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PROPERTIES OF SURFACE WATER; ADSORPTION KINETICS AND MECHANISM OF ARSENIC AND LEAD IONS REMOVAL USING A MATRIX TECHNIQUE

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ABSTRACT

In this article, the effectiveness of adsorption techniques in removing arsenic(As) and lead(Pb) ions from the typical heavy metals contaminated surface (T_{ac}) of the Aponmu River at different pH values (7.2, 6.4, 3.2 and 11.5) was determined using powdered eggshell. The initial dosage of selected water characteristics (pH, dissolved Oxygen, chloride, suspended solids, turbidity, As, dissolved oxygen (DO), Pb, and chemical oxygen demand (COD)) of the raw water was determined. The findings established that the average dosages of the selected pollutants were 6.48, 88.73 mgl^{-1}, 255.67 mgl^{-1}, 97.44 mgl^{-1}, 290.44 NTU, 0.79 mgl^{-1}, 0.55 mgl^{-1}, 3.71 mgl^{-1} and 188.36 mg-1, for pH, dissolved Oxygen, chloride, suspended solids, turbidity, As, Pb, DO, and COD, respectively. In the case of adsorption, P_e was able to remove 99.98 % and 99.99 % of As and Pb dosage, respectively. Adsorption kinetics were in the range of 0.12878 and 0.37051, 0.0782 and 0.31757 for As and Pb respectively. It was concluded that adsorption mechanisms for these selected toxic pollutants (As and Pb) were mainly ion exchange and precipitation.

Keywords: Adsorption Kinetics, Matrix Technique, Water Quality, Microsoft Excel Functions, Heavy Metals

INTRODUCTION

Some metalloids and metals, which are usually dispersed in a human environment (land, air and water) are known to be toxic and harmful pollutants (Pawar et al., 2018). The availability of these toxic and harmful contaminants can be attributed to the speedy progress of urbanization and industrialization (Lakshmia et al., 2024). The availability and accumulation of these dangerous toxic metalloid ions, metallic ions and radicals in the sea and marine environment are major worldwide concerns due to their serious impacts on human and aquatic survival (Pawar et al., 2018). These toxic and harmful metal ions include cadmium, Pb, and mercury and the toxic and harmful metalloids include arsenite and arsenate. These pollutants are harmful, inhibit and toxic to biological activities and functions. These specified pollutants are important pollutants that are dangerous for plants, human and aquatic life based on their high toxicity values, even at very low-level dosages (Pawar et al., 2018). Arsenic as one of the utmost toxic and harmful chemicals in the air, water and soil, poses a great risk to the lives of millions of individuals and aquatic animals worldwide. These inorganic species of As compounds and radicals are categorised as Group 1 carcinogens ((Pawar et al., 2018; Lakshmia et al., 2024; Gomez et al., 2024; Kaya 2024). Long-term contact with As causes bladder, skin, kidney, liver, and lung cancers. As also causes hindrance in the mental progress of children (Gomez et al., 2024; Kaya 2024; Topal et al., 2024). These impacts are evidence that came from epidemiological research and studies of As- pesticide- workers, ore smelters, as well as people and aquatic animals exposed to As-containing surface and ground drinking water (Pawar et al., 2018). Among the several removal approaches and techniques for As removal include adsorption, coagulation, electrochemical, electro-coagulation, electro-adsorption, electrodialysis, ion exchange, irradiation, membrane and nano-filtration, pH adjustment and chemical precipitation removal techniques (Abiodun et al., 2023; Alka et al., 2020; Amen et al., 2020; Aristizabal-Henao et al., 2020; Arun et al., 2021; Garba, 2019; Liu et al., 2022; Obijole et al., 2022; Oke et al., 2022). The adsorption removal technique is among the most common remediation techniques utilised for the treatment of toxic, harmful, hazardous and dangerous chemicals contaminated wastewater and water due to the low cost of the facilities, availability of adsorbents, simplicity of the techniques, accessibility of the process and high efficiency of the removal techniques (Abiodun et al., 2023; Alka et al., 2020; Amen et al., 2020; Aristizabal-Henao et al., 2020; Arun et al., 2021; Garba, 2019; Khanam et al., 2019; Liu et al., 2022; Obijole et al., 2022; Oke et al., 2022). Subsequently, numerous research studies have been conducted and are still going on to advance suitable and sustainable adsorbents for removing these dangerous, hazardous, toxic and harmful pollutants from contaminated air, water and land (Pawar et al., 2018). In the last five decades, various adsorbents, mathematical equations and several expressions or functions have been utilised to establish adsorption removal techniques and processes for removing pollutants such as arsenic from water (surface and ground) and wastewater (industrial and domestic). Adsorption kinetics are vital in several engineering and science processes (for the design of facilities to remove environmental pollutants, Garba, 2019).

Adsorption kinetics refers to studying and analysing the rate at which a solute interacts with an adsorbent. Understanding adsorption kinetics is crucial in various scientific and industrial applications due to its wide-ranging implications and utility. In summary, adsorption kinetics provide critical insights into the rates, mechanisms and routes of adsorption processes across various fields, enabling the optimization of materials and processes for enhanced performance and efficiency. In addition, adsorption kinetics parameters interpret adsorption isotherm data, which can be used by environmental scientists and engineers to establish adsorption mechanisms and processes. . Figure 1 presents some of the treatment techniques for the removal of As and Pb ions from the air, water and land . Figure 2a presents a schematic and summary of adsorption knowledge available in the literature. Figure 2b shows the adsorption mechanism of cationic pollutants by selected adsorbents. Figure 2c presents the schematic diagram of the adsorption mechanism and mass

transfer steps. It has been established that the least squares, linearized and non-polynomial methods built into these Microsoft Excel packages and functionalities were to compute several variables in the several model equations and expressions (Al-Ghouti and Da'ana, 2020; Wang and Guo, 2020; Outram et al., 2021, Raji et al., 2023; Amoko et al., 2023; 2024), but evaluation of matrix transformation and utilisation M_t , which depends on lineraization and least square method for the adsorption kinetic models are rare in literature. Using matrices for solving equations involves the application of matrix algebra and linear algebra techniques to analyze and solve complex processes, which is particularly useful for systems involving multiple components and interactions. In summary, using matrices for adsorption kinetics offers numerous advantages in handling complexity, improving computational efficiency, facilitating data analysis, and enhancing the accuracy of models and predictions.

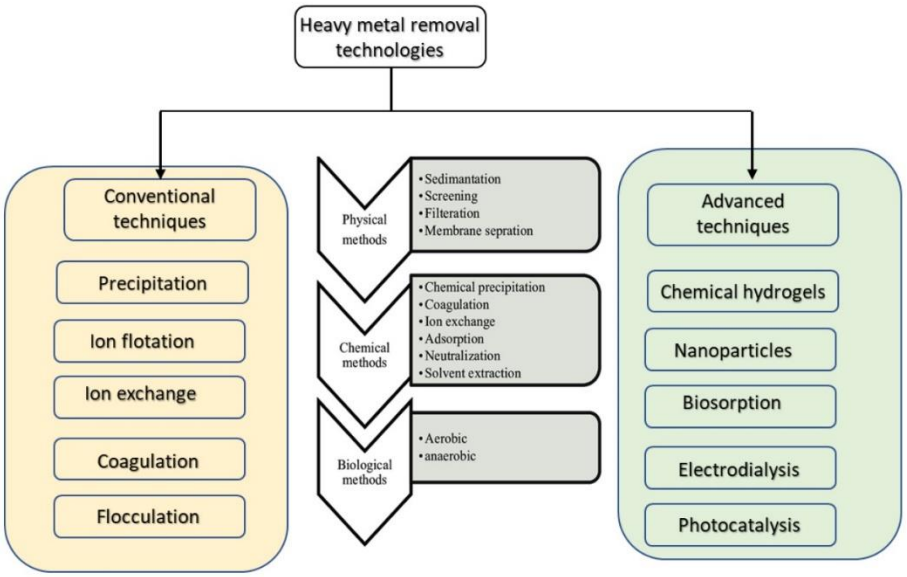

Figure 1: Some of the frequently utilised treatment techniques for the reduction of As and Pb from the environment (Source: Abiodun et al., 2023 and Obijole et al., 2022)

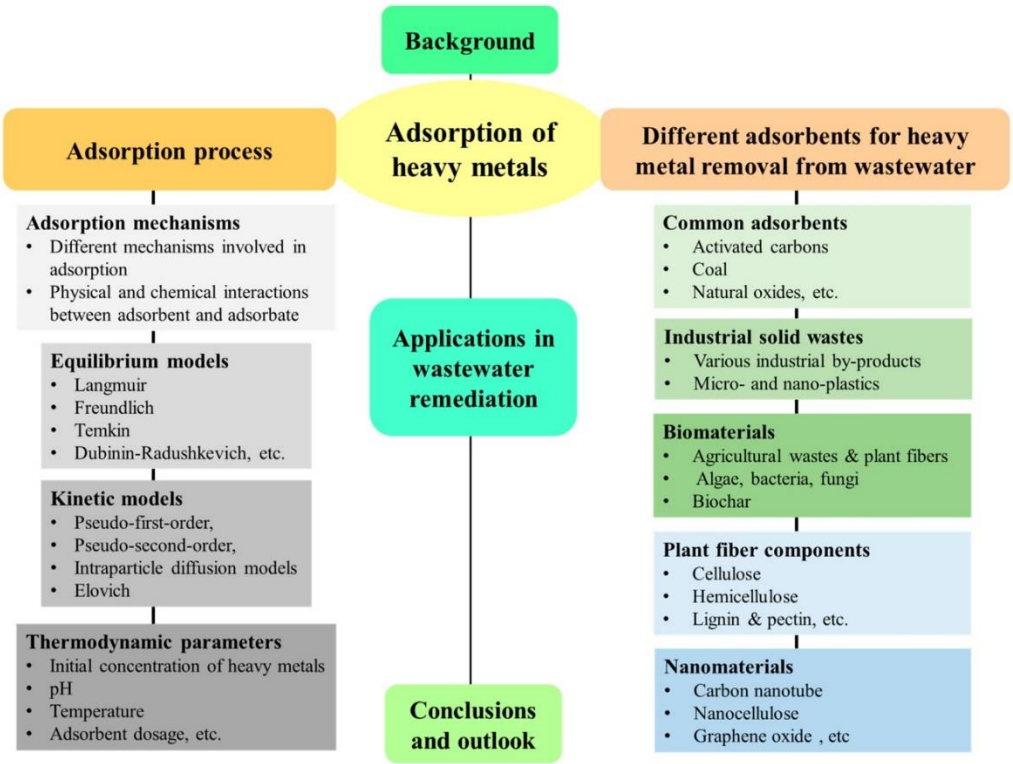

Figure 2a: Schematic and summary of adsorption knowledge available in literature (Source: Raji et al., 2023; Amoko et al., 2023; 2024)

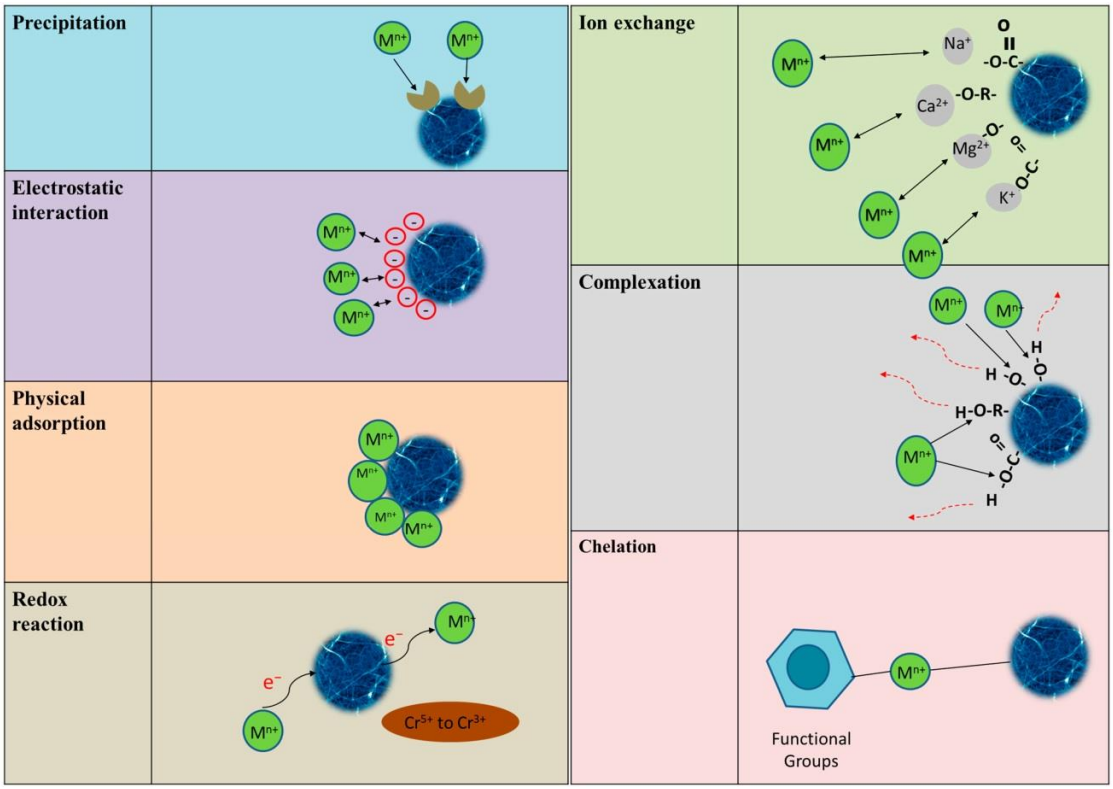

Figure 2b Adsorption mechanism of cationic pollutants by selected adsorbents (Source: Raji et al., 2023)

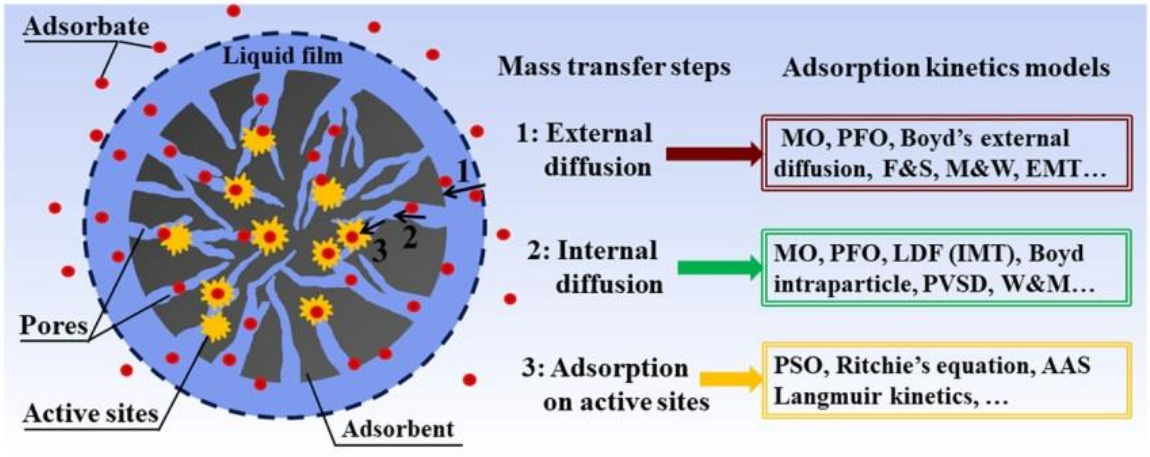

Figure 2c: schematic diagram of the adsorption mechanism and mass transfer steps (Source: Wang and Guo , 2020)

This approach is particularly beneficial for multicomponent systems, dynamic processes, and optimization tasks, making it a powerful tool in both research and industrial applications of adsorption technology (Al-Ghouti and Da'ana, 2020; Wang and Guo, 2020; Outram et al., 2021, Raji et al., 2023; Amoko et al., 2023; 2024). The main focus of this paper is to evaluate the performance of P_{II} in removing As and Pb ions from T_{ac} and solve selected commonly used adsorption kinetic models using matrix functions in Microsoft Excel, establish the accurateness and preciseness of matrix transformation and technique in solving commonly used adsorption kinetic models with specific consideration to the utilization of least squares and built-in matrix functions in Microsoft Excel and compared with typical adsorption kinetics with a critical aim of attaining sustainable development goals number 3 which is on good health and well-being, number 6 focus on clean water and sanitation; number 14 highlighted issues on life below water and number 15 with special attention on life on land (Dalampira and Nasti, 2019), through exact, adequate and precise design parameters for environmental pollution control facilities and to further knowledge in computer software applications.

MATERIALS AND METHODS

All reagents and chemicals utilised in this research study had solid and aqueous solution purity of 95 % or more. Distilled water was utilised in the preparations of all standard solutions. All facilities and equipment utilised in the experiments were standardised and calibrated using standard techniques. The coefficient of determinations of these calibrations and standardizations between experimental and simulated values were equal or greater than 96 %. Figure 3 presents the summary of the materials and methods. This section of materials and methods is breakdown as follows:

Collections of water Samples and Raw water Properties Determinations

Raw water samples were collected from Aponmu river in Ilara-Mokin during the rainy season. Selected properties (turbidity, pH, total suspended solids, dissolved solids, salinity and chloride dosage, Pb and As dosages) were determined using standard methods and procedures specified in the Standard Methods for Water and Wastewater Examination such as Van Loosdrecht et al. (2016) and APHA (2019). Statistical parameters (average, minimum, maximum, skewness, standard deviation, and coefficient of variation) of the measured characteristics and parameters were computed using standard equations and expressions.

Preparation and Determination of Properties of the Adsorbent

As a continuation of our previous research and studies, Amoko et al.(2023) on adsorption (Ads) of As from aqueous solution, Amoko et al.(2024) on Ads equilibrium models; Fehintola et al.(2018) on the mechanism of As Ads by P_{II}; Obijole et al.(2022) on reviews of techniques for As reduction, Oke et al.(2008) on As Ads with its kinetic and Ads equilibrium models., powdered eggshells (P_{II}) were utilised as adsorbents for As and Pb ions removal or reduction from typical As and Pb contaminated surface water. The microstructure of P_{II} was examined utilising a scanning electron microscope (SEM, Carl Zeiss Smart Evo 10 of secondary electron imaging (SEI) detector, system vacuum of 89e06Torr and WD of 9.14 mm at different magnifications). This examination of the microstructure of P_{II} was steered with the support of the backscattered electron detector, delivering compositional contrast and the secondary electron detector (SED) delivering topographical evidence of P_{II}. Energy Dispersive Spectroscopy (EDS) of P_{II} was utilised to establish the elemental composition of the acknowledged phase while check-ups of P_{II} were conducted in the high vacuum mode.

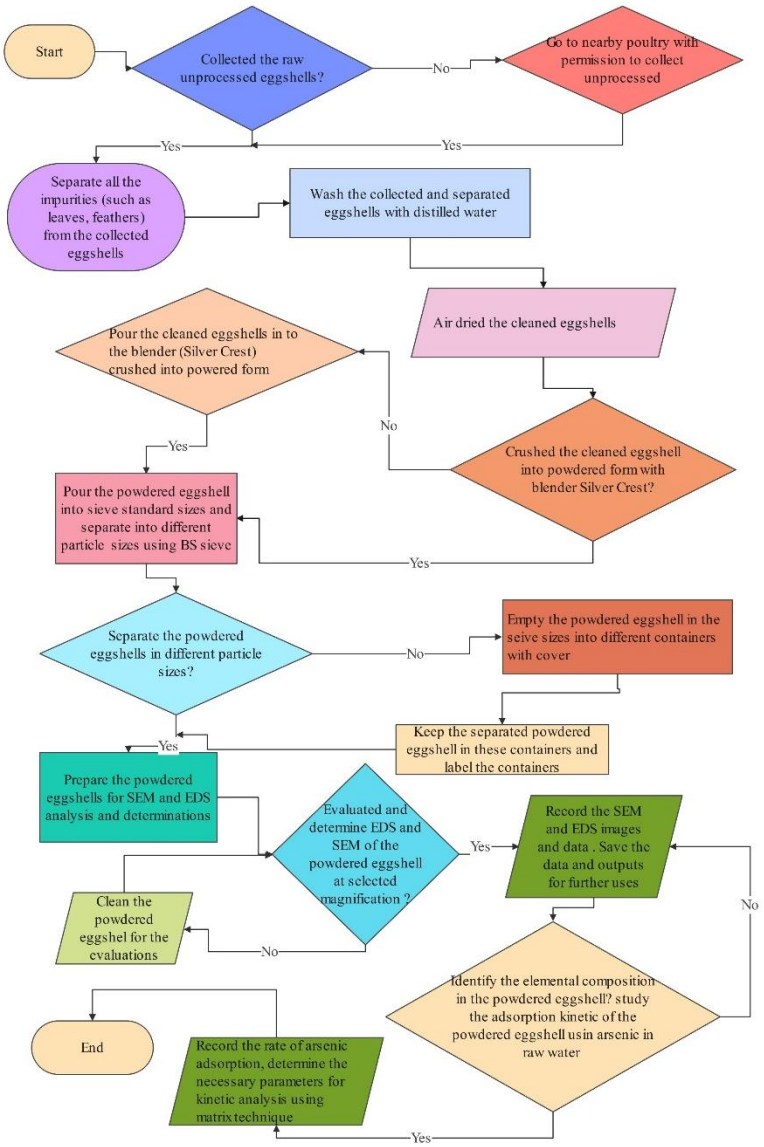

Figure 3: Flowchart for the overall methodology of the study

Estimation of Ads Capacities of the Adsorbent

The Ads capacities of the adsorbent for T_{ac} (Aponmu River in Elizade University, Ilara- Mokin, Nigeria, Figure 4, at different pH values such as .2, 6.4, 3.2 and 11.5) were evaluated using these selected Ads kinetics models. These pH values were adjusted using NaOH or HCl. The details of preparations of P_{II}, and properties of the adsorbent are presented in some of the previous studies such as Amoko et

al. (2023; 2024); Obijole et al. (2022) and Oke et al. (2008). Ads kinetics isotherms were determined utilising different masses of the adsorbent and dosages of As Ads equilibrium and kinetics. It was computed and evaluated as follows:

$$q_t = \frac{(C_{tn} - C_{tf})}{M_{ad}} V_{in} \quad (1)$$

Where: q_t is the Ads capacity of the P_{II} at equilibrium (mg/g), C_{tn} is the initial dosage of A_{se} in the aqueous solution (mgl^{-1}), C_{tf} is the experimental dosage of A_{rs} in the aqueous solution at equilibrium (mgl^{-1}), M_{ad} is the weight of adsorbent (P_{II}) added (g) and V_o is the volume of prepared As aqueous solutions utilised. The dosage of As in both raw and treated water samples was determined using procedures and techniques as stated in Standard Methods as stated in APHA (2019) and Van Loosdrecht et al. (2016).

Evaluation of Ads Kinetics and Impacts of Selected Operational Factors

Impacts of initial pH of Pb and As aqueous solutions on Ads capacity were established utilising Analysis of Variance (ANOVA) at a 95 % confidence level. Regression analysis of the pollutant removed and Ads kinetic concerning time and pH values were established.

Figure 4: Detailed sampling point at Elizade Reservoir(Source: Google Earth Pro Map, 2024)

RESULTS AND DISCUSSION

Results from this research and study are presented and discussed in the following categories:

Properties and Characteristics of the Water Samples

Table 1 presents a statistical briefing and summary of the selected water characteristics and quality parameters of the raw water measured. The Table established that the average dosages of physical parameters (turbidity, suspended solids, and dissolved solids) were 881.12 mg/l, 97.44 mg/l, and 290.44 NTU, respectively. The average dosages of chemical parameters (pH, chloride, DO and COD) were 6.48, 255.67 mgl^{-1}, 3.71 mgl^{-1}; and 188.36 mgl^{-1} , respectively. The average dosages of selected toxic and health-related parameters (As, and Pb) were 0.79 mg/l, and 0.55 mg/l, respectively. High dosages of these selected parameters in Aponmu River can be attributed to anthropogenic or human-caused activities such as farming (rearing of animals production of cash crops and annual crops), mining and industrial activities, which support erosion and discharge of various chemicals. This observation on the influence of anthropogenic or human-caused activities on characteristics or water quality of surface water agrees with conclusions and observations made in the studies such as Wera et al.. (2019), Cunha Richard et al. (2020), Jahangiry Fard et al. (2019), Luo et al. (2020) .and Lee et al. (2020).

Properties of the Adsorbent

Figure 5 presents the Scanning Electron Microscope (SEM) of the adsorbent at various amplifications. The results of the Scanning Electron Microscope (SEM) are shown in Figure 5. The Scanning Electron Microscope (SEM) discovered that micrographs were utilised to evaluate the surface pore variations and morphology of the P_{weg} as an adsorbent before the Ads process. Based on these features and facts, it was established that the surface of the utilised P_{II} was permeable with a huge number of pores which brands it suitable for the Ads of A_{rs}. Figures 5a, b, c and d display the results of the SEM. Figures 5a (at 40 x 10^{-6} m and magnification of 750) and 5b (at 30 x 10^{-6} m and magnification of 1000) delivered an indication of the microstructural geomorphology of the P_{II}. These two figures also offer information on assorted homogeneousness and the isolation of the micro-constituents. In these two figures, a fair dispersal of constituents of P_{II} was observed with a manifest lack of segregation in the P_{II}. Nevertheless, at a lower magnification of the micrograph (Figure 5c), it was revealed that small sections of agglomeration exist, where the boundary tends to form clusters. Also at lower magnification, the aperture structure is superficial. The pores are consistently sized and saturate the whole structure. These physical pores cover the surface area of the P_{II} and support the Ads process of the adsorbent. Figure 5 (c and d) provides structural details and geometry. Figures 5c and 5d revealed the topographic anatomy of the pores. It is superficial in these figures that the pores are consistent and not blind pores. It also confirms the all-embracing nature of the pores. From these figures (5a, b and c), the constituent parts of the P_{II} are discernible. The porosity is understood to be an outcome of constituent parts assembling against each other. These results were in line with the previous research findings and studies such as Ajala et al. (2018); Hee-Jong (2019) and Hess et al. (2018) on the composition of eggshells.

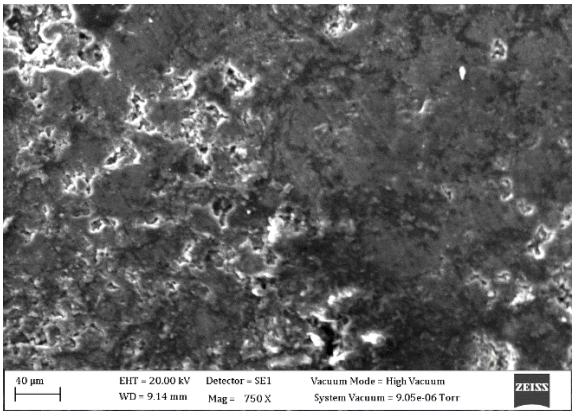

Figure 5a: SEM of Pll at 40 x 10-6 m and magnification of 750X

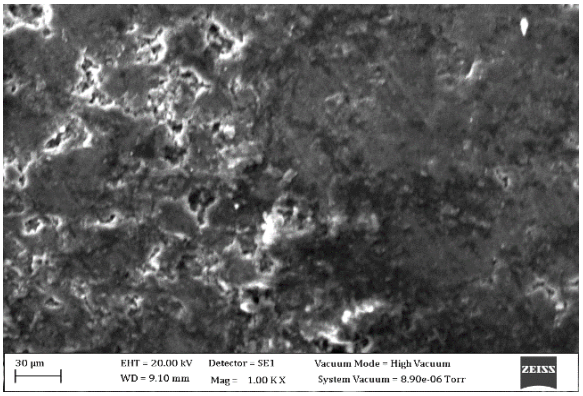

Figure 5b: SEM of Pll at 30 x 10-6 m and magnification of 1.0KX

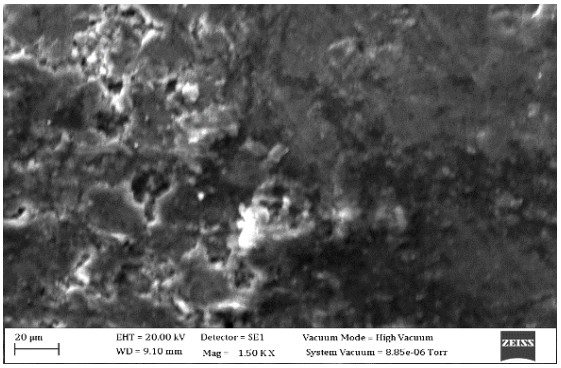

Figure 5c: SEM of Pll at 20 x 10-6 m and magnification of 1.5KX

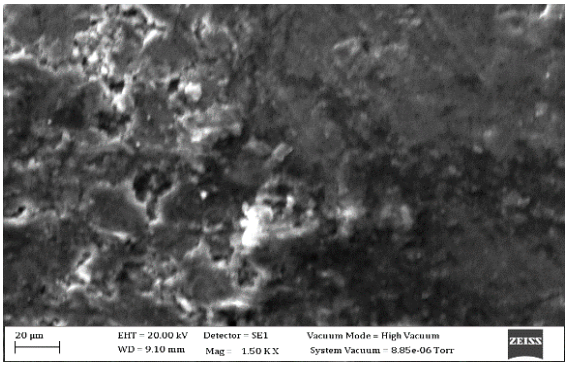

Figure 5d: SEM of Pll at 20 x 10-6 m and magnification of 1.5KX

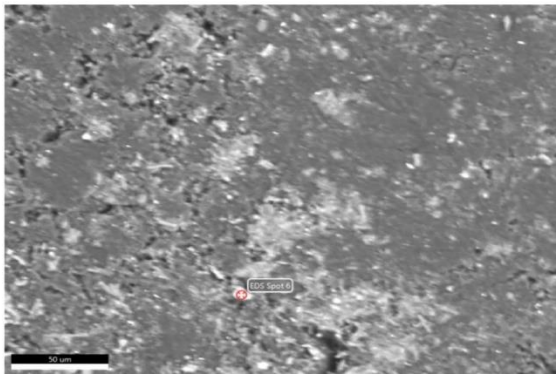

Figure 6ai: EDS of Pll at Spot 6 at 20 x 10-6 m

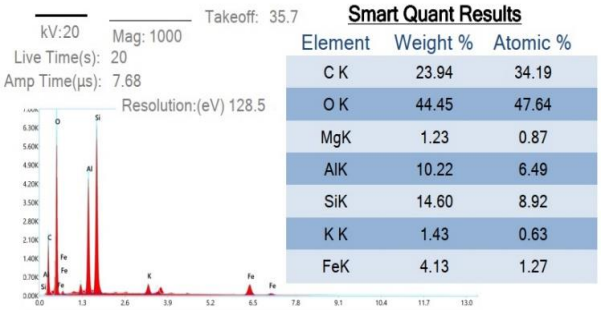

Figure 6aii: Smart Quant Results of Spot 6 at 20 x 10-6 m

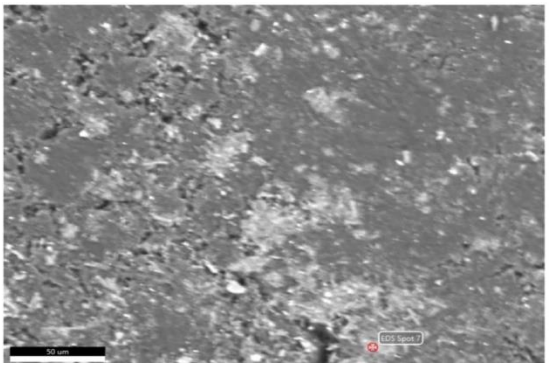

Figure 6bi: EDS of Pll at Spot 7 at 20 x 10-6 m

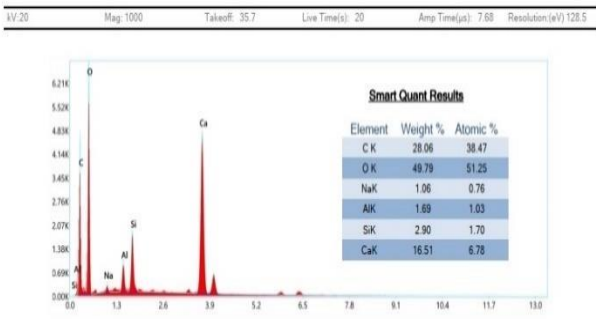

Figure 6bii: Smart Quant Results of Spot 7 at 20 x 10-6 m

Table 1: Statistical briefing and summary of water characteristics and water quality measured

Description	Average	Minimum	Maximum	Skewness	Standard Deviation	Coefficient of Variation
pH	6.48	6.20	6.76	0.01	0.281	4.34
Dissolved Solid (mg/l)	881.12	876.80	884.73	-0.76	4.012	0.46
Chloride (mg/l)	255.67	247.89	266.86	1.36	9.936	3.89
Suspended Solids (mg/l)	97.44	85.76	117.81	1.68	17.701	18.17
Turbidity (NTU)	290.44	270.00	307.59	-0.76	19.009	6.54
As (mg/l)	0.79	0.73	0.86	0.74	0.067	8.48
Pb (mg/l)	0.55	0.42	0.65	-1.07	0.119	21.72
Chemical Oxygen Demand (mg/)	188.36	185.89	192.01	1.43	3.228	1.71
Dissolved Oxygen (mg/l)	3.71	2.72	4.82	0.48	1.057	28.45

Figure 6 presents the results of the EDS of the adsorbent at 20 x 10^{-6} m. These two figures of 6a, and 6b established that the major configuration of the P_{II}. These two figures pin that the major configurations of the P_{II} are Sodium, Oxygen, Aluminium, Carbon, Magnesium, Silicon, Potassium, Iron and Calcium. The proportions of these elemental compositions are Aluminium (1.03 – 6.49 %), Calcium (0.00 - 6.68 %), Silicon (1.70 – 8.92 %), Carbon (34.19-38.47 %), Iron (0.00 – 1.27 %), Oxygen (47.64- 51.25%), Sodium (0.00-0.76%), Magnesium (0.00- 0.87%) and Potassium (0.00- 0.87 %). These results established that Carbon, Oxygen, Silicon, Aluminium and Calcium had the highest weight proportions (Figures 8a and 8b). Higher proportions of Carbon and Oxygen can be attributed to the availability of organic matter such as eggshell membranes. The other metallic elements in the adsorbent structure were Mg, Na, K, Fe with their equivalent weight proportions. SEM and EDS of eggshells pinned that the compositions and components of eggshells are similar but vary with changed proportions of these elemental and metallic configurations. These observations of SEM and EDS established several studies such as Ajala et al. (2018), Hee-Jeong (2019), and Hess et al. (2018).

Removal of As and Pb ions and Ads Capacities of P_e

Figure 7 presents the dosage of As and Pb in the contaminated water concerning the treatment time, respectively. Figure 7a revealed that the rate of Ads of As dosage from contaminated water decreases with increasing treatment time, which is in the form of a negative exponential. Figure 7b revealed that the rate of Ads of Pb dosage from contaminated water declines with increasing treatment time, which is in the form of a negative exponential. The figure established that the removal of As by the adsorbent was in the two phases of non-linear for the first phase which can be attributed to the availability of pores and electrostatic attractions. The removal of As in the second phase can be attributed to electrostatic attraction only as the pores within the adsorbent might have been filled up. These observations support conclusions and observations made in previous studies such as Caballé-Serranoet al. (2019); Hu et al. (2022); Mahmoud et al. (2021); Najafinejad et al. (2023); Güzel et al. (2024); Günes et al. (2024); Roe. (2024); Zhang et al. (2021); Xu et al. (2022); Wang et al. (2013; 2022); Miao et al. (2022); Medykowska et al. (2022); Liu et al. (2022); Khanam et al. (2019); González-López et al. (2022); Gendy et al. (2021); Crini and Lichtfouse (2019).

Figure 8 presents the proportion of As and Pb dosage removed from contaminated water with respect to the treatment time, respectively.

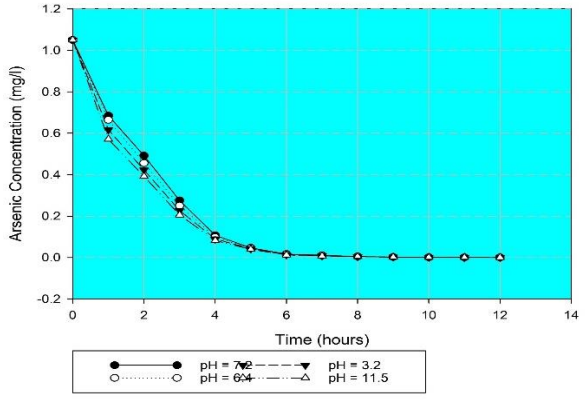

Figure 7a: Concentration of Arsenic in the contaminated water during adsorption and time of treatment

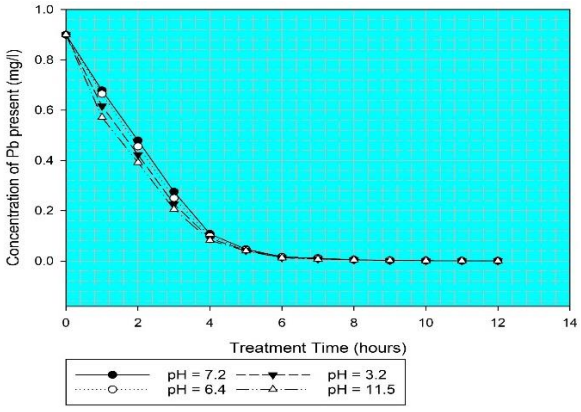

Figure 7b: Concentration of Lead ion in the contaminated water during adsorption and time of treatment

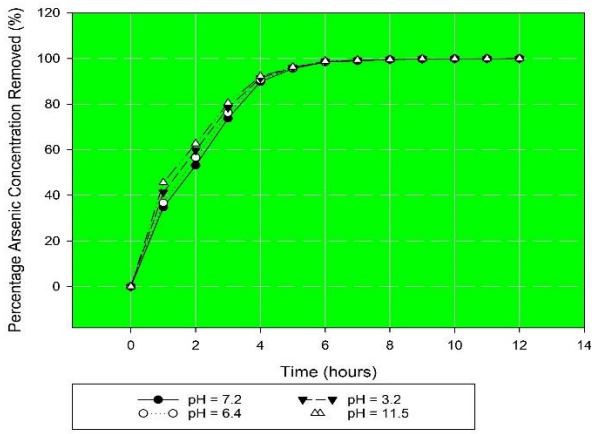

Figure 8a: Proportion of arsenic removed onto powdered eggshell at different pH and Time

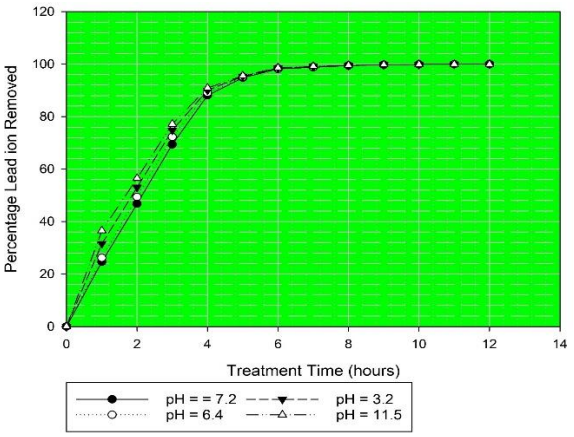

Figure 8b: Proportion of lead removed onto powdered eggshell at different pH and Time

Figure 8a revealed that the cumulative removal rate of As dosage from contaminated water increases with increasing treatment time, which can be established to be in the form of positive exponential expression. In addition, Figure 8b revealed that the cumulative removal rate of Pb dosage from contaminated water increases with increasing treatment time, which can be established to be in the form of positive exponential expression. The shape of these Figures (8a and 8b) is the reverse of Figure 7. Figure 8 revealed that the proportion of As and Pb removed from the contaminated water improves with cumulative treatment time, which is in the form of a positive exponential. The figure established that the removal of As and Pb by the adsorbent was in the two phases of non-linear for the first phase which can be attributed to the availability of pores and electrostatic attractions. The removal of As in the second phase can be attributed to electrostatic attraction only as the pores within the adsorbent might have been filled up. These observations support conclusions and observations made on the proportion of heavy metals or adsorbates removal in previous studies such as

Impacts of Operational Factor (pH) on Ads Kinetics and Mechanism of P_e

Figure 9 presents the Ads kinetics of As and Pb dosage removed from contaminated water with respect to the treatment time, respectively. Figure 9a revealed that the cumulative Ads kinetics of As dosage from contaminated water increases with increasing treatment time, which can be established to be in the form of positive exponential expression. In addition, Figure 9b revealed that the cumulative Ads kinetics of Pb dosage from contaminated water increases with increasing treatment time, which can be established to be in the form of positive exponential expression. The shape of these Figures (9a and 9b) is the reverse of Figure 7, but similar to Figure 8. Figure 9 revealed that the Ads kinetics of As and Pb removed from the contaminated water improves with cumulative treatment time, which is in the form of positive exponential. The figure established that the removal of As and Pb by the adsorbent was in the two phases of non-linear for the first phase which can be attributed to the availability of pores and electrostatic attractions. The removal of As in the second phase can be attributed to electrostatic attraction only as the pores within the adsorbent might have been filled up. These observations support conclusions and observations made on kinetics and mechanism of Pb, As and other metals removal in previous studies such as Zhang et al. (2021), Xu et al. (2022); Wang et al. (2022), Wang and Guo (2023), Wang and Guo (2020), Tong et al. (2019), Sen and Chattoraj (2021), Raji et al. (2023), Obijole et al. (2022), Nethaji et al. (2022); and Liu et al. (2022).

Table 2a shows the impacts of pH and Time on the performance of the adsorbent using typical As-contaminated water. In the case of Time, the Table revealed that the F- value was 501.488 and p was 2.1 x 10^{-33} ($F_{11, 33}$ = 501.488 and p was 2.1 x 10^{-33} which is less than 0.05), which indicates that treatment time in the Ads process is a significant factor in the Ads of As from typical surface water. Similarly, in the case of the initial pH of the typical raw surface water, the Table revealed that the F- value was 4.781 and p was 0.0071 ($F_{3, 33}$ = 4.781 and p was 0.007 which is less than 0.05), which indicates that initial pH of the aqueous solution during the Ads treatment process is a significant factor in the Ads of As from typical surface water. In addition, Table 2b shows the impacts of pH and Time on the performance of the adsorbent using typical Pb-contaminated water. In the case of Time, the Table revealed that the F- value was 561.9341 and p was 3.25 x 10^{-34} ($F_{11, 33}$ = 561.9341 and p was 3.25 x 10^{-34} which is less than 0.05), which indicates that treatment time in the Ads process is a significant factor in the Ads of Pb from typical surface water. Similarly, in the case of the initial pH of the typical raw surface water, the Table revealed that the F- value was 4.866138 and p was 0.006535 ($F_{3, 33}$ = 4.866138 and p was 0.006 which is less than 0.05), which indicates that initial pH of the aqueous solution during the Ads treatment process is a significant factor in the Ads of Pb from typical surface water. The influence of pH and mechanism of Ads of As and Pb by powdered eggshells can be attributed to several factors such as composition of the eggshells (these cations: Al^{3+}; Fe^{2+} or Fe^{3+} and Ca^{2+} carry charges which can precipitate or facilitate removal of Pb and As ions from the aqueous solution through coagulation or precipitation process), chemical, precipitation and electrostatic reactions of the components is a made of calcium salt also known as calcite material. It has been proposed that in the occurrence of water, some metallic elements such as aluminium, iron and calcium salts undergo placement or displacement reactions as presented or indicated in equation (2) as follows (Bai et al., 2023; Zhang et al., 2021; Xu et al., 2022; Wang et al., 2022; Wang and Guo, 2023):

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

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

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

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

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

In equation (2a) forms the aluminium hydroxide bayerite ($Al(OH)_3$) and hydrogen, in equation (2b) the final product is aluminium hydroxide boehmite (AlO(OH)) and hydrogen, and in equation (2c) the products are aluminium oxide and hydrogen. All these reactions and products of aluminium salts are thermodynamically supported or favourable reactions starting from room temperature to the melting point of aluminium (660^0C). In addition, all these reactions are highly exothermic reactions. Starting from the room temperature to a temperature of 280^0C, $Al(OH)_3$ is the most stable product, while from 280 to 480^0 C, AlO(OH) is the most stable. Above 480 ^{0}C, Al_2O_3 is the most stable product. This result shows that the P_{ll} underwent the reaction in equations (3 and 4) with Pb and As ions, which altered the pH value and the product formed reacted with As ion to precipitate the pollutant as calcium, aluminium and iron salts (Zhang et al., 2021; Xu et al., 2022, Wang et al., 2022; Wang and Guo, 2023). Ads-precipitation reaction (this process is mainly controlled by the molecule's transport and electron transfer rate at the interface of adsorbent and adsorbate as follows (Sen and Chattoraj, 2021; Raji et al., 2023):

$R + M \rightarrow M - R_{ads}(adsorption\ reaction)$ (3)

$M - R_{ads} + e^- \rightarrow M - R_{ads,ox}(direct\ charge\ electron\ reaction)$ (4)

R and M are As molecules and adsorbent surfaces, respectively.

The influence of pH on Ads kinetics parameters of As and Pb ions by powdered eggshells and the mechanism of Ads can be attributed to several factors which include the composition of the eggshells and the pollutant reaction (carbon, Oxygen and Silicon, which are passive and inactive to pH reaction and adjustment) such as equation (5) to (15):

For As ion removal (Sen and Chattoraj, 2021; Raji et al., 2023):

$H_3AsO_3 \rightarrow H^+ + H_2AsO_3^-$ pKa = 9.22 (5)

$H_2AsO_3^- \rightarrow H^+ + HAsO_3^{2-}$ pKa = 12.3 (6)

$H_3AsO_4 \rightarrow H^+ + H_2AsO_4^-$ pKa = 2.2 (7)

$H_2AsO_4^- \rightarrow H^+ + H_2AsO_4^{2-}$ pKa = 7.08 (8)

$HAsO_4^{2-} \rightarrow H^+ + AsO_4^{3-}$ pKa = 11.5 (9)

Where; pKa is the pH at which disassociation of reactant is 50 % complete

For Pb ion removal (Sen and Chattoraj, 2021; Raji et al., 2023):

Metal ion exchange:

$Z(OH)_n + Pb \rightarrow Pb(OH)_2 + Z^{n+}$ (10)

Complexation: $R - NH_2 + Pb^{2+} \rightarrow R - NH_2 - Pb^{2+}$ (11)

$R - C = O + Pb^{2+} \Leftrightarrow R - C = O - Pb^{2+}$ (12)

$R - OH + Pb^{2+} \Leftrightarrow R - OH - Pb^{2+}$ (13)

Ion-Exchange: $(R - OH)_2^- + Pb^{2+} \Leftrightarrow (R - OH)_2 - Pb^{2+} + 2H^+$ (14)

$R - NH_3^+ + Pb^{2+} \Leftrightarrow R - NH_2 - Pb^{2+} + H^+$ (15)

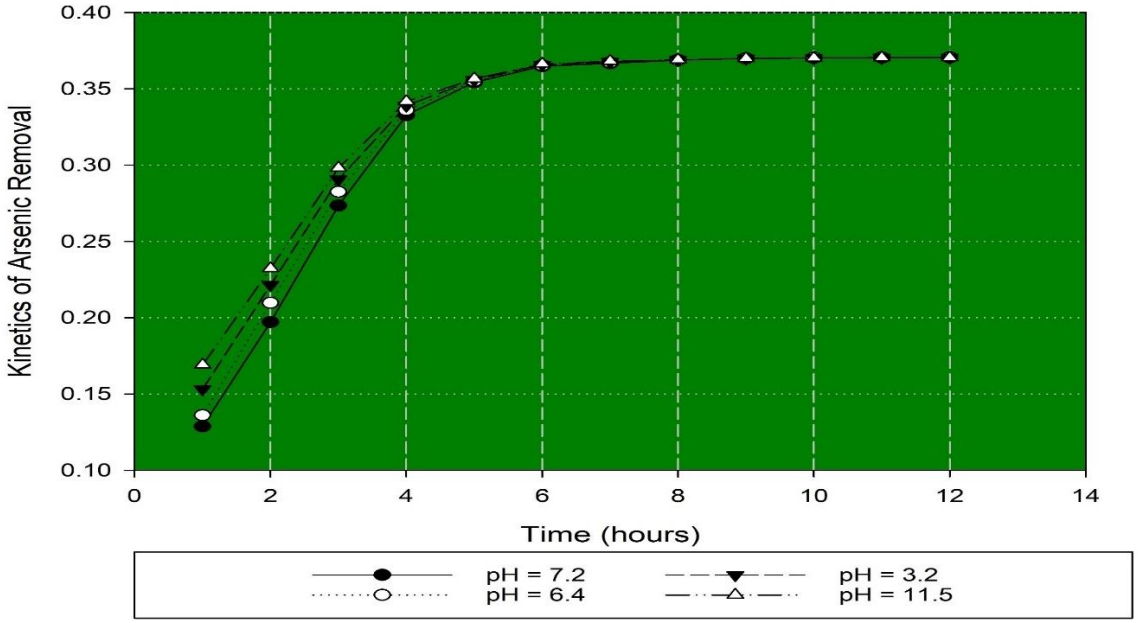

Figure 9a: Kinetics of arsenic removal onto powdered eggshell at different pH and Time

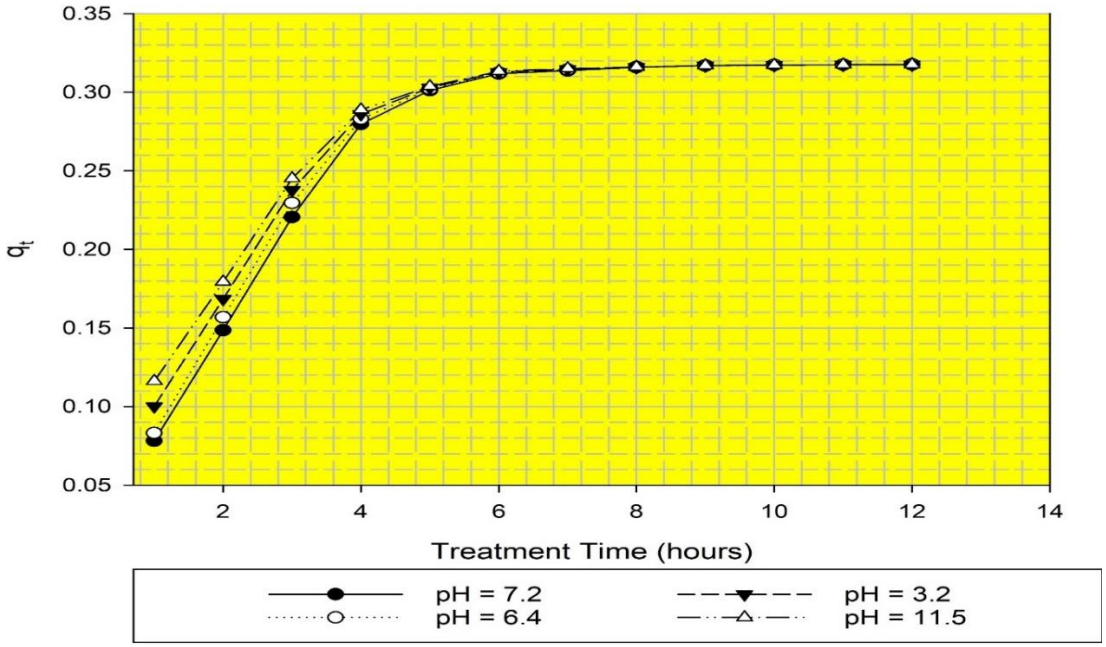

Figure 9b: Kinetics of lead removal onto powdered eggshell at different pH and Time

Table 2a: Effects of pH and Time on the performance of the adsorbent using typical As-contaminated water

Source of Variation (SV)	Sum of Squares (SS)	Degree of freedom (df)	Mean Sum of square(MSS)	F-value	P-value	F crit
Within the Time	0.239777	11	0.021798	501.488	2.1×10^{-33}	2.093254
Between the pH	0.000623	3	0.000208	4.781	0.007108	2.891564
Error	0.001434	33	4.35×10^{-5}			
Total	0.241835	47				

Table 2b: Effects of pH and Time on the performance of the adsorbent using typical Pb- contaminated water

SV	SS	df	MSS	F-value	P-value	F crit
Within the Time	0.237958	11	0.021633	561.9341	3.25×10^{-34}	2.093254
Between the pH	0.000562	3	0.000187	4.866138	0.006535	2.891564
Error	0.00127	33	3.85×10^{-5}			
Total	0.23979	47				

CONCLUSION

Based on the study and the findings, the following key conclusions can be drawn as follows:

Arsenic and Pb ions can be adsorbed by P_e at different pHs (acidic, neutral and basic media);

pHs and treatment time are significant factors that influence Ads kinetics.

Ads of Pb and As ions increases with increasing pH and time

Ads mechanism of Pb and As ions onto P_e was based on ion-exchange and complex reactions based on the composition of the adsorbent

DATA AVAILABILITY STATEMENT

The data supporting this research's findings are available on request from the corresponding author.

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