exchange, adsorption, coagulation and flocculation, advanced oxidation, membrane filtration, and many others (Vishali and Mullai, 2016; Shakoor *et al.,* 2018; Wang *et al.,* 2023a). With the exemption of adsorption, the other practices have some disadvantages which include higher sludge formation, higher operational cost, or ineffectiveness of a broad range of A_{sic} removal are identified in the above techniques, making adsorption among the best alternative technology (Attar *et al.,* 2018; Adekunbi *et al.,* 2019; Suwannahong *et al.,* 2021; Guo *et al.,* 2023, Wang *et al.,* 2023b). Adsorption techniques are capable of removing pollutants from raw water and industrial wastewater (El-Khaiary and Malash, 2011; Al-Ghouti and Da'ana, 2020; El Hammari *et al.,* 2023). The adsorption technique has many advantages as being cost-effective, easy to operate, simple mechanism, and insensitive to pollutants (Vishali and Mullai, 2016; Shakoor *et al.,* 2018; Al-Ghouti and Da'ana, 2020; Liu *et al.,* 2023a). Many researchers have reported different types of adsorbents for the removal of pollutants from aqueous solutions. These adsorbents include commercial activated carbon, carbon material made from solid wastes and coal-based sorbents like rice husk, waste newspaper, date pits, coir pith, sugarcane bagasse, neem sawdust, orange and cassava peel, banana pith, cotton waste, natural materials like clay, glass powder, zeolite, and silica (Vishali and Mullai, 2016; Shakoor *et al.,* 2018; Dada *et al.,* 2019; 2021). Biomasses as adsorbents include bacteria, fungi, and yeast, both living and dead cells are used as

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adsorbents for the treatment of raw water and industrial wastewater. Researchers have observed in their studies the capacity of the adsorbents to remove A_{sic} from surface and groundwater (Shakoor *et al.,* 2018; Attar *et al.,* 2018; Lopez-Luna *et al.,* 2019). In applications, equilibrium isotherms experiments are essential tools in use for assessing the performance of new adsorbents or applications of materials in surface and groundwater treatment (Daus *et al.,* 2004; Singh and Pant, 2004, Shih, 2005, El-Khaiary and Malash, 2011; An *et al.,* 2011; Millar *et al.,* 2015; Analia *et al.,* 2019; Al-Ghouti and Da'ana, 2020; Outram *et al.,* 2021). Equilibria data are often fitted to a range of mathematical models to interpret the removal behaviour of treatment media (El-Khaiary and Malash, 2011; Millar *et al.,* 2015; Kumar and Sivanesan, 2006; Al-Ghouti and Da'ana, 2020; Outram *et al.,* 2021). Figure 1 presents some of the adsorption equilibrium isotherms models and their categories based on the number of variables in the equation. One of the principal functions of isotherm equilibrium and kinetics modelling is to estimate the maximum adsorbate loading (Millar *et al.,* 2015; El-Khaiary and Malash, 2011; Al-Ghouti and Da'ana, 2020; Outram *et al.,* 2021). The adsorbate loading offers researchers and engineers a means of comparing the differences between experimental situations, water quantity and quality, and materials with regard to A_{sic} removal performance. The problem with this method of performance evaluation is that the loading estimates are susceptible to errors that originated from mathematical factors and experimental design (Millar *et al.,* 2015; El-Khaiary and Malash, 2011; Al-Ghouti and Da'ana, 2020; Outram *et al.,* 2021). The uncertainty of these estimates is rarely assessed or acknowledged in the majority of published literature. Furthermore, the impacts of experimental design, such as repeats and equipment selection, on loading estimates are not quantified. Factually, batch adsorption equilibrium isotherms experiments were interpreted through non-linearized and linearized expressions of the appropriate adsorption or ion exchange models. A deficiency of computing facilities was the initial primary reason for the derivation of linearized adsorption models, yet nowadays numerous publications still utilize this method to contempt the accessibility of powerful computational services. Millar *et al*. (2015) and Mohammad *et al.,* (2019; 2020) demonstrated that the linearized approach introduces inaccuracies in the fitted models, whereby lower goodness of fit and overestimated loading and constant values were observed. El-Khairy and Malash (2011) emphasised the incorrectness of linearizing adsorption equilibrium isotherm models due to deviations in the error structure of the data. Several documents illustrated the variation in outcomes between three linearized forms of the Langmuir adsorption model using a single set of sorption data (Hamadaoui and Naffrechoux 2007; El-Khaiary and Malash, 2011; Millar *et al.,* 2015; Al-Ghouti and Da'ana, 2020; Outram *et al.,* 2021). It has been recommended that the explanation of adsorption isotherm data through linearized and least squares analysis using GAUSS, Microsoft Excel Solver, Maple, Sigma Plot, Mathcad, Dataplot, MATLAB, Origin, Ardnial, Mathematica, Freemat, Flepro and SPSS functionality can significantly increase the robustness of equilibrium isotherm data analysis (Millar *et al.,* 2015; El-Khaiary and Malash, 2011; Adekunbi *et al.,* 2019; Al-Ghouti and Da'ana, 2020; Outram *et al.,* 2021; Suwannahong *et al.,* 2021). It has been reported that the linearized and least squares methods built into these computer functionalities were to solve several variables in the adsorption models (Song *et al.,* 2006; Kumar *et al.,* 2004; Al-Ghouti and Da'ana, 2020; Outram *et al.,* 2021). The focal focus of this paper is to establish the accurateness of linearized and non-linear 2-parameter adsorption equilibrium models with specific consideration to the utilization of least squares and Microsoft Excel Solver with a critical aim of attaining sustainable development goals 3 (good health and well-being, Liu *et al.,* 2023b), 6 (clean water and sanitation); 14 (life below water) and 15 (life on land, Dalampira and Nastis, 2019).

2. Materials and Methods

2.1. Data Collection and analysis

As a continuation of our previous research and studies (Obijole *et al.,* 2022; Oke *et al.,* 2008), powdered eggshells (P_{oes}) were utilised as adsorbents for A_{sic} removal or reduction from synthetic wastewaters. The microstructure was examined utilising a scanning electron microscope (Carl Zeiss Smart Evo 10). This was conducted with the aid of the backscattered electron detector, providing compositional contrast and the secondary electron detector providing topographical information. Energy Dispersive Spectroscopy (EDS) was used to confirm the elemental composition of identified phase while examinations were conducted in the high vacuum mode. Adsorption equilibrium isotherms were evaluated as follows (Amoko *et al.,* 2015; Obijole *et al.,* 2022; Adekunbi *et al.,* 2019; Oke *et al.,* 2008):

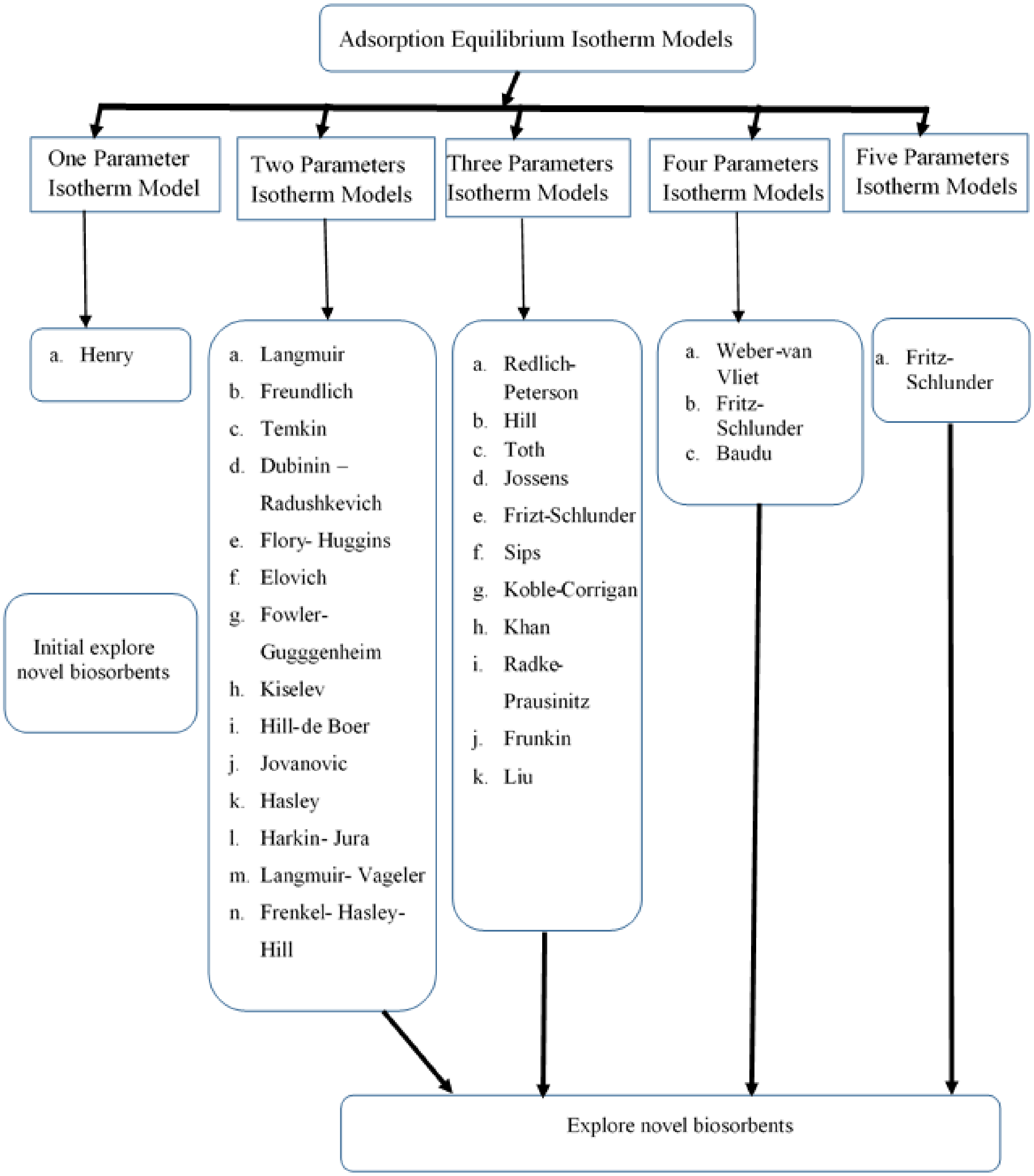


Figure 1. The significance of adsorption equilibrium isotherm models in use to establish performance of adsorbents (Adopted from Rangabhashiyam et al., 2014)

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

Where: q_e is the adsorption capacity of the P_{oes} at equilibrium (mg/g), C_0 is initial the concentration of A_{sic} in the solution (mg/l), C_e is the experimental concentration of A_{sic} in the solution at equilibrium (mg/l), M is the mass of adsorbent (P_{oes}) added (g) and V is the volume of prepared A_{sic} solution used.

The concentration of A_{sic} in both raw and treated water samples was determined using procedures as stated in Standard Methods (APHA, 2015; van Loosdrecht *et al.,* 2016). Parameters of standard adsorption equilibrium isotherm models (mainly 2–parameters, Table 1) were evaluated using Microsoft Excel Solver (MES). These adsorption equilibrium isotherms models were utilised to compute adsorption capacity and the adsorption capacity was evaluated using standard statistical methods (Model Selection Criterion (MSC), Coefficient of Determination, Akaike Information Criterion, and Correlation Coefficient). Microsoft Excel Solver was utilised for the evaluation of the standard adsorption isotherm's variables based on the accuracy and accessibility at no additional installation and operational costs. The procedure used for the Microsoft Excel solver can be summarized as follows (Adekunbi *et al.,* 2019; Umaru *et al.,* 2021; Suwannahong *et al.,* 2021):

a) Excel solver was added to Microsoft Excel,

b) Target of the numerical analysis, $\left(\left(q_p - q_t\right)^2 = 0\right)$,

   operation and changing cells were set, Where; q_p is the experimental adsorption capacity and q_t is the calculated adsorption capacity using the adsorption equilibrium isotherms; and

c) Microsoft Excel Solver was allowed to iterate at 200 iterations with 0.005 tolerance (Figure 2).

MSC indicates higher accuracy, validity and a good fit of the methods. MSC was computed using equation (2) as follows (Amoko *et al.,* 2015; Adekunbi *et al.,* 2019; Umaru *et al.,* 2021; Suwannahong *et al.,* 2021):

$$MSC = \ln\left(\frac{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y}_{obs}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2}\right) - \frac{2p}{n} \tag{2}$$

Where, Y_{obsi} is the A_{sic} concentrations from the experimental study; $\overline{Y}_{obs}$ is the average A_{sic} concentrations from the experimental study; p is the total number of fixed parameters to be estimated in the methods; n is the total number of A_{sic} concentrations calculated, and Y_{cali} is the A_{sic} concentration calculated using the methods. The coefficient of determination (CD) can be interpreted as the proportion of expected data variation that can be explained by the obtained data. Higher values of CD indicate higher accuracy, validity and good fitness of the device. CD and correlation coefficient can be computed as follows (Obijole *et al.,* 2022; Adekunbi *et al.,* 2019; Oke *et al.,* 2008; Amoko *et al.,* 2015):

$$CD = \frac{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{cali}}\right)^2 - \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{cali}}\right)^2} \tag{3}$$

$$R = \sqrt{\frac{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{cali}}\right)^2 - \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{cali}}\right)^2}} \tag{4}$$

The AIC was derived from the Information Criterion of Akaike (Idi *et al*. 2020). It allows a direct comparison among models with a different number of parameters. The AIC presents the information on a given set of parameter estimates by relating the coefficient of determination to the number of parameters. The AIC was determined using Equation (5) as follows (Obijole *et al.,* 2022; Adekunbi *et al.,* 2019; Oke *et al.,* 2008; Amoko *et al.,* 2015):

$$AIC = n\left(\ln \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2\right) + 2p \tag{5}$$

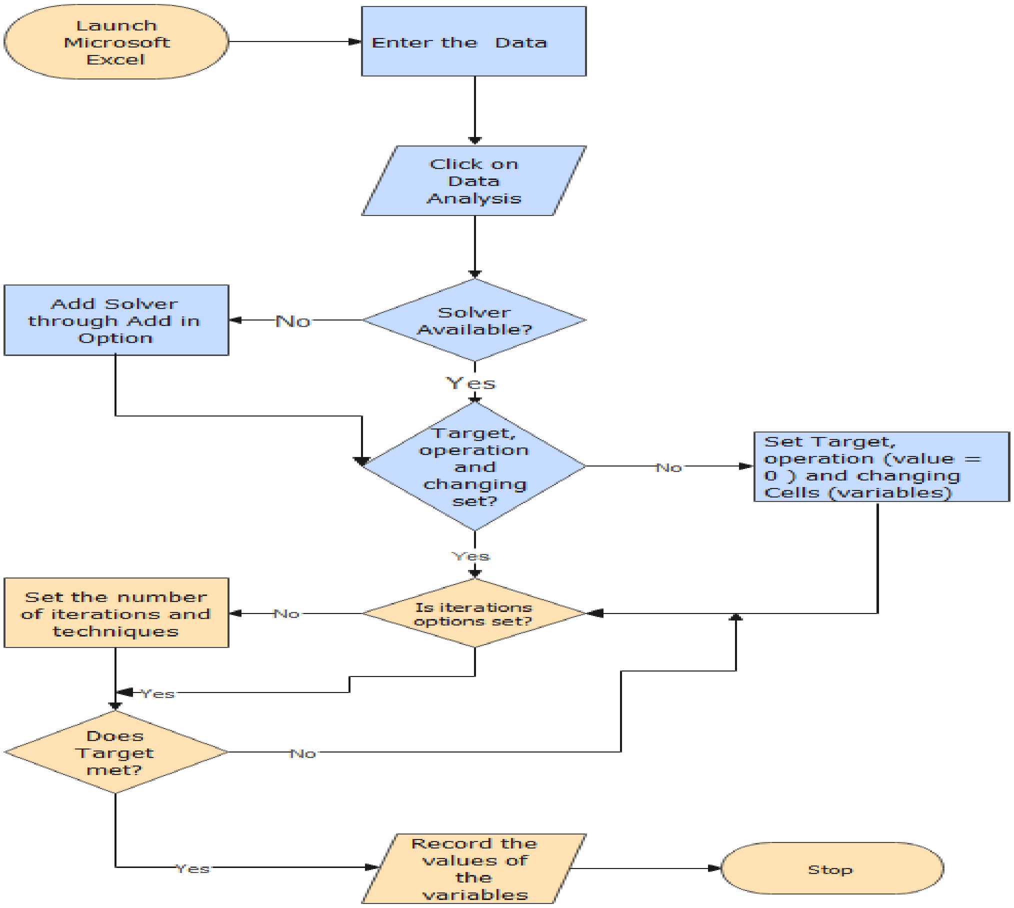


Figure 2. Flow Chart for using Microsoft Excel Solver in the computation of the Isotherm's parameters

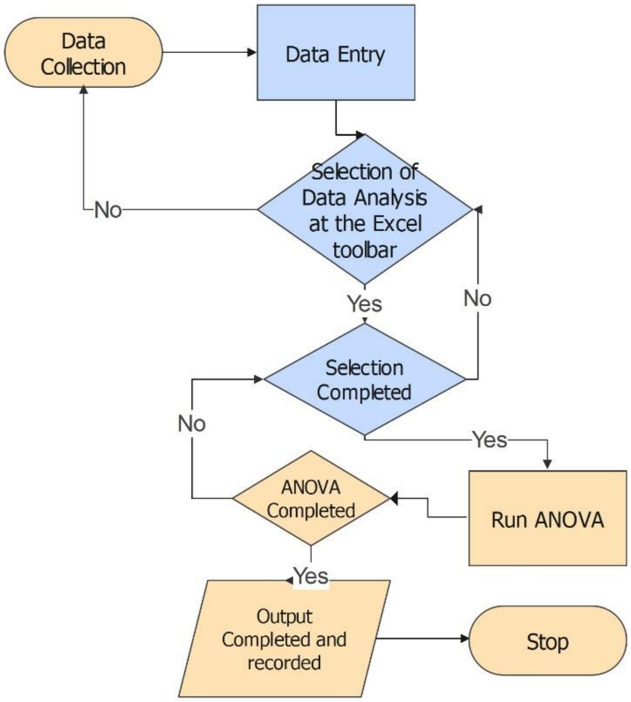


Figure 3. Flow chart for the ANOVA of the data

Table 1, Adsorption equilibrium isotherm models for single component aqueous solutions

Model (References)	**Non-Linear Relationship**	**Linear Relationship**	**Parameters**
Langmuir (Hamdaoui and Naffrechous, 2014; Obijole *et al.,* 2022; Adekunbi *et al.,* 2019; Oke *et al.,* 2008; Garba, 2019; Ayawei *et al.,* 2017; Olafadehan *et al.,* 2022; Karri *et al.,* 2017; Suwannahong *et al.,* 2021)	$q_e = \frac{a_L b_L C_e}{1 + a_L C_e}$	$\left(\frac{C_e}{q_e}\right) = \frac{C_e}{b_L} + \frac{1}{b_L a_L}$ $\left(\frac{1}{q_e}\right) = \frac{1}{a_L b_L C_e} + \frac{1}{b_L}$ $q_e = b_L - \frac{b_L q_e}{a_L C_e}$ $\left(\frac{q_e}{C_e}\right) = b_L a_L - a_L q_e$ $\left(\frac{1}{C_e}\right) = b_L a_L \frac{1}{q_e} - a_L$	a_L and b_L
Freundlich (Hamdaoui and Naffrechous, 2014; Vishali and Mullai, 2016; Karri *et al.,* 2017)	$q_e = K_f C_e^{1/N_f}$	$Log\left(q_e\right) = log\left(K_f\right) + \frac{1}{N_f} Log\left(C_e\right)$	K_f and N_f
Temkin (Hamdaoui and Naffrechoux, 2007; Al-Ghouti and Da'ana, 2020)	$q_e = \frac{RT}{b_t} \ln\left(a_t C_e\right)$	$q_e = a_t + 2.3 b_t \log C_e$	a_t and b_t
Dubinin–Radushkevich (Atallah *et al.*, 2020)	$q_e = X_m Exp\left(-k\varepsilon^2\right)$	$\ln\left(q_e\right) = \ln\left(X_m\right) - k\varepsilon^2$	X_m and k
Halsey A (Hamdaoui and Naffrechous, 2014; Al- Ghouti and Daana, 2020; Outram *et al*., 2021).	$q_e = \left(\frac{K_H}{C_e}\right)^{\frac{1}{N_H}}$	$\log\left(q_e\right) = \left(\frac{1}{N_H}\right)\log K_H - \frac{1}{N_H}\log C_e$	K_H and N_H
Halsey B (Hamdaoui and Naffrechous, 2007)	$q_e = K_{Hf}\left(\frac{C_e}{C_0}\right)^{\frac{1}{N_{Hf}}}$	$\log\left(q_e\right) = \log K_H - \frac{1}{N_{Hf}}\log\left(\frac{C_e}{C_0}\right)$	K_{Hf} and N_{Hf}
Halsey C(Rangabhashiyum *et al.,* 2014)	$q_e = \exp\left(\frac{\ln\left(K_{Hr}\right) - \ln\left(C_e\right)}{N_{Hr}}\right)$	$\ln\left(q_e\right) = \frac{1}{N_{Hr}}\left(\ln\left(K_{Hr}\right) - \ln C_e\right)$	K_{Hr} and N_{Hr}

Model (References)	Non-Linear Relationship	Linear Relationship	Parameters
Frenkel- Halsey- Hill (Hamdaoui and Naffrechous, 2014; Inyinbor *et al.,* 2016; Olafadehan *et al.,* 2022).	$q_e = Exp\left(\frac{\ln\left(\left(K_{fhh}\right)-\ln\left(C_e\right)\right)}{N_{fhh}}\right)$	$\ln\left(q_e\right) = \left(\frac{1}{N_{fhh}}\right)\ln K_{fhh} - \frac{1}{N_{fhh}}\ln C_e$	K_{fhh} and N_{fhh}
Harkin Jura- A (Rangabhashiyam *et al.,* 2014; Olafadehan *et al.,* 2022).	$q_e = \left(\frac{\left(A_{hj}\right)}{B_{hj}+\log\left(C_e\right)}\right)^{0.5}$	$\log\left(q_e\right)^2 = \log\left(A_{hj}\right)+\log\left(B_{hj}+\log C_e\right)$	A_{hj} and B_{hj}
Harkin Jura -B (Rangabhashiyam *et al.,* 2014; Olafadehan *et al.,* 2022).	$q_e = \left(\frac{\left(A_{hj}\right)}{B_{hj}-\log\left(C_e\right)}\right)^{0.5}$	$\log\left(q_e\right)^2 = \log\left(A_{hj}\right)+\log\left(B_{hj}-\log C_e\right)$	A_{hj} and B_{hj}
Jovanovic (Ayawei *et al.* (2017)	$q_e = q_m\left(1-\exp^{kC_e}\right)$	$\log\left(q_e\right)=\log\left(q_m\right)+\log\left(1-\exp^{kC_e}\right)$	q_m and k
Elovich (Hamdaoui and Naffrechous, 2014; Al- Ghouti and Daana, 2020; Outram *et al.*, 2021).	$\left(\frac{q_e}{q_{mE}}\right) = K_E C_e\left(\exp^{-\frac{q_e}{q_{mE}}}\right)$	$\ln\left(\frac{q_e}{C_e}\right)=\ln\left(K_E q_{mE}\right)-\frac{q_e}{q_{mE}}$	K_E and q_{mE}
Folwer –Guggenhien (Hamdaoui and Naffrechoux, 2007; Al-Ghouti and Da'ana, 2020)	$K_{FG}C_e=\frac{\theta}{1-\theta}\exp\left(\frac{2\theta W}{RT}\right)$	$\ln\left(\frac{C_e\left(1-\theta\right)}{\theta}\right)=-\ln\left(K_{FG}\right)+\frac{2\theta W}{RT}$	K_{FG} and W
Hill-de Boer (Al- Ghouti and Daana, 2020; Outram *et al.*, 2021).	$K_{Hd}C_e=\frac{\theta}{\left(1-\theta\right)}\exp\left(\frac{\theta}{\left(1-\theta\right)}-\frac{K_2\theta}{RT}\right)$	$\ln\left[C_e\frac{\left(1-\theta\right)}{\theta}\right]-\frac{\theta}{\left(1-\theta\right)}=-\ln\left(K_{Hd}\right)-\frac{K_2\theta}{RT}$	K_{Hd} and K_2
Kiselev (Al- Ghouti and Daana, 2020; Outram *et al.*, 2021).	$K_1C_e=\frac{\theta}{\left(1-\theta\right)\left(1+K_n\theta\right)}$	$\frac{1}{C_e\left(1-\theta\right)}=\frac{K_1}{\theta}+K_1K_n$	K_1 and K_n
Flory – Huggins (Al- Ghouti and Daana, 2020; Outram *et al.*, 2021).	$\frac{\theta}{C_e}=K_{FH}\left(1-\theta\right)^{N_{FH}}$; $\theta=1-\frac{C_e}{C_0}$	$\log\left[\frac{\theta}{C_e}\right]=\log\left(K_{FH}\right)+N_{FH}\log\left(1-\theta\right)$	K_{FH} and N_{FH}
Langmuir – Vageler (Attar *et al.,* 2018; Al-Ghouti and Da'ana, 2020)	$q_e = \left(\frac{C_f q_{\max}}{C_f+K_{LV}}\right)$; $C_f=\frac{C_0V}{m}$	$\log\left(q_e\right)=\log\left(C_f q_{\max}\right)-\log\left(C_f+K_{LV}\right)$	q_{max} and K_{LV}

3. Results and Discussion

3.1. Surface Morphology and Pore variations of the P_{oes}

SEM micrographs were used to study the surface morphology and pore variations of the P_{oes} adsorbent before the adsorption process, and its results are shown in Figure 4. Based on these figures, it can be observed that the surface of the applied P_{oes} was porous with a large number of pores which makes it appropriate for the adsorption of A_{sic}. Figures 4a, b, c and d show the results of the SEM. Figures 4a and 4b deliver an overview of the microstructural morphology of the P_{oes}. These two figures also provide information on mixed homogeneity and the segregation of the micro-constituents. In these figures, a fair distribution of constituents is observed with a marked absence of segregation. However, the higher magnification micrograph (Figure 4b), revealed that small regions of agglomeration exist, where the border tends to form clumps. Also at higher magnification, the pore structure is apparent. The pores are evenly sized and permeate the entire structure. These pores extend the surface area of the P_{oes} and also aid in the adsorption of impurities. Figure 4 provides topographical details and geometry. Figures 4c and 4d revealed the topology of the pores. It is apparent in these micrographs that the pore are interconnected and not blind pores. It also confirms the extensive nature of the pores. From these figures (4a, b and c), the particles of the P_{oes} are discernable. The porosity is seen to be a result of particles stacking against each other. Figure 5 presents the results of the SEM and EDS spot A. These figures (Figures 5a, and 5b) revealed the major composition of the P_{oes}. These figures revealed that the major compositions of the P_{oes} are Aluminium (1.25 – 7.58 %), Calcium (3.7 – 10.12 %), Silicon (11.15 – 25.62 %), Carbon (27.75%) and oxygen (48.75 – 58.13%) had the highest weight percentages (Figure 4 a, and 4b). The other elements in the adsorbent structure were Na, Mg, K, and Fe and their corresponding weight percentages. Figures 6a, 6b and 6c present SEM and EDS of eggshells from the literature. The figures revealed that the compositions of eggshells were similar but with different proportions elemental composition.

3.2. Performance of the Adsorption Equilibrium Isotherms Model

Tables 2 and 3 show the values of the non-linear and linearized 2 parameters adsorption equilibrium models, respectively. These two tables revealed that the values of the non-linear and linear 2-parameter adsorption equilibrium models were not the same for both non-linear and linear. This reflection is in agreement with literature such as Walsh and Diamond (1995); Farouq and Yousef (2005); Vasanth (2007) Subramanyam and Ashutosh (2012); Yaneva *et al.* (2013); Inyinbor *et al.* (2016); Atallah *et al.* (2020) and Olafadehan *et al.,* (2022). Tables 2 and 3 provide the values of the 2 parameters in the adsorption equilibrium isotherm models and the values of MSC, AIC, CD and R, respectively. Table 2 revealed that the values of the parameters for non-linear regression of the adsorption equilibrium isotherm models range from -0.001 (B_{hj} for Harkin-Jura A) to 383.900 (b_L for Langmuir). Table 3 established that the values for non-linear regression of the adsorption equilibrium isotherm models range from -229.552 (for W of Fowler-Guggenheim adsorption model) to 1.55 x 10^{13} (for X_m of Dubinin-Redunshikevich adsorption model). These Tables revealed that the values of these adsorption equilibrium isotherm models were not the same for both non-linear and linearized regressions, which indicates that analysing adsorption equilibrium data must be done using both linearized and non-linear regressions to establish a better-fit model. It can be said here that the conventional technique of selection of the best-fit adsorption equilibrium models based on only the regression coefficient is not permanently the appropriate technique for choosing an adsorption equilibrium model for the adsorption equilibria. Based on any of these measures model of selection criterion, coefficient of determination, correlation coefficient and Akaike Information Criterion, better fits can be obtained for any adsorption equilibrium models by using both non-linear and linearized regressions adsorption equilibrium isotherm models.

From these Tables (Tables 2 and 3) the lowest value of MSC came from Table 3(0.012, linearized form of Langmuir, Langmuir B) and the came from linearised Kiselev adsorption equilibrium model (8.896). Table 2 also revealed that some adsorption equilibrium models had negative values MSC, while Table 3 prevealed the non-linear adsorption equilibrium models produced positive values of MSC. Negative values of adsorption equilibrium models indicated that care must be taken in the selection of such adsorption equilibrium models. In respect to AIC, the highest and the lowest can from Table 2, which is the linearised form of the adsorption equilibrium models. In the case of CD and R values, Table 3 revealed higher values than Table 2, which indicated that non- linear regression of the adsorption equilibrium models performed better than linerilized form the the models. Based on the statistical evaluations and values of CD and R, MSC, and AIC the performance and quality of the adsorption isotherm fittness can be organised in order of increasing the weightage of the correctness as follows (MSC, AIC, CD and R):

a) Based on CD and R the quality of the isotherm fit can be organised in order of increasing weightage of the accuracy as follows:

   (i) In respect of non-linear regression of adsorption equilibrium isotherm models, the performance and quality of the fitness expressed as the values of CD and R revealed that Fowler- Guggenheim (0.992 and 0.996), which is greater than Freundlich (0.972 and 0.986) and Halsey- A (0.972 and 0.986) are greater than Langmuir – Vageler(0.926 and 0.962) is greater than Dubinin– Radushkevich (0.876 and 0.936), which are greater than Hill-de Boer (0.864 and 0.930) is greater than Kiselev(0.782 and 0.884) is greater than Temkin (0.751 and 0.867) is greater than Jovanoaic (0.518 and 0.719) is greater than Langmuir (0.498 and 0.706) is greater than Flory – Huggins (0.460 and 0.678) is greater than Elovich (0.415 and 0.644) is greater than Halsey C (-0.222 and 0.471) is greater than Harkins-Jura-A (0.199 and 0.446) is greater than Halsey B (-0.055 and 0.234) is greater than Harkins-Jura-B (0.022) is greater than Frenkel- Hasley- Hill (-0.010 and 0.100). The details are as presented in Table 2.

(ii) In the case of linearised adsorption equilibrium isotherm models, the performance and quality of the isotherm fittness can be arranged in order of increasing weightage of the accuracy line with CD and R as follows: Kiselev (0.9998 and 0.9999) was greater than Harkins-Jura –A (0.993 and 0.997), which was greater than Temkin(0.986 and 0.994) was greater than Dubinin- Redunshikevich (0.986 and 0.931) was greater than Fowler-Guggenheim (0.9615 and 0.9806) was greater than Langmuir A (0.921 and 0.960) greater than Langmuir C (0.912 and 0.955) was greater than Freundlich (0.902 and 0.950) was greater than Hasley B (0.891 and 0.944) was greater than Frenkel Hasley- Hill (0.851 and 0.923) was greater than Langmuir D (0.851 and 0.922) was greater than Hasley A(0.807 and 0.898) was greater than Elovich 0.756 and 0.8697) was greater than Langmuir B (0.698 and 0.835) was greater than Hasley C (0.449 and 0.670) was greater than Jovanoaic (0.367 and 0.606) was Langmuir – Vageler (-0.276 and 0.525) was greater than Harkins-Jura –B (-0.101 and 0.318) was greater than Flory – Huggins (0.086 and 0.293) was greater than Langmuir E (0.047 and 0.216) was greater than Hill-de Boer (0.0357 and 0.1891). The details are presented in Table 3.

b) Based on MSC the quality of the isotherm fit can be arranged in order of increasing weightage of the accuracy as follows:

(i) In the case of non-linear regression of adsorption equilibrium isotherm models, the performance and quality of the fitness expressed as the values of MSC revealed that Fowler-Guggenheim greater (5.134) was than Freudlich (3.906) was greater than Halsey A (3.906) was greater than Langmuir – Vageler (2.936) was greater than Dubinin–Radushkevich (2.419) was greater than Kiselev (1.856) was greater than Temkin (1.725) was greater than Jovanoaic (1.062) was greater than Langmuir (1.023) was greater than Flory – Huggins (0.949) was greater than Elovich (0.869) was greater than Harkins-Jura-A (0.556) was greater than Hill-de Boer (0.375) was greater than Harkins-Jura-B (0.355) was greater than Frenkel-Hasley- Hill (0.323) was greater than Halsey B (0.280) was greater than Halsey C (0.133). The details are presented in Table 2

(ii) In the case of linear regression of adsorption equilibrium isotherm models, the performance and quality of the fitness expressed as the values of MSC revealed that Langmuir – Vageler (-26.661) was less than Kiselev (8.896) was greater than Temkin (4.701) was greater than Dubinin-Redunshikevich (4.621) was greater than Fowler-Guggenheim (3.591) was greater than Langmuir C (2.768) was greater than Freundlich (2.655) was greater than Hasley B (2.551) was greater than Langmuir D (2.235) was greater than Hill-de Boer (2.159) was greater than Elovich (1.746) was greater than Harkins-Jura –A (1.688) was greater than Frenkel Hasley- Hill (1.428) was greater than Harkins-Jura –B (1.226)was greater than Hasley A (1.206) was greater than Hasley C (0.930) was greater than Flory – Huggins (0.423) was greater than Langmuir E (0.381) was greater than Langmuir A (0.204) was greater than Jovanonic (0.045) was greater than Langmuir A (0.012). The details are presented in Table 3.

c) Based on AIC the quality of the isotherm fit can be arranged in order of increasing weightage of the accuracy as follows:

i. In the case of non-linear regression of adsorption equilibrium isotherm models, the performance and quality of the fitness expressed as the values of AIC revealed that Fowler-Guggenheim (-20.032) was greater than Freudlich (-19.243) was greater than Halsey A (-19.243) was greater than Dubinin–Radushkevich (-10.316) was greater than Temkin (-5.039) was greater than Hill-de Boer (-3.234) was greater than Langmuir – Vageler (-2.263) was greater than Jovanoaic (-1.943) was greater than Langmuir (--1.905) was greater than Flory – Huggins (-1.465) was greater than Elovich (-0.968) was greater than Harkins-Jura-A (1.261) was greater than Kiselev (1.550) was greater than Frenkel- Hasley- Hill (2.846) was greater than Halsey C (3.401) was greater than Halsey B (5.748) was greater than Harkins-Jura-B (7.246). The details are presented in Table 2.

ii. In the case of linear regression of adsorption equilibrium isotherm models, the performance and quality of the fitness expressed as the values of AIC revealed that Kiselev (-42.227) was greater than Temkin (-24.013) was greater than Dubinin-Redunshikevich (-23.531) was greater than Freundlich (-17.928) was greater than Fowler-Guggenheim (-7.373) was greater than Langmuir D (-1.548) was greater than Jovanonic (-0.076) was greater than Langmuir B (0.122) was greater than Langmuir C (0.319) was greater than Langmuir A (1.421) was greater than Hasley C (2.431) was greater than Hasley A (7.432) was greater than Harkins-Jura –B (7.550) was greater than Frenkel Hasley- Hill (8.763) was greater than Harkins-Jura –A (10.323) was greater than Hasley B (10.471) was greater than Elovich (11.350) was greater than Hill-de Boer (13.150) was greater than Flory – Huggins (14.203) was greater than Langmuir E (20.768) was greater than Langmuir - Vageler (160.163). The details are presented in Table 3.

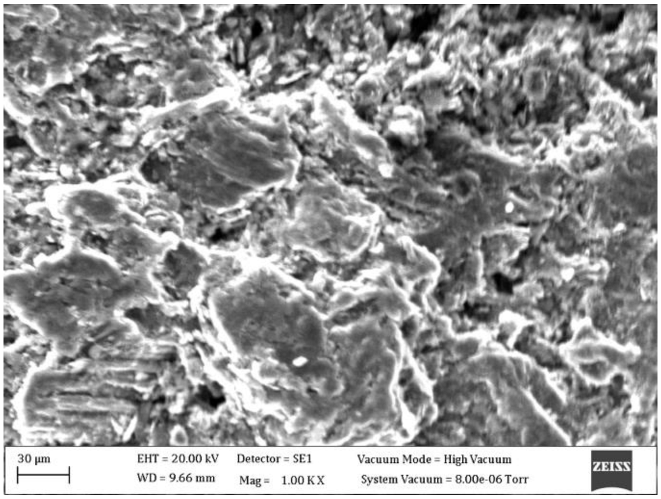


Figure 4a: SEM of P_{oes} at 100KX

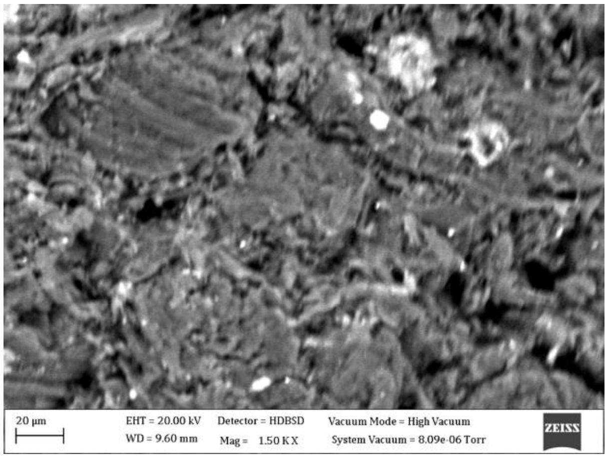


Figure 4b: SEM of Poes at 150KX

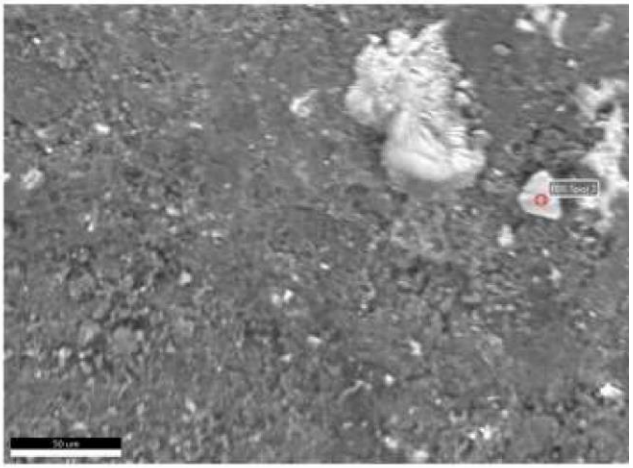


Figure 4c: EDS of Poes at Spot A

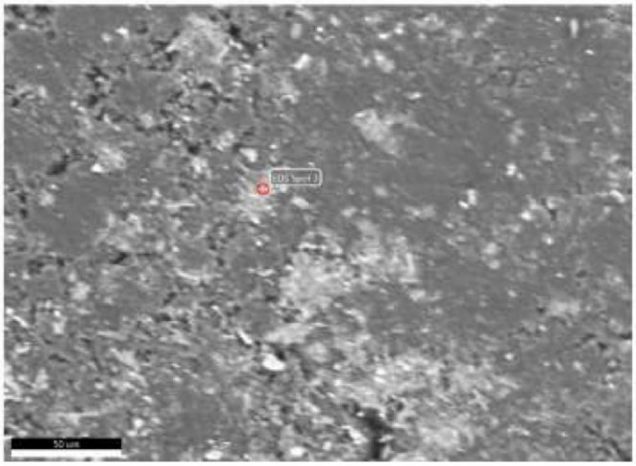
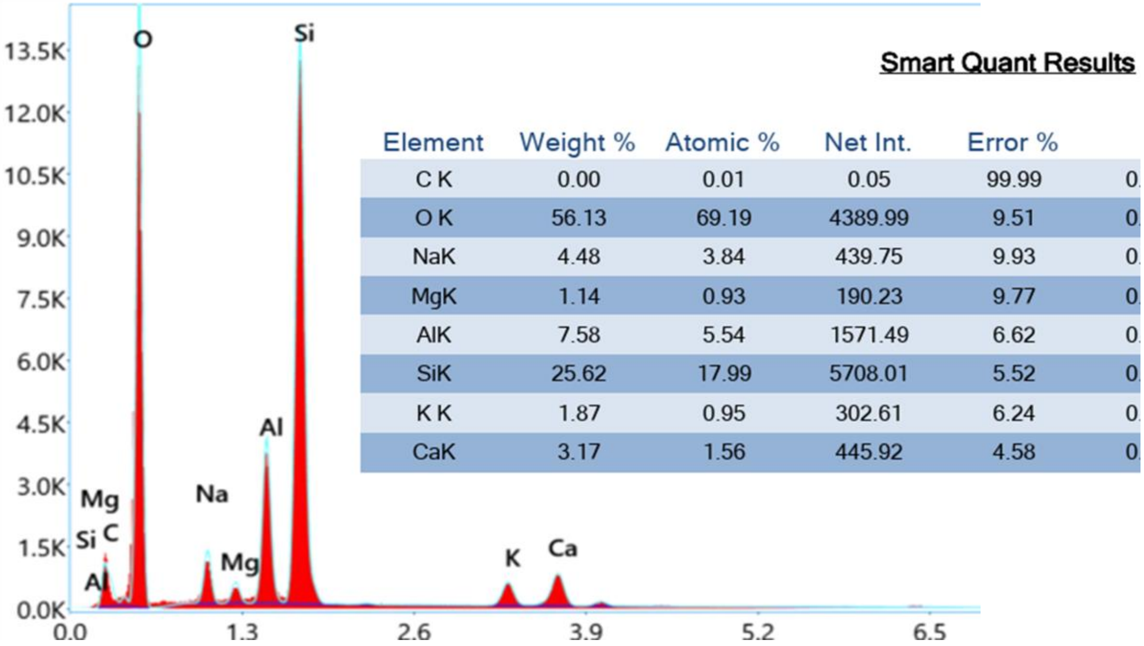


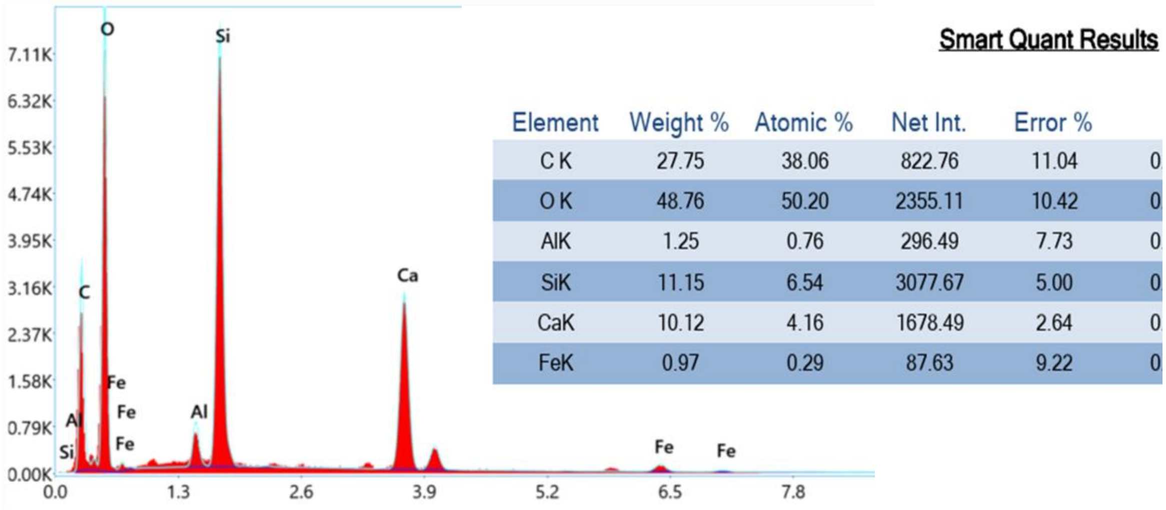
Figure 4d: EDS of Poes at Spot B



Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	
C K	0.00	0.01	0.05	99.99	0
O K	56.13	69.19	4389.99	9.51	0
NaK	4.48	3.84	439.75	9.93	0
MgK	1.14	0.93	190.23	9.77	0
AlK	7.58	5.54	1571.49	6.62	0
SiK	25.62	17.99	5708.01	5.52	0
K K	1.87	0.95	302.61	6.24	0
CaK	3.17	1.56	445.92	4.58	0

Figure 5a: EDS of Poes at Spot A with elemental composition



Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	
C K	27.75	38.06	822.76	11.04	0
O K	48.76	50.20	2355.11	10.42	0
AlK	1.25	0.76	296.49	7.73	0
SiK	11.15	6.54	3077.67	5.00	0
CaK	10.12	4.16	1678.49	2.64	0
FeK	0.97	0.29	87.63	9.22	0

Figure 5b: EDS of Poes at Spot B with elemental composition

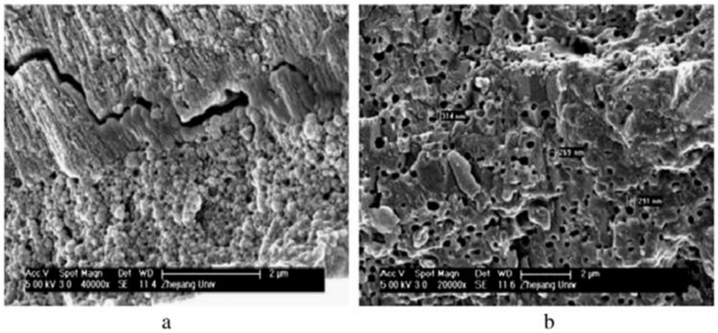


Figure 6a: SEM of similar P_{oes} (Source: Guru and Dash, 2014).

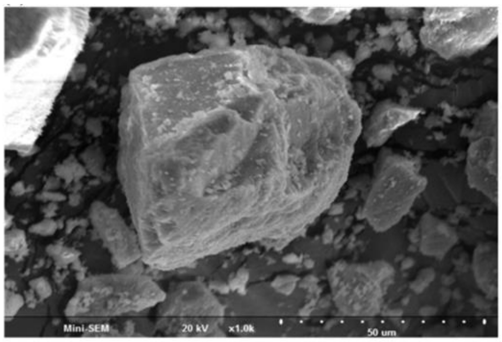


Figure 6c: SEM of similar P_{oes} (Source: Hee-Jeong and Seung-Mok, 2015).

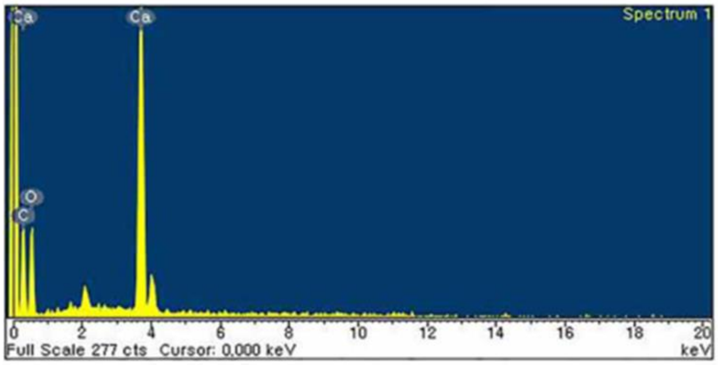


Figure 6b: EDS of similar P_{oes} (Source: Hee-Jeong, 2019).

Table 2. Adsorption equilibrium Parameters for Non- Linear regression adsorption equilibrium models

Model	Parameters				MSC	AIC	CD	R
Langmuir	a_L	0.00646	b_L	383.900	1.023	-1.905	0.498	0.706
Freudlich	K_f	32.65536	N_f	0.286	3.906	-19.243	0.972	0.986
Halsey A	K_H	0.36874	N_H	0.286	3.906	-19.243	0.972	0.986
Halsey B (Hamdaoui and Naffrechous, 2014)	K_{Hf}	0.35892	N_{Hf}	3.988	0.280	5.748	-0.055	0.234
Halsey C(Rangabhashiyum et al., 2014)	K_{Hf}	0.54212	N_{Hf}	2.699	0.133	3.401	-0.222	0.471
Temkin	b_t	93.58712	a_t	3.984	1.725	-5.029	0.751	0.867
Harkins-Jura-A	A_{hj}	-0.42063	B_{hj}	-0.001	0.556	1.261	0.199	0.446
Harkins-Jura-B	A_{hj}	0.261	B_{hj}	1.0987	0.355	7.246	0.022	0.148
Jovanoaic	q_m	-0.70699	k	2.220	1.062	-1.943	0.518	0.719
Flory - Huggins	K_{FH}	4.29978	N_{FH}	1.104	0.949	-1.465	0.460	0.678
Langmuir - Vageler	q_{max}	1.09765	K_{LV}	0.353	2.936	-2.263	0.926	0.962
Frenkel- Hasley- Hill	K_{fhh}	0.00767	K_{fhh}	52.249	0.323	2.846	-0.010	0.100
Elovich	q_{mE}	311.39892	K_E	0.008	0.869	-0.968	0.415	0.644
Fowler-Guggenheim	W	0.23400	K_{FG}	1.165	5.134	-20.032	0.992	0.996
Hill-de Boer	K_{Hd}	1.68613	K_2	0.818	0.375	-3.234	0.864	0.930
Kiselev	K_1	1.63415	K_n	1.810	1.856	1.550	0.782	0.884
Dubinin–Radushkevich	k	25.118	X_m	17.647	2.419	-10.316	0.876	0.936

Table 3. Adsorption equilibrium Parameters for Linear regression adsorption equilibrium models

Summary	Equilibrium Isotherm Models' Parameters				MSC	AIC	CD	R
Langmuir - Vageler	q_{max}	0.0043	K_{LV}	577.5954	-26.661	160.163	-0.276	0.525
Hill-de Boer	K_{Hd}	1.968	K_2	0.702	2.159	13.1498	0.0357	0.1891
Flory - Huggins	K_{FH}	60.4332	N_{FH}	2.9421	0.423	14.203	0.086	0.293
Elovich	q_{mE}	1790.223	K_E	0.006	1.746	11.3499	0.7564	0.8697
Fowler-Guggenheim	W	-229.552	K_{FG}	1.668	3.591	-7.3725	0.9615	0.9806
Kiselev	K_1	0.174	K_n	3.252	8.896	-42.2267	0.9998	0.9999
Langmuir E	b_L	2105.1295	a_L	0.001	0.381	20.768	0.047	0.216
Langmuir D	b_L	2105.1295	a_L	0.001	2.235	-1.548	0.851	0.922
Langmuir C	b_L	1.7797	a_L	2.276	2.768	0.319	0.912	0.955
Langmuir B	b_L	1093.3217	a_L	0.002	0.012	0.122	0.698	0.835
Langmuir A	b_L	726.2891	a_L	0.003	0.204	1.421	0.921	0.960
Jovanonic	q_m	3.648	k	0.641	0.045	-0.076	0.367	0.606
Harkins-Jura -A	A_{hj}	0.2216	B_{hj}	4.044	1.688	10.323	0.993	0.997
Harkins-Jura -B	A_{hj}	1.255	B_{hj}	1.336	1.226	7.550	-0.101	0.318
Frenkel Hasley- Hill	K_{fhh}	0.1014	N_{fhh}	1.037	1.428	8.763	0.851	0.923
Hasley A	K_H	1.625	N_H	8.014	1.206	7.432	0.807	0.898
Hasley B	K_H	45.582	N_H	0.262	2.551	10.471	0.891	0.944
Hasley C	K_H	2.333	N_H	0.262	0.930	2.431	0.449	0.670
Temkin	b_t	2.816	a_t	3.857	4.701	-24.013	0.986	0.994
Dubinin- Redunshikevich	k	-22.015	X_m	1.55×10^{13}	4.621	-23.531	0.986	0.9931
Freundlich	K_f	45.582	N_f	0.262	2.655	-17.928	0.902	0.950

From these results, it is obvious that Freundlich and Fowler- Gugggenheim isotherm offer the best fit for A_{sic} adsorption at equilibrium for both non-linear and linear adsorption equilibrium isotherm models. On the contrary Langmuir adsorption equilibrium isotherm model is not consistent with the performance indicators (MSC, AIC, CD and R) for both non-linear and linear regression analysis of the adsorption equilibrium data. Moreover, compared to other adsorption equilibrium isotherms, the parameter sets of the Freundlich and Halsey A isotherms for A_{sic} were remarkably consistent and quite similar for both non-linear and linear transform values. In certain adsorption equilibrium isotherms models, it was found that these parameters acquired using linearization adsorption equilibrium isotherms models are better than the values derived by non-linear regression adsorption equilibrium isotherms. This phenomenon is common in cases where the parameters are not consistent, and diverge widely and with ambiguous parameters. The adsorption equilibrium isotherms models with inconsistent parameters include Langmuir (Langmuir E, Langmuir D, Langmuir A and Langmuir B), Elovich, Fowler-Guggenheim, and Dubinin-Redunshikevich adsorption equilibrium isotherms models.

4. Conclusion

P_{oes} particles are an excellent source of various inorganic materials for A_{sic} adsorption. Freundlich isotherm can be adjudged as the best-fit isotherm for A_{sic} adsorption in linear as well as non-linear systems based on the performance indicators and consistency of the parameters. Langmuir isotherm, which is among the most common use isotherm was able to offer a fair indication of the relative ranking of the linear isotherm fits based on the selected performance indicators with inconsistency in the parameters. In the non-linear regression analysis, the Langmuir, Elovich, Fowler-Guggenheim, and Dubinin-Redunshikevich isotherms produced very inconsistent results quite different from that obtained by linear regression from which it can be inferred that these adsorption equilibrium isotherm models are not particularly reliable models for A_{sic} adsorption. The linear and non-linear regression analysis of the adsorption equilibrium data gave different models as the best fitting isotherm based on the performance indicators (MSC, CD, R and AIC), which indicated significant differences between the analytical techniques. The performance of some adsorption equilibrium isotherm models such as Jovanonic, Hasley C, Harkins-Jura –B, Frenkel Hasley-Hill, Harkins-Jura –A, Hill-de Boer, Flory – Huggins, and Langmuir – Vageler show some degree of reliability. Therefore, to ensure reliable results of adsorption equilibrium data analysis through the adsorption isotherm models, these data sets must be evaluated by both linear and non-linear regression analyses.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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