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Adsorption Mechanisms and Structures of Arsenic Removed

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ABSTRACT

The toxicity of arsenic ions and salts in the environment (air, water, and land) has made it among the most common elements that have to be removed or reduced in the environment. This paper proposed possible mechanisms of arsenic removal or reduction by powdered raw eggshells through adsorption techniques. 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 using a Silver Crest blender. Energy Dispersive Spectroscopy and scanning electron microscope images of the powdered eggshell were evaluated at selected magnifications. The study revealed that 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 48.75and 58. 13% of the adsorbent as oxygen) had the highest weight percentages. The other elements present in the adsorbent structure were Na, Mg, K, and Fe. It was revealed based on the components of eggshell and previous studies that the possible mechanisms of arsenic removal by powdered eggshell include:

$$\equiv\left[Fe-OH\right]_{(s)}+H_2AsO_4^-\rightarrow\equiv Fe-OAsO_3H+OH^-$$

$$XMnOOH_2^++H_2AsO_4^-\rightarrow XMnOOH-H_2AsO_4$$

$$XMgOH_2^++H_2AsO_4^-\rightarrow\left(XMgOH_2\right)_2-H_2AsO_4$$

$$SOH+H_3AsO_4 \rightleftharpoons SHAsO_4^-+H_2O+H^+$$

$$M\left(OH\right)_2+H_2AsO_4^-\leftrightarrow M\left(OH_2\right)_s-H_2AsO_{4(s)}^-$$

The study concluded that the removal or reduction of arsenic by powdered eggshells is a function of the following factors pH of the aqueous solution, the composition of the aqueous solution, the presence of hydroxyl groups ions and the nature of the aqueous solution. The mechanism of arsenic removal includes redox, H-bond and surface complexation formations, electrostatic attraction, oxic and anoxic reactions.

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INTRODUCTION

Environmental pollution control and protection have been critically considered in scientific and engineering communities (Koohzad *et al.,* 2019). The effluents that are incessantly discharged into the environment through industries and municipal activities play the most notable role in the pollution of the environment, groundwater and surface waters. The food-chain pyramid obtains metals through anthropogenic and non-anthropogenic pollution. Man, which is at the peak of this pyramid takes pre-concentrated heavy metals, some of which are harmful and toxic to man and animals (Deliyanni *et al.,* 2015; Wei et al., 2016). In addition, different crops would absorb heavy metals from soil enrichment heavy metal, which in turn would enter into a complex food chain. The presence of these heavy metals would then cause grave ecological problems and risks (Wakeel *et al.,* 2020).

In humans, long-term exposure or contact with these contaminated and polluted soils tend to impact negatively on the central nervous, respiratory and gastric systems (Wang *et al.,* 2022; Khanam *et al.,* 2019; Tseng *et al.,* 2019). Arsenic, which is one of these heavy metals is a carcinogenic and toxic metalloid. Arsenic is a naturally presence metalloid that exists throughout the environment in food, soil, water, and air. The consumption and exposure to high echelons of arsenic concentration by animals and humans has been associated with cancer of the bladder, kidney, lungs and skin. In addition, exposure and intake of high concentrations of arsenic have been related to cancer of the cardiovascular and neurological systems (Babaeivelni *et al.,* 2014).

Further studies and literature on the effects of human and relevant human 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); Lin et al. (2018); 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.* (2018; 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); Han et al. (2009); Ajala *et al.* (2018); Guo *et al.* (2022); Ghosh and Sil (2015); Calatayud Laparra Llopis (2015); Bailey and Fry (2015) and Calatayud *et al.* (2022). Figure 1a presents the different targets and signalling pathways of arsenic toxicity. Figure 1b presents the effects of arsenic exposure on animals. 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. Table 1 presents some of the previous studies on arsenic reduction and removal utilizing adsorption treatment methods.

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. Figure 2 shows several ways adsorption can take place in the environment. Figure 3 presents the summary of phytoremediation processes in plants. Figure 4 describes adsorption mechanisms in both oxic and anoxic as a function of pH values. Figure 5 explains the potential mechanisms of adsorption and immobilization of pollutants on biochar-based adsorbents. Figure 6 presents a schematic diagram of developing and manufacturing bio-char-based nanocomposites. 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. 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 used 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. 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.

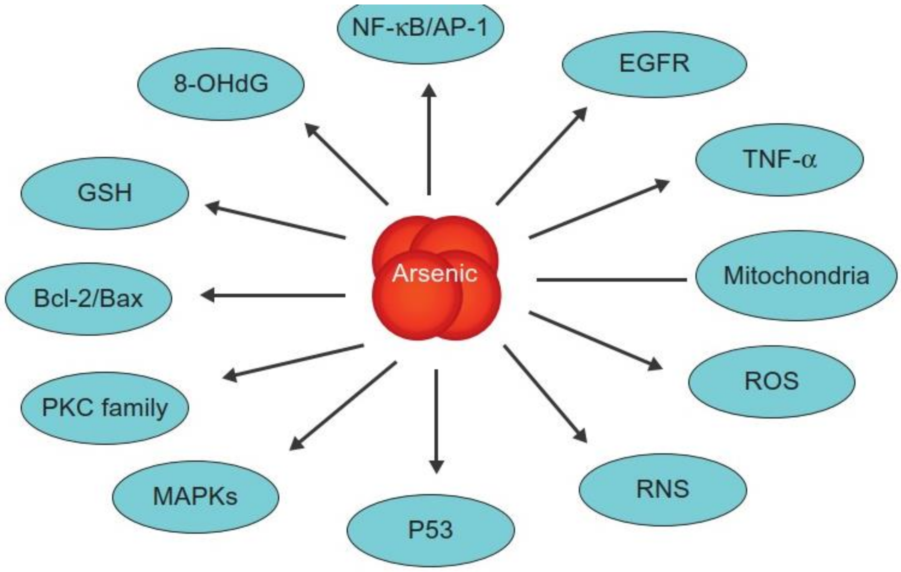


Figure 1a Different targets and signaling pathways of arsenic toxicity (Source: Ghosh and Sil, 2015)

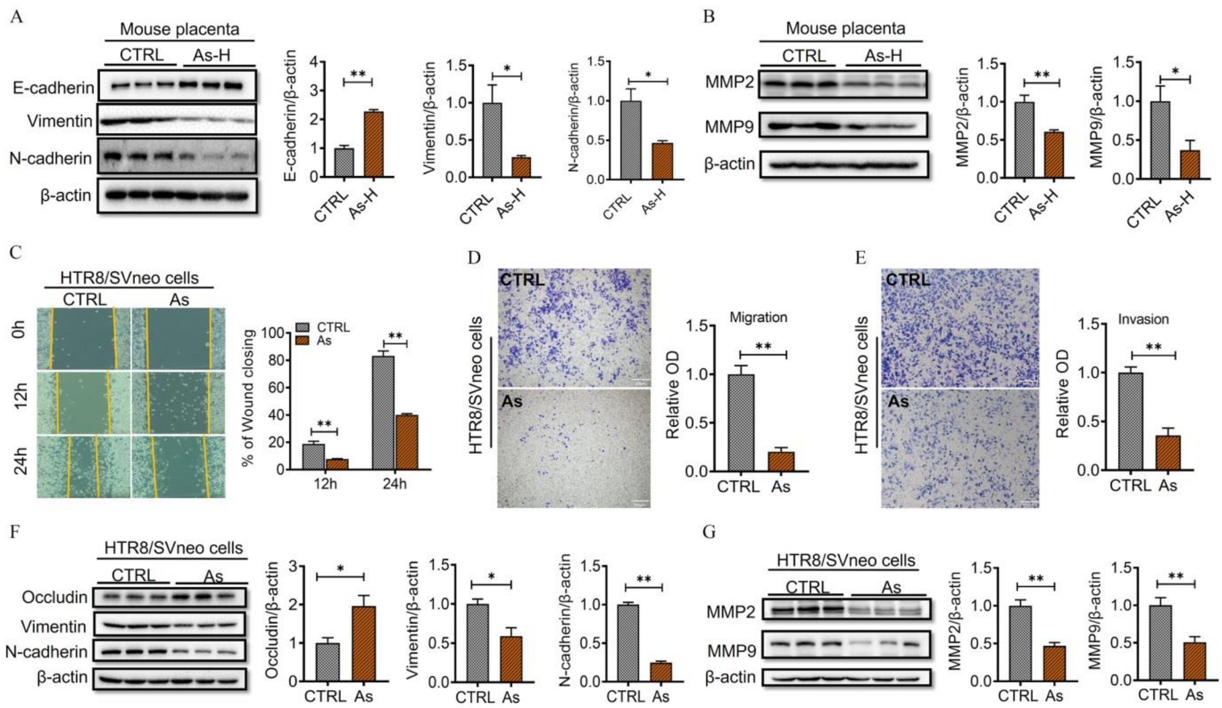


Figure 1b The effects of arsenic exposure on animals (Source: Song *et al.*, 2023)

Table 1 some of the previous studies on arsenic reduction and removal utilizing adsorption treatment methods (Source: Amen *et al.*, 2020).

Biochar-based sorbents	Temperature (°C)	Optimum sorbent dose (g L^{-1})	Initial As(III)/As(V) concentration (mg L^{-1})	Arsenic species	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	pH	Maximum sorption (m g^{-1})
Pristine biochars								
Rice husk	300	8	0.90	As(V)	155	0.153	6.7–7	2.59 (μg/g)
Municipal solid waste	300	16	0.90	As(V)	5	0.029	6.7–7	3.54 (μg/g)
Sewage sludge	300	16	0.90	As(V)	51	0.058	6.7–7	4.25 (μg/g)
Pine wood char	400	10	0.01–0.1	As(III)	2.73	0.41	5.0	2.6
Oak bark char	400	10	0.01–0.1	As(III)	25.4	0.86	5.0	3.0
Pine bark char	400	10	0.01–0.1	As(III)	1.88	1.06	5.0	13
Oak wood char	400–450	10	0.01–0.1	As(III)	2.04	0.73	5.0	4
	500	1	4	As(V)	475	0.2	6	3.9
	500	1	4	As(III)	475	0.2	7	3.1
Perilla leaf biochar	300	1	0.05–7.0	As(III)/As (V)	473	0.1	9.7	4.7/3.8
	700	1	0.05–7.0	As(III)/As (V)	3.2	0.01	10.6	11.0/7.2
Pine wood	600	2.5	10	As(V)	67.4	0.066	NA	0.91
Rice husk biochar	500	2	0–200	As(V)	23.2	0.009	9.5	0.35
Empty fruit bunch biochar	300–350	2	0–200	As(V)	46.3	0.008	10.2	0.42
Sewage sludge	500	10	1	As(III)	70	NA	3–3.5	0.07
Loblolly pine wood biochar	NA	NA	NA	As(V)	NA	NA	NA	10
Mulberry wood	NA	NA	NA	As(III)	NA	NA	3.5–9.5	5
Tectona leaves Biochar (TB 800)	800	4	NA	As(III)	34.55	0.1929	NA	0.66
		2	NA	As(V)			NA	1.3
Lagerstroemia leaves biochar (LB 800)	800	4	NA	As(III)	6.18	0.0499	NA	0.45
		4	NA	As(V)			NA	0.71
Modified biochars								
Magnetic-Pine wood	600	2.5	10	As(V)	463	0.022	NA	0.59
	600	2.5	10	As(V)	67.4	0.066	NA	0.91
Hydrogel Rice husk	300	0.167–16.7	1–150	As(V)	51	0.058	6.7–7	28
Mn-oxide Pine wood	600	2.5	20	As(V)	193.1	NA	NA	0.43
nZVI-Bamboo	400	2	5–400	As(V)	NA	NA	NA	24
KOH-activated MSW	NA	5	50	As(III)	NA	0.357	8.3	31
Fe-impregnated Hickory chips	550	1	50	As(V)	49.1	NA	NA	2.1
Red mud-modified rice straw	600	NA	1–50	As(V)	NA	NA	NA	5.9
Fe-modified corn stem	620	NA	0.2–50	As(III)	NA	NA	NA	8.2
Fe-coated Fruit bunch	700	5	55	As(III)	NA	NA	NA	31
		5	50	As(V)	NA	NA	NA	15
Fe-coated Rice husk	700	5	50	As(III)	NA	NA	NA	31
		5	50	As(V)	NA	NA	NA	17
AIOOH-nano-composite Cotton wood	600	2	50	As(V)	NA	NA	NA	17
Bismuth-impregnated wheat straw	500	0.1	50	As(III)	190.40	0.09	NA	16
Fe-oxide Rice husk	550	0.5	2	As(V)	77.3	NA	NA	6
MnO-modified loblolly pine wood	NA	NA	NA	As(V)	NA	NA	NA	10
Calcium-based magnetic raw straw	400	0.05	NA	As(III)	NA	NA	5	6.3
Ni/Mn-LDHs pinewood	600	0.05	0–40	As(V)	282.8	NA	7	6.3
nZVI-pine wood	600	NA	NA	As(V)	211.7	NA	4.1	124
GracilariaAlgal-based Fe-biochar	300	NA	0.113	As	NA	NA	NA	62
Oedogonium Algal-based Fe-biochar	300	NA	0.113	As	NA	NA	NA	67
$FeCl_3$/Coffee ground under CO_2	700	NA	12.4–95	As(V)	512	0.249	4.5	8.9
$FeCl_3$/Coffee ground under N_2	NA	NA	NA	As(V)	8.3	0.018	NA	13
Titanium-modified corncobs biochar	550	0.5	100	As(V)	450.43	0.052	NA	118
Fe-modified biochar powder	500	NA	1–30	As(III)	123.8	0.07	NA	56
Fe-modified biochar beads	500	NA	1–30	As(III)	NA	NA	NA	48

NA: not available data.

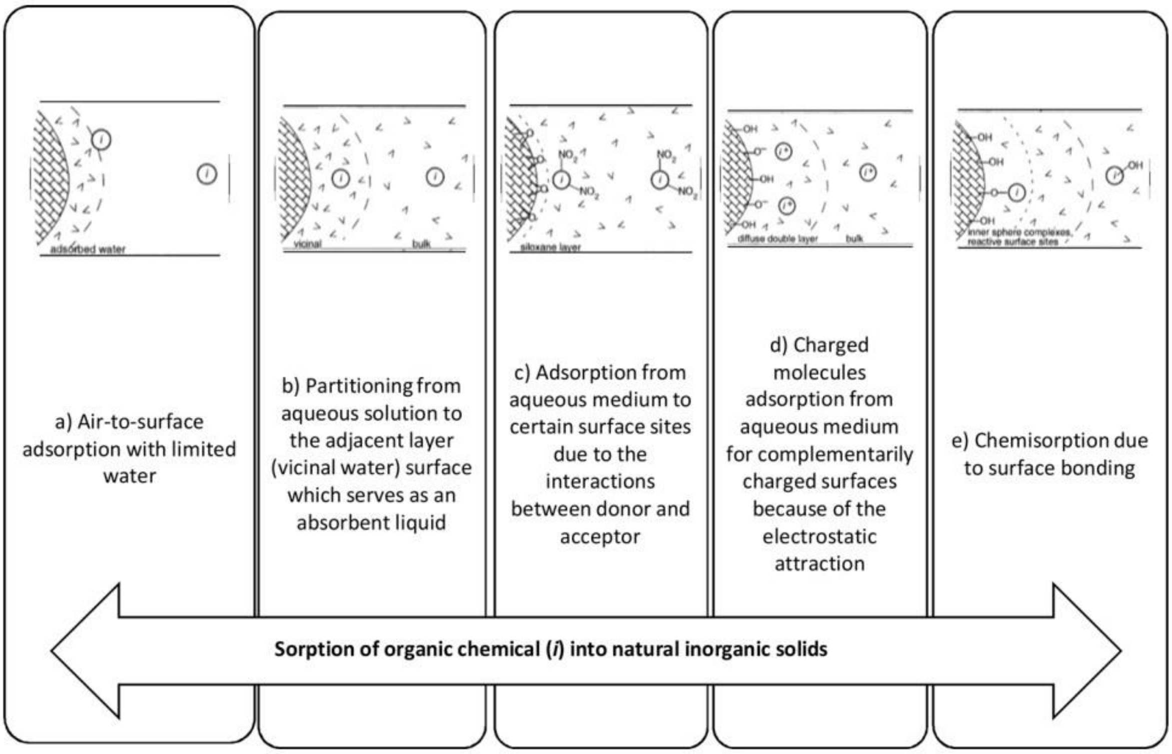


Figure 2 Several ways adsorption can take place in the environment (Source: Al-Ghouti and Da'ana, 2020).

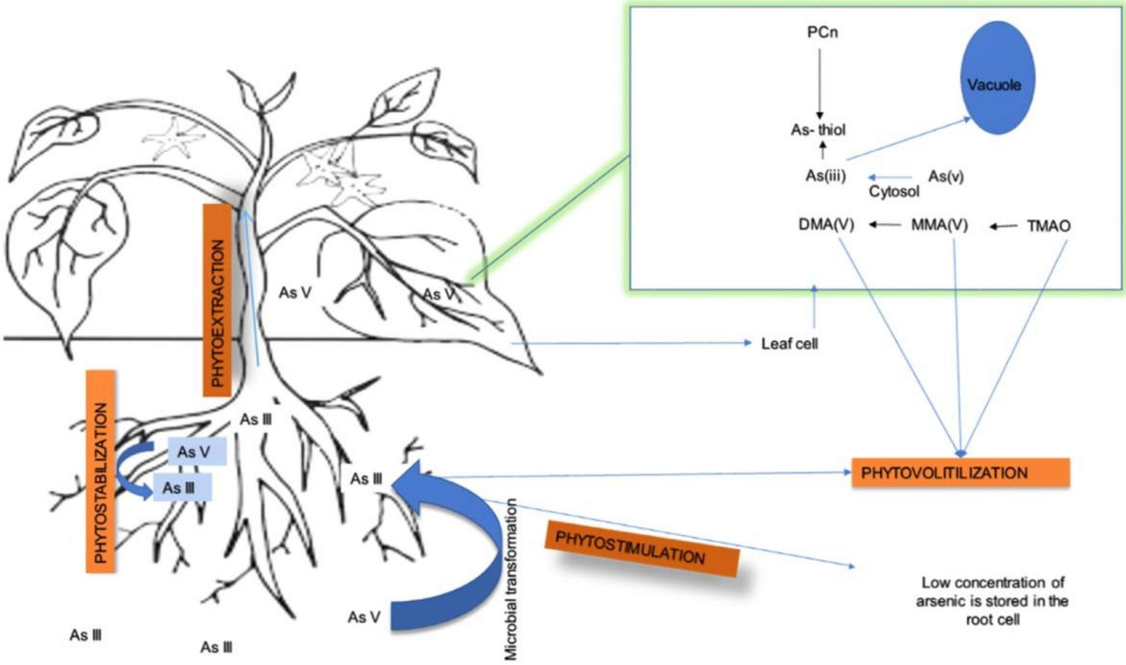


Figure 3 the summary of phytoremediation processes in plants (Source: Alka *et al.*, 2020),

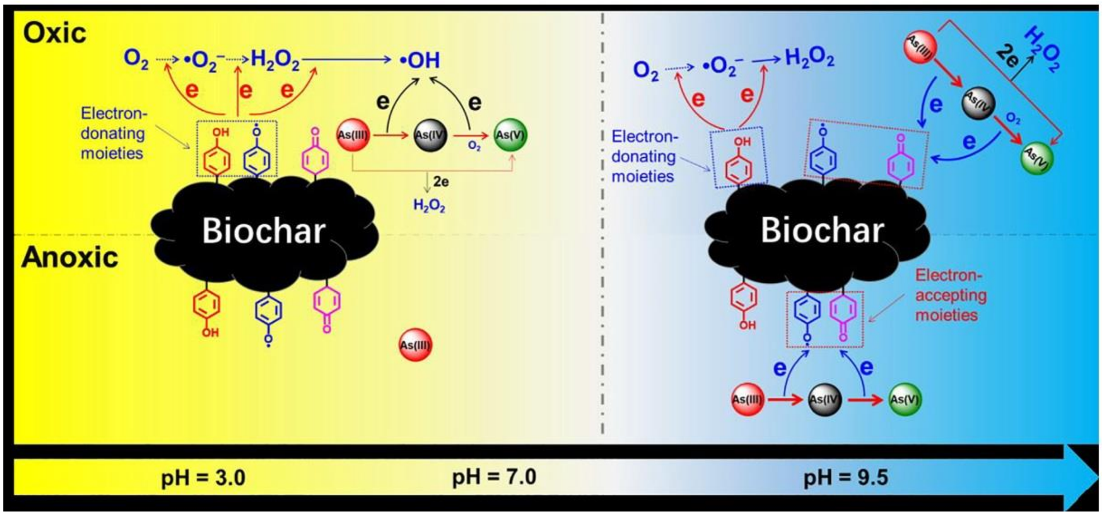


Figure 4 adsorption mechanisms in both oxic and anoxic as a function of pH values (Source: Amen *et al.*, 2020)

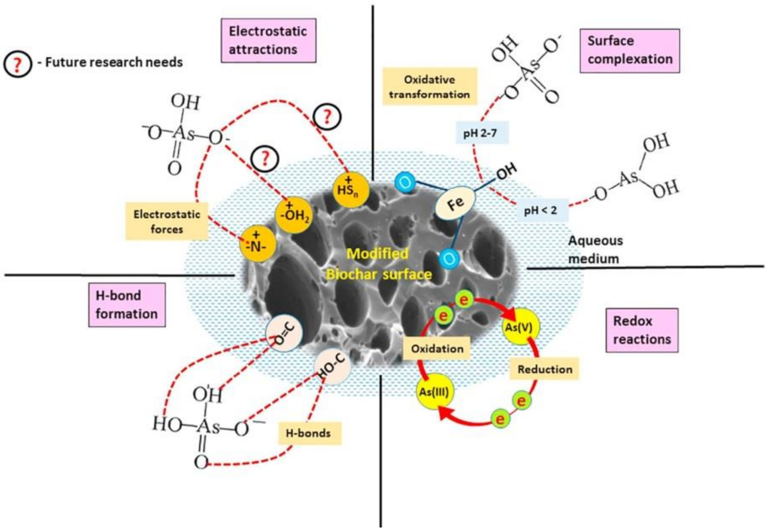


Figure 5 the potential mechanisms of adsorption and immobilization of pollutants on biochar-based adsorbents (Source: Amen *et al.*, 2020),

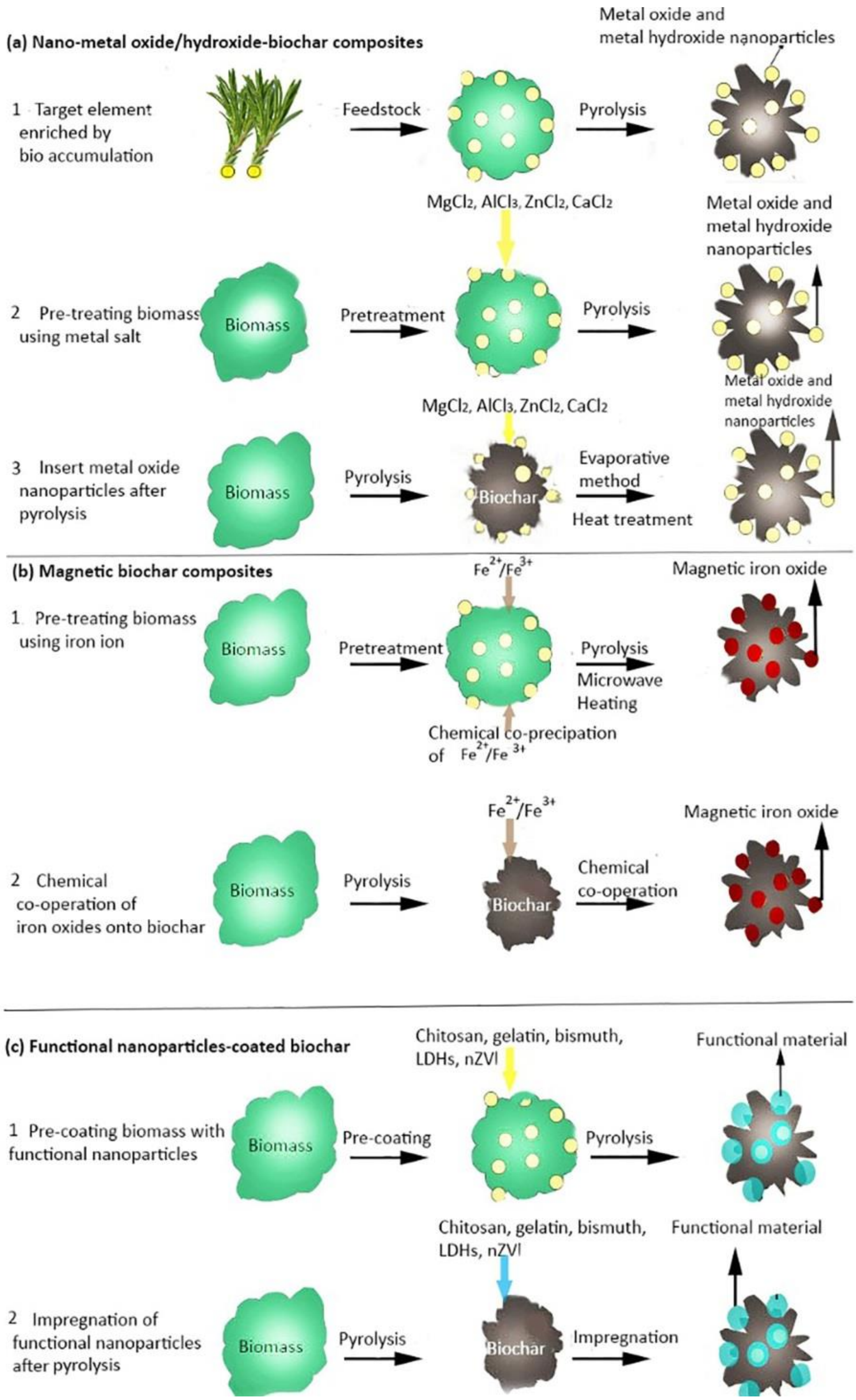


Figure 6: Schematic diagram of developing and manufacturing bio-char based nanocomposites (Source: Amen *et al.*, 2020),

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 7a presents the mechanism of arsenic species adsorption in the environment. Figure 7b shows the mechanism of arsenic removal or reduction by adsorption using activated charcoal. Figure 7c describes the mechanism and path of arsenic removal and reduction by adsorption using Fe. Figure 7d provides the path of arsenic adsorption by Fe compound. Figure 8 shows the required mechanisms for the development and production of biochar as an adsorbent.

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.* (2019a and b); Yin *et al.* (2019); Zhou *et al.* (2019); Fan *et al.* (2020); Zhu and Yan (2016); Sudhakar *et al.* (2018); Lin *et al.* (2018); 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.* (2019); Liu *et al.* (2015); Zhang *et al.* (2003); 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 and mechanism of arsenic removal by powdered eggshells are rare or not available in the literature. The main objectives of this research work are to present the arsenic adsorption mechanism by powdered eggshells from chicken eggshells.

MATERIALS AND METHODS

Powdered eggshell was prepared from raw and unprocessed chicken eggshells collected from an institutional agricultural farm in 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)*. 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. The mechanisms of arsenic removal by powdered eggshell were proposed based on the composition of the eggshell from the study and previous studies on the adsorption of pollutants by either membrane or eggshell. Figure 9 presents the summary of the powdered eggshell preparation processes and a flowchart of the methods with the materials utilised in this study.

Figure 7a Mechanism of arsenic species adsorption in the environment (water and air; Source Liu *et al*., 2015)

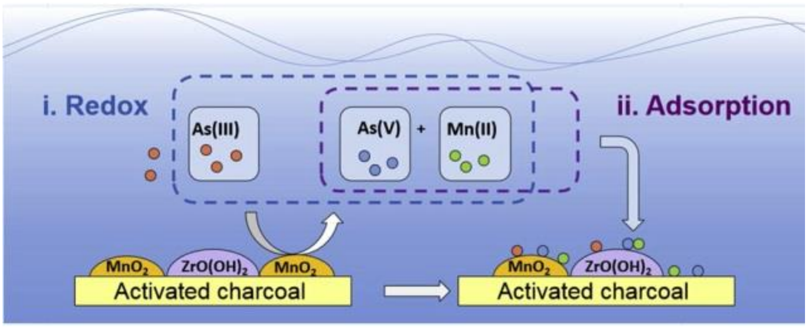


Figure 7b Mechanism of arsenic removal or reduction by adsorption using activated charcoal (Source: Yin et al., 2019)

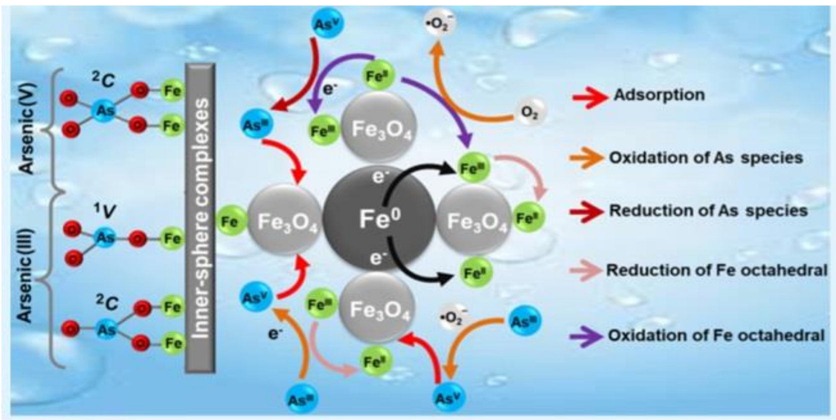


Figure 7c Mechanism and path of arsenic removal and reduction by adsorption using Fe (Source: Zubair et al., 2020)

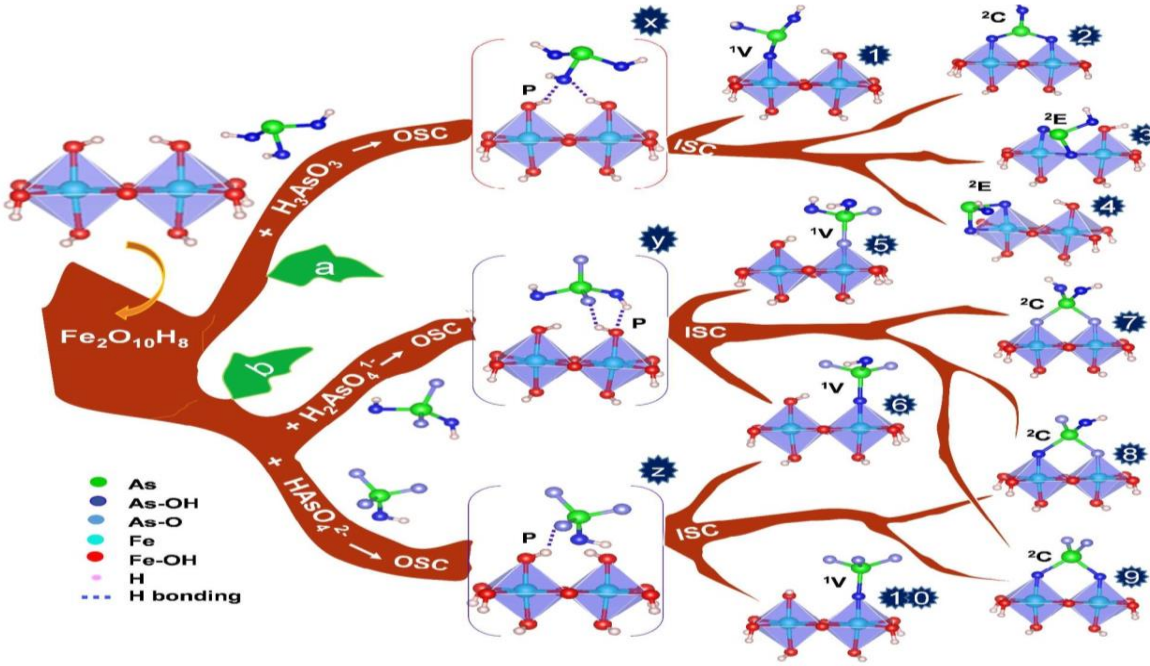


Figure 7d: Path of arsenic adsorption by Fe compound (Source: Sudhakar et al., 2018)

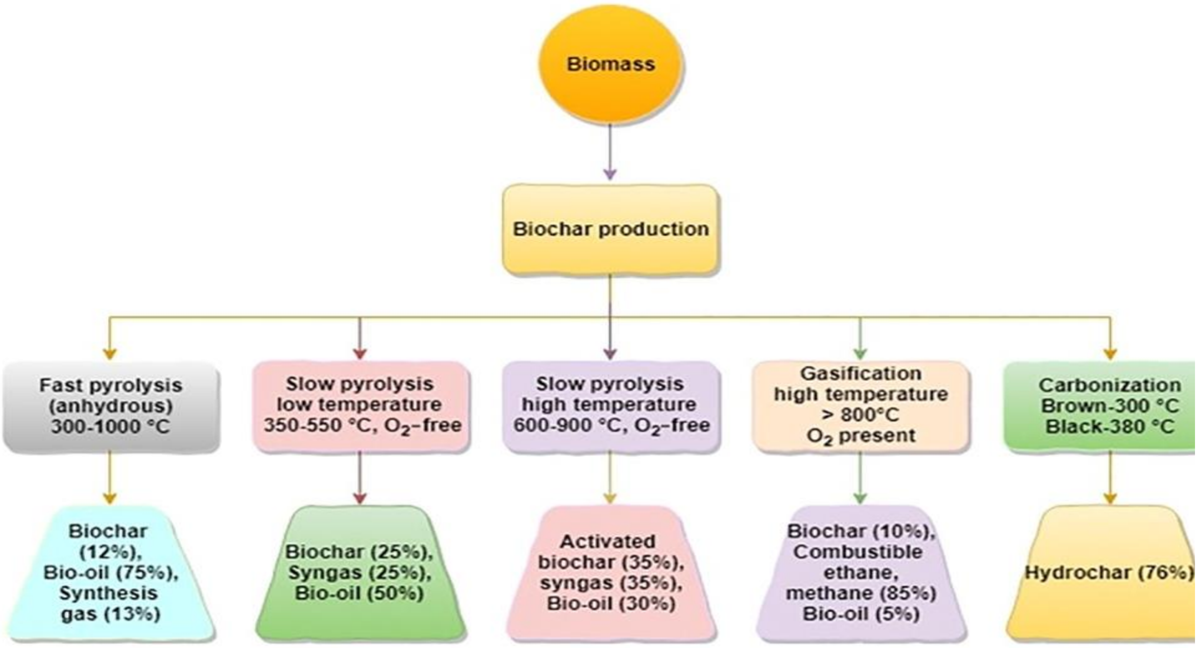


Figure 8: the required mechanisms for the development and production of biochar as an adsorbent (Source: Amen et al., 2020)

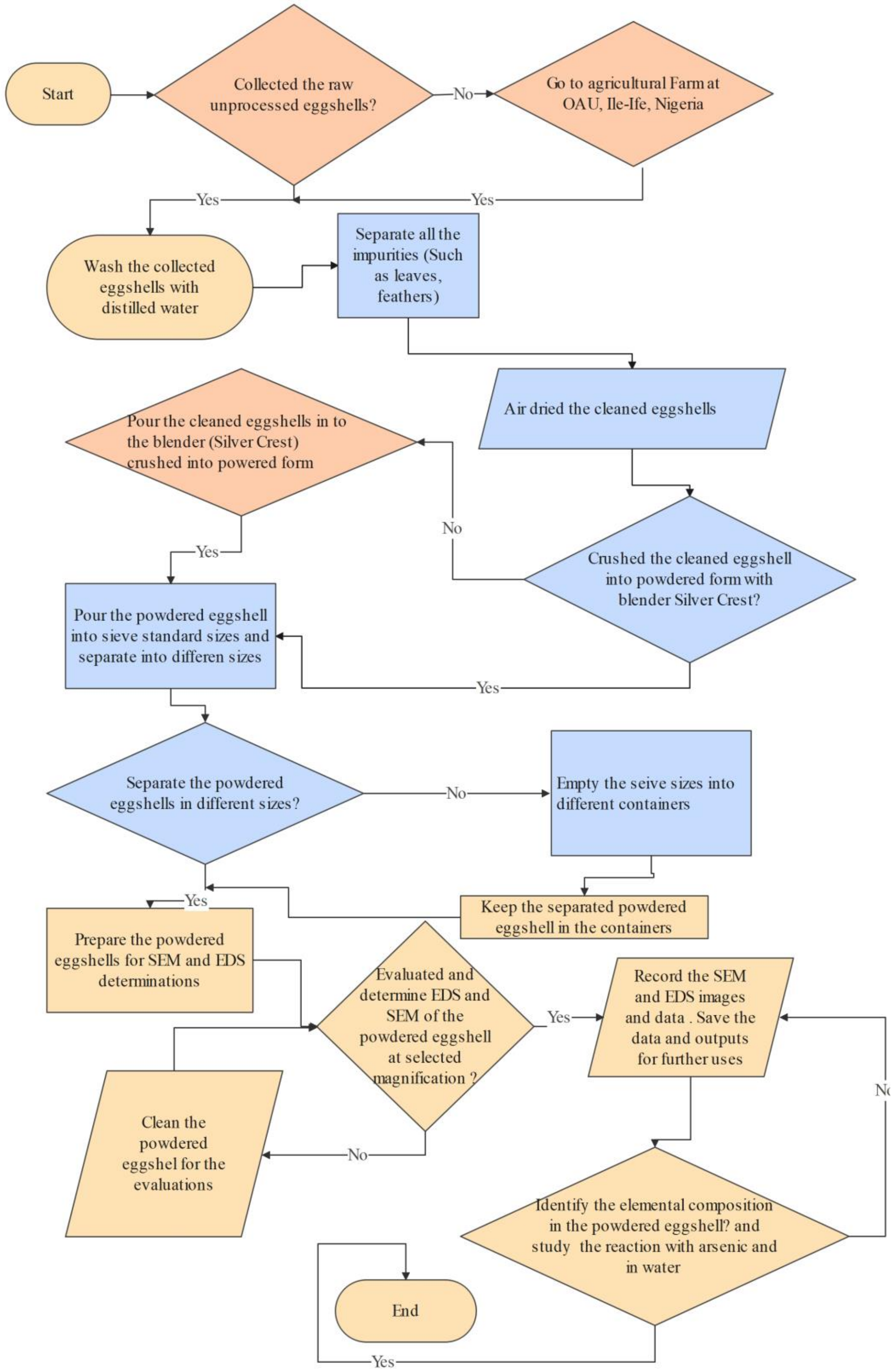


Figure 9 the summary of the powdered eggshell preparation processes and a flowchart of the methodology utilised in this study

RESULTS AND DISCUSSION

Figures 10a, 10b, 10c and 10d 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 mega-pores and micropores, which makes it appropriate for the adsorption of arsenic from the aqueous solutions. Figures 10a, 10b, 10c and 10d 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 (1000 X and 1500 X) there are smaller regions of accumulation. These regions tended to form clumps with the border and the pore structure is apparent. The pores are permeated 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. From previous studies, Guru and Dash (2014); Hee-Jeong and Seung-Mok (2015), Hee-Jong (2019) and Koohzad *et al.* (2019) reported some similar observations of pores for selected absorbents in the removal of arsenic. These results of microstructural geomorphology agreed with previous studies and research works.

Figures 11a, 11b, 11c, 11d and 11e 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 12 presents the results of the Energy Dispersive Spectroscopy. These figures (Figures 12a, and 12b) 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 12a, and 12b). 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 the 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. Arunlertaree et al. (2007) documented that the elemental composition of raw chicken eggshell includes Calcium carbonates ($CaCO_3$; 96.48%); Sulphur (2.31 %); Magnesium (0.404 %); phosphorus (0.505 %) and strontium (0.074%) and the elemental composition of boiled chicken eggshell include $CaCO_3$ (96.48%); Sulphur (3.59 %); Magnesium (0.440 %); phosphorus (0.469 %) and Strontium (0.073%). Markovski et al. (2014) reported that the elemental composition of dried chicken eggshells includes Calcium (12.2%); Iron (1.53 %); Magnesium (1.31 %); Manganese (0.532 %), Potassium (0.081 %) and Carbonates (52.8 %). Soares et al. (20 16) stated that the composition of eggshells can be summarised as total pore volume 0.98 x 10^{-6} litres per gram of eggshells, Calcium carbonates (89.6 grams of $CaCO_3$ per 100 grams of eggshell) and organic matters (2. 1%). Mittal et al. (2016) reported that the major constituents of the eggshell are carbonates, sulphates and phosphates of calcium, magnesium and organic matter. Traces of Na, K, Mn, Fe, Cu, and Sr metals are also present in eggshells.

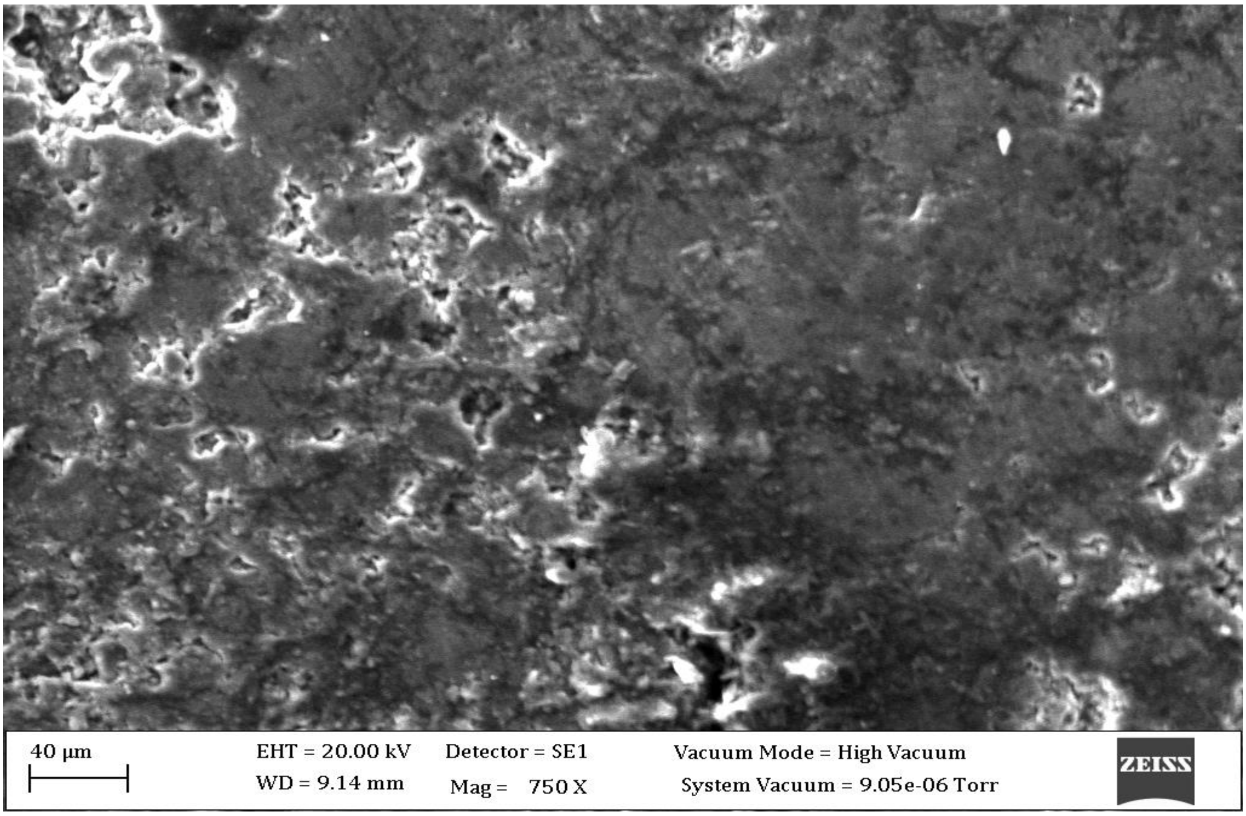


Figure 10a Surface morphology of the powdered eggshell at 750 X magnification

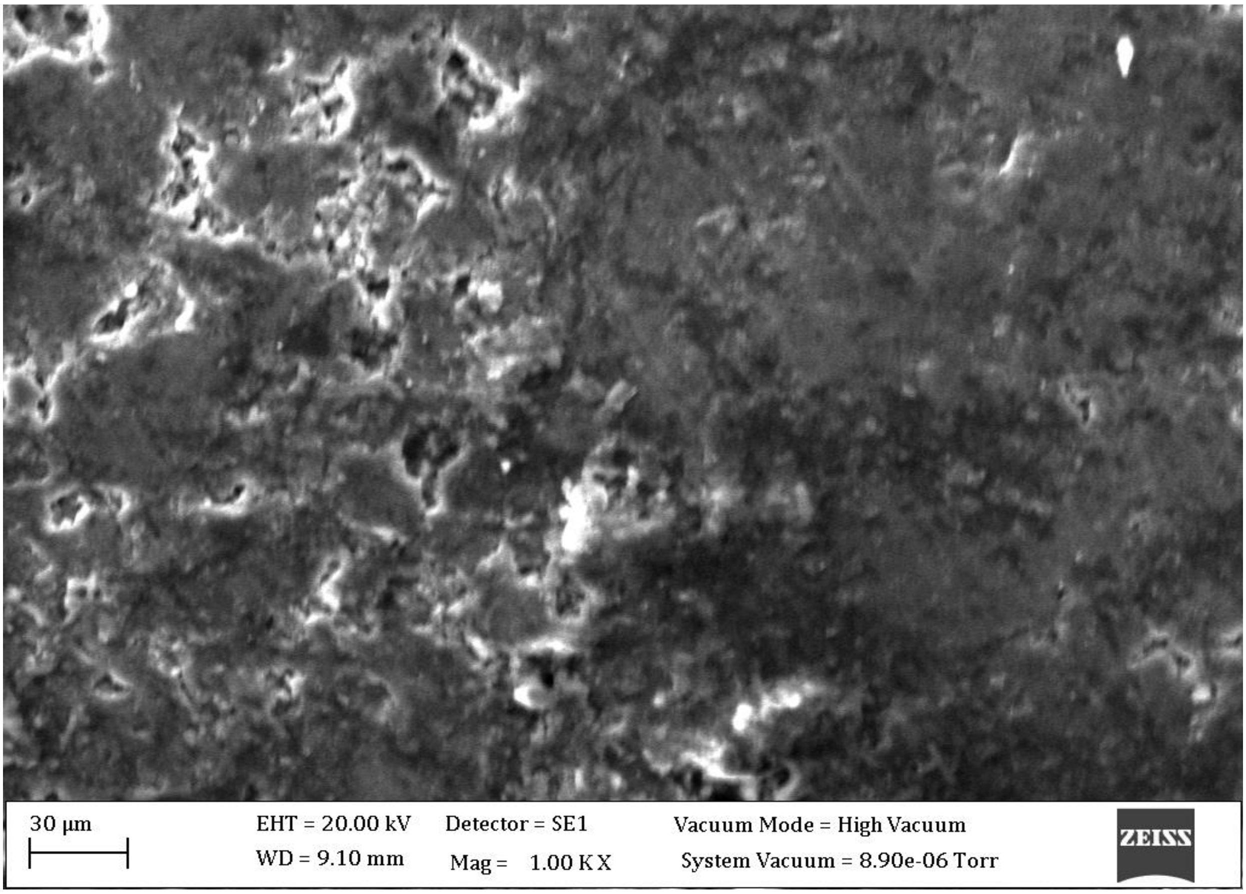


Figure 10b Surface morphology of the powdered eggshell at 1000 X magnification

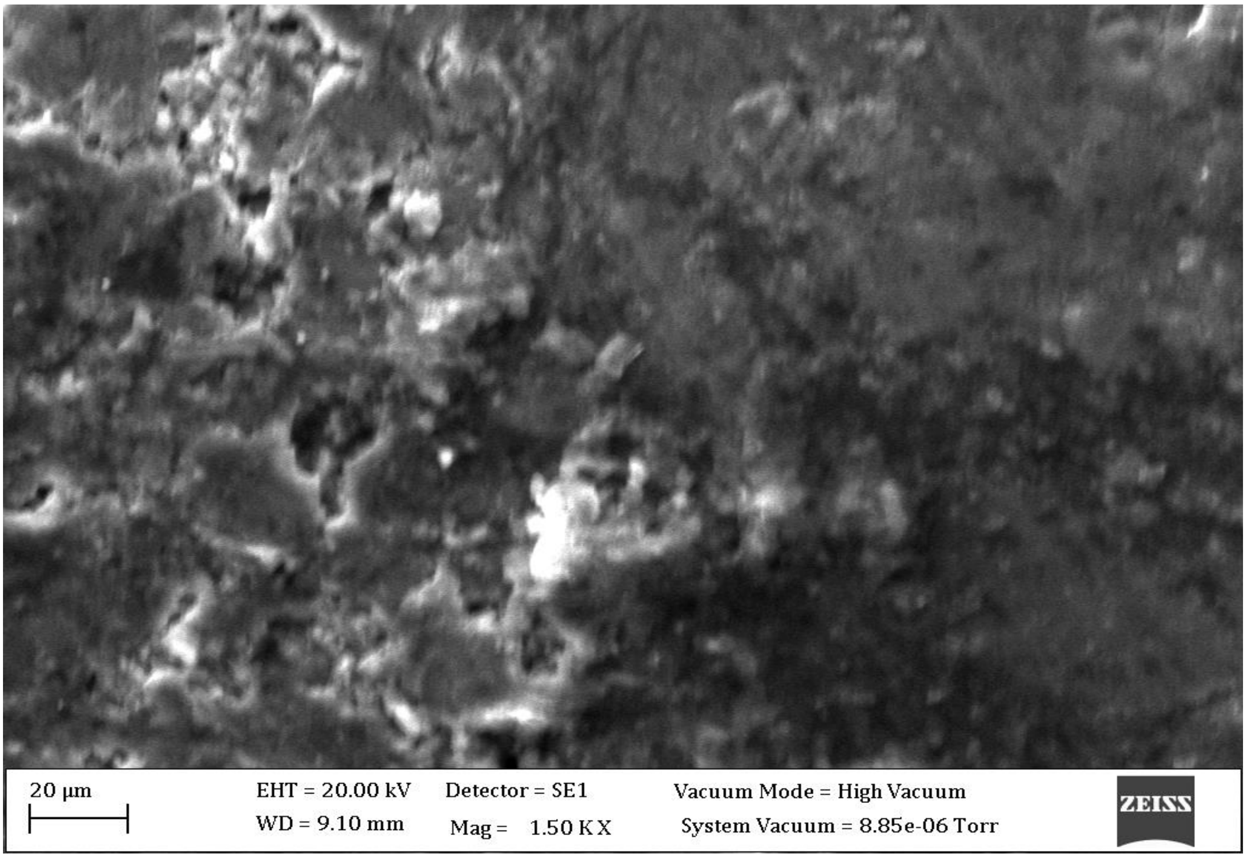


Figure 10c Surface morphology of the powdered eggshell at 1500 X magnification

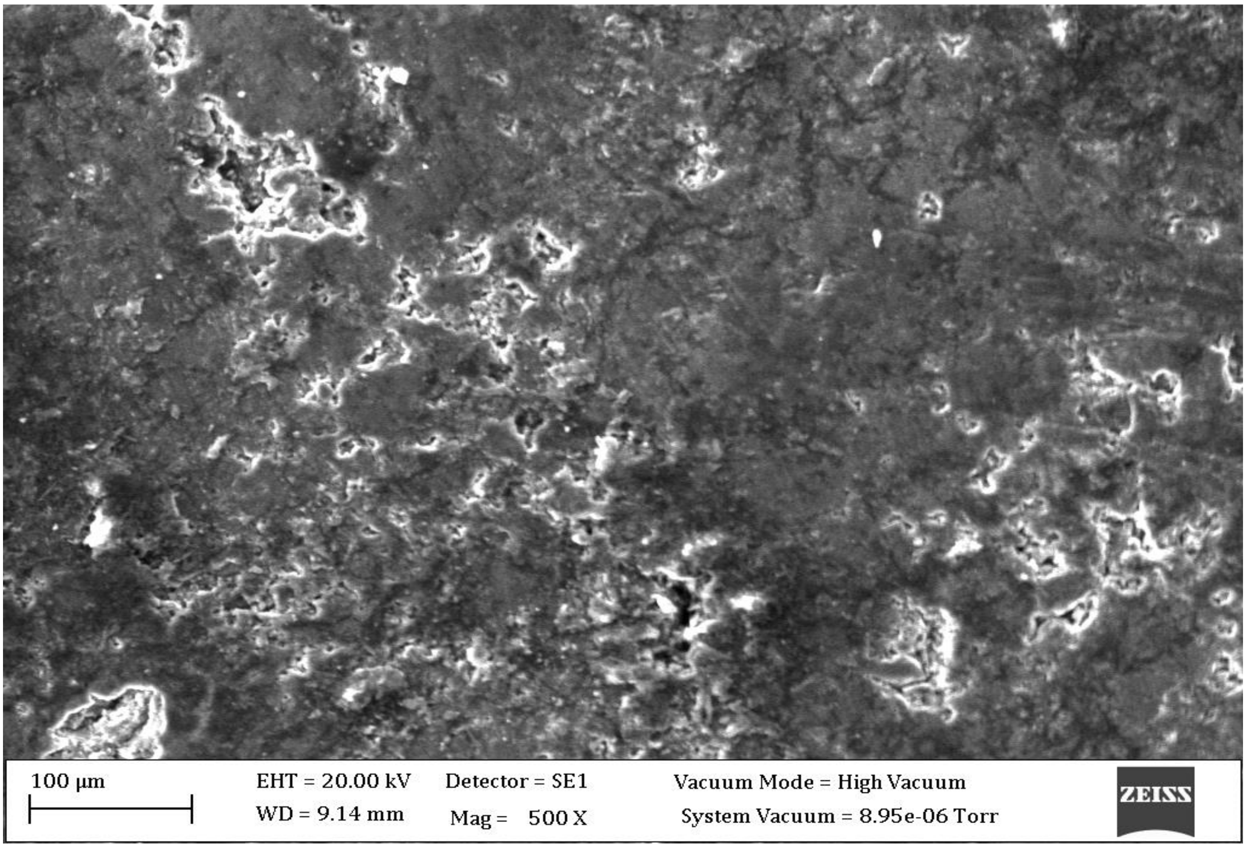


Figure 10d Surface morphology of the powdered eggshell at 500 X magnification

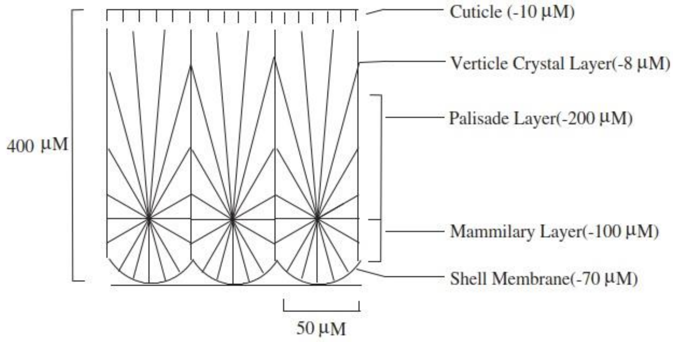


Figure 11a: Scanning Electron Microscope micrographs of similar powdered eggshell (Source: Guru and Dash, 2014)

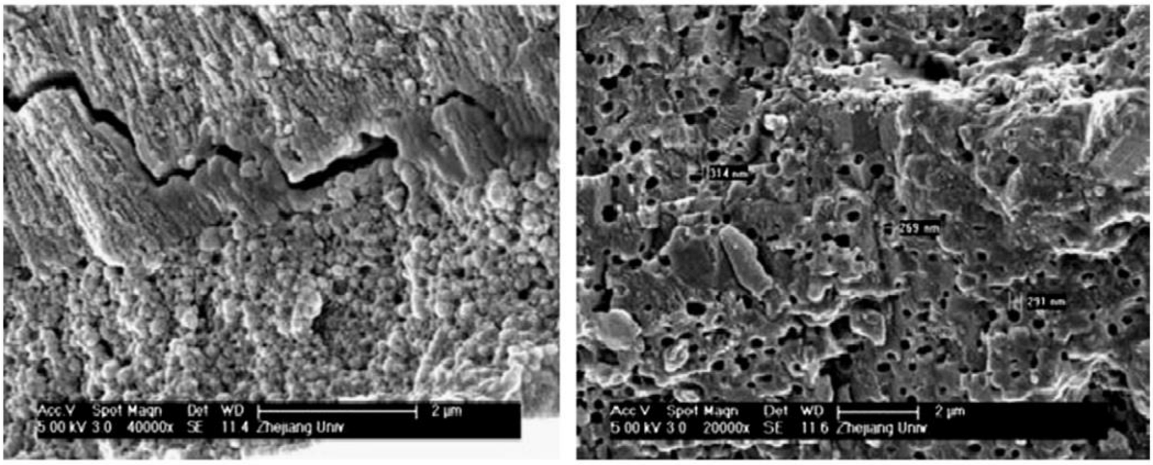


Figure 11b: the Scanning Electron Microscope micrographs of label (a) in the figure stands for image of chicken eggshell; label (b) in the figure stands for image of crystalline sheet (Source: Guru and Dash, 2014)

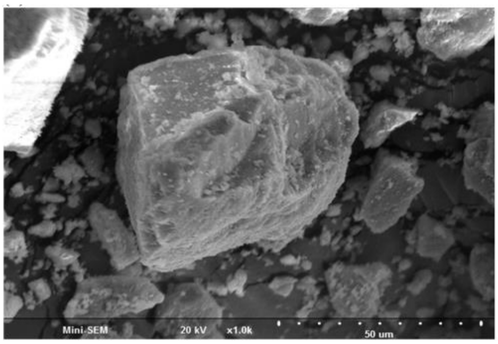


Figure 11c the scanning electron microscope micrographs of similar powdered eggshells (Source: Hee-Jeong and Seung-Mok, 2015).

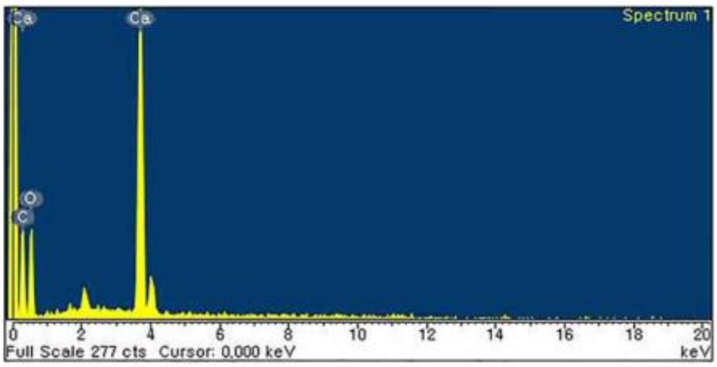


Figure 11d Energy Dispersive Spectroscopy of similar powdered eggshells (Source: Hee-Jeong, 2019).

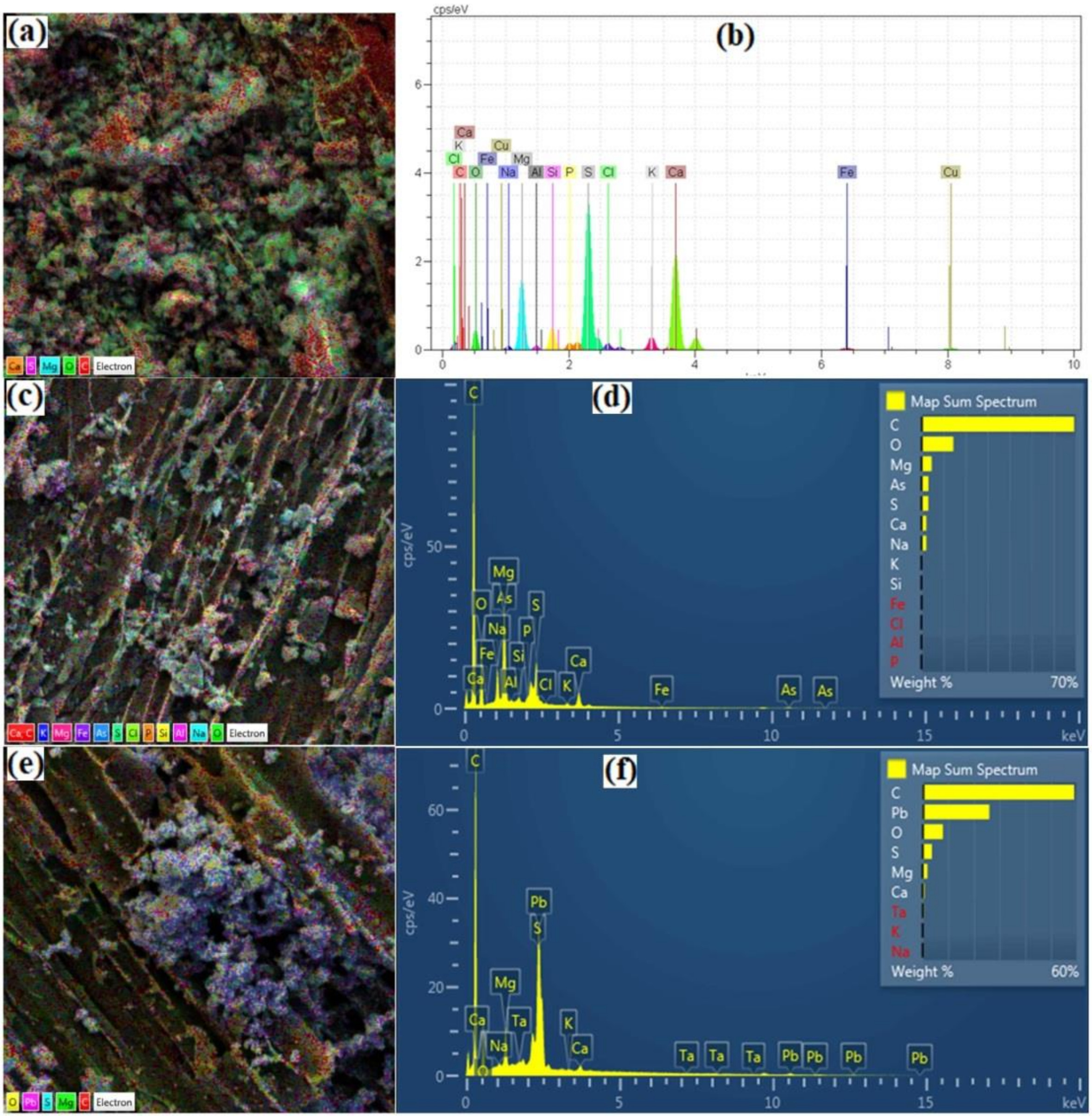
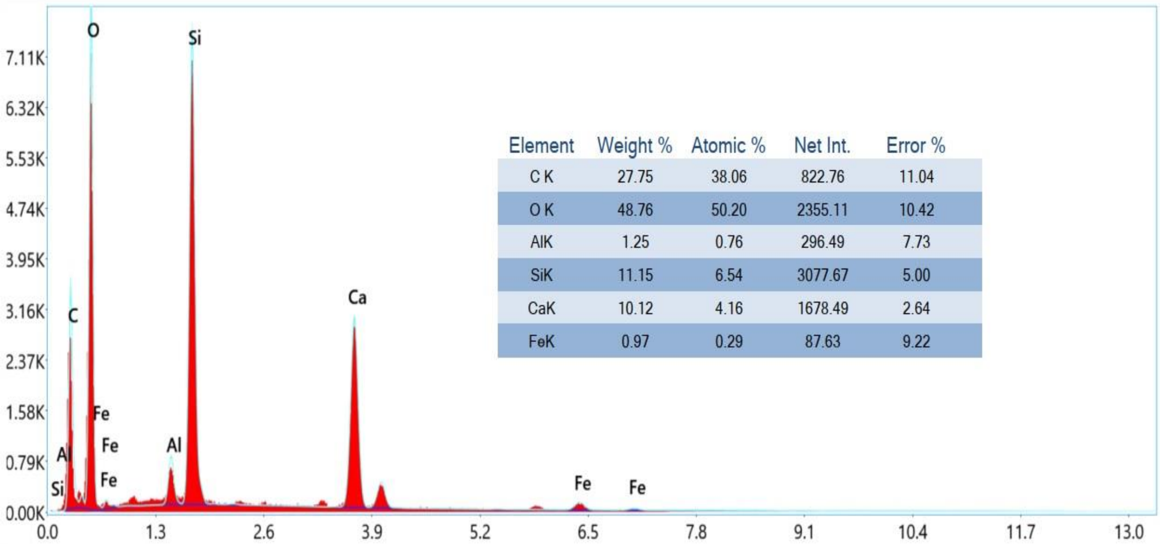
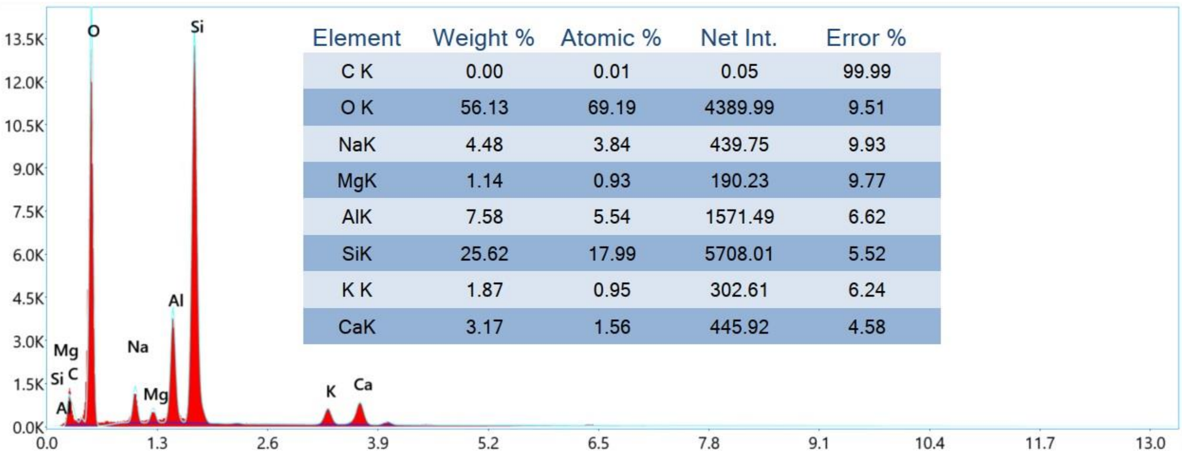


Figure 11e Energy Dispersive Spectroscopy view of carbon adsorbent labels (a and b) in the figure are the view before adsorption of ions; labels (c and d) in the figure are for view after adsorption of arsenic and the labels (e and f) in the figure are for after adsorption of lead ions (Source: Koohzad *et al.*, 2019)



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

Figure 12a Energy Dispersive Spectroscopy view of powdered eggshell adsorbent at spot A



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

Figure 12 b Energy Dispersive Spectroscopy view of powdered eggshell adsorbent at spot B

The density of eggshell. is about 2.53 g/cm'. The portion of the major constituents of eggshell are calcium carbonate (94%), organic matter (4%) calcium phosphate 1% and magnesium carbonate (1%). The membrane surface shows positively charged sites, which are produced by basic side chains of amino acids. The membrane of eggshell has a very high surface area with unique functional groups such as thiol (—SH). hydroxyl (OH). carboxyl (—COOH), amide (—$CONH_2$), and amino (—NH_2). 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 I.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 %. Further reported in the literature such as Guru and Dash (2014) documented that an eggshell is a highly well-organized structure, which comprises five structurally dissimilar layers. From the inside to the outwards, the structure includes the shell membranes (inner and outer), palisade layer, mammillary layer, vertical crystal layer and cuticle (Figure 11a). The arrangement from the inner membranes is the mineralized layer is the mammillary layer (which contains randomly orientated calcite (as $CaCO_3$) crystals). These calcite crystal layers are large with a size of greater than I 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. Figure 11b shows the structure of the cuticle sheet. The loose and viscous—elastic porous structures provide eggshells more flexibility, and improved chemical adsorption performance. The crystalline sheet shown in Figure 11 b has a typical porous structure. Figure 11d presents Energy Dispersive Spectroscopy pictures of the eggshells and eggshell membrane particles.

The diameters of round micropores range from 200 nanomillimeters to 400 nanomillimeters. These pores function as exchangers of matter between the outside and inside of eggshells while having enough space and pores to prevent desorption. In comparison with the microstructure of sea turtle eggshells, hen eggshells are more compact, which suggests that a moist environment influences the porous structure of eggshells (Guru and Dash, 2014). Another report stated that eggshell is mainly composed of calcium carbonate and behaves as known adsorbents analogous to those containing calcite and calcareous soil (Ajala *et al.,* 2018). Further analysis of the composition of the eggshell revealed the presence of carbon and oxygen in the eggshell in the right proportion as a good alternative adsorbent for the removal and reduction of heavy metals and dyes from aqueous solutions. Evaluation of the adsorption performance of eggshell revealed that during its utilization for the adsorption, Fe(III) ions from aqueous solutions aid the adsorption processes, a pseudo-second order kinetics was observed and the adsorption equilibrium data better fits the Langmuir (Type 2) model than Freundlich and others types of Langmuir isotherm models with an activation energy value of -13.40 kJ mol $^{-1}$. Enthalpy, entropy and Gibb's free energy changes show the reversible and exothermic nature of the adsorption of performance of the eggshell (Guru and Dash, 2014; Ajala et al., 2018). With reference to the composition of the powdered eggshell, literature, documented reports and previous studies the mechanisms of arsenic adsorption unto powdered eggshell can be summarised as follows:

a) **Surface complexation formation and reaction**: The surface complexation reactions for the arsenic reduction and removal mechanisms can be as follows (Wang *et al.,* 2016; equations 1 to 5):

$$\equiv [Fe-OH]_{(s)} + H_2AsO_4^- \longrightarrow \equiv Fe-OAsO_3H + OH^- \quad (1)$$

$$\equiv [Fe-OH]_{(s)} + H_2AsO_4^- \longrightarrow \equiv Fe-O_2AsO_2H + OH^- \quad (2)$$

$$\equiv [Fe-OH]_{(s)} + H_2AsO_4^{2-} \longrightarrow \equiv Fe-OAsO_3H^- + OH^- \quad (3)$$

$$\equiv [Fe-OH]_{(s)} + H_2AsO_4^{2-} \longrightarrow \equiv Fe-O_2AsO_2H^- + OH^- \quad (4)$$

$$\equiv 2\left[Fe - OH\right]_{(s)} + H_2AsO_4^{2-} \longrightarrow \equiv 2FeO - AsO_2H + 2OH^- \qquad (5)$$

These reductions and removal of arsenic by powdered eggshell through Fe(III)-exchanged molecular sieves yielded in the release of hydroxide and increased the pH of the aqueous solution. The formation of inner- sphere complexations between Fe hydroxide on the surface of the molecular sieves and arsenate could cause the enhanced removal and reduction of arsenic (Wang et al., 2016).

b) **Reaction with surface aluminol:** The study indicated that the chemical composition of minerals in the powdered eggshell include aluminium (Al) content, which acted as an important factor in the arsenic adsorption. The adsorption may be derived from a greater number of surface Al-OH groups, which yielded and resulted in a higher capacity for a ligand exchange reaction. They presented their hypothetical ligand exchange reaction for H_2AsO_4 as follows (Yazdani *et al.,* 2016; Liu *et al.,* 2015; equation 6):

$$\equiv \quad Al_{(s)} - OH \quad + H_2AsO_4^- \longrightarrow \quad \equiv Al_s - H_2AsO_4 + OH^- \qquad (6)$$

Where; the surface aluminol sites of the minerals is represented with the symbol $=Al_s$-OH. The reactions that occur during the adsorption process depend on the arsenate oxyanion and dominant protonation status of the surface aluminol sites (Yazdani *et al.,* 2016). While the aluminol groups are suggested to be the adsorption reactive sites, terminal silanol groups are supposed to have lower arsenic adsorption capacities, which is in good agreement with the results of adsorption on some adsorbents (Silicon to Aluminium ratio of 72)

c) **Reaction of Arsenic with other elements in the aqueous solution:** In the presence of the elemental composition in the powdered eggshell the mechanisms that were involved in the removal or reduction of arsenic from the aqueous solution by adsorption onto powdered eggshell can be considered to follow these reactions and interactions as follows (Li *et al.,* 2012, equations 7 to 10):

$$XMnOOH_2^+ + H_2AsO_4^- \longrightarrow XMnOOH_2 - H_2AsO_4 \quad (7)$$

$$XMnOOH_2^+ + H_2AsO_4^{2-} \longrightarrow \left(XMnOOH_2\right)_2 - H_2AsO_4 \quad (8)$$

$$XMgOH_2^+ + H_2AsO_4^- \longrightarrow XMgOH_2 - H_2AsO_4 \quad (9)$$

$$XMgOH_2^+ + H_2AsO_4^{2-} \longrightarrow \left(XMgOH_2\right)_2 - H_2AsO_4 \quad (10)$$

Where; X is the elemental composition of the powdered eggshell. An increment in the protonation will increase the positively charged sites and enhance the attractive force between the adsorbent surface and As(V), which will in turn increase the adsorption. In the alkaline pH region, $HAsO_4^{2-}$ is the dominant As(V) type in the aqueous solution. Higher pH is unfavourable for protonation of the adsorbent surface, and negatively charged sites dominate, which enhances repulsion, and the adsorption decrease

d) **Chemisorption reaction of metals and Arsenic:** The chemisorption reaction mechanism of arsenic adsorption onto eggshell in aqueous solutions based on detected elements present can be summarised as follows (Mukhopahyay et al., 2017, equations 11 to 14):

$$M\left(OH\right)_{(s)} + H^+ \leftrightarrow M\left(OH_2\right)_{(s)}^+ \quad (11)$$

$$M\left(OH\right)_{(s)} + H_2AsO_{4(aq)}^- \leftrightarrow MHAsO_{4(s)}^- + H_2O_{(aq)} \quad (12)$$

$$M\left(OH\right)_{(s)} + H_2AsO_{4(aq)}^- \leftrightarrow MHAsO_{4\ (s)}^{2-} + H_2O_{(aq)} + H^+{}_{(aq)} \quad (13)$$

$$M\left(OH\right)_{(s)} + H_2AsO_{4(aq)}^- \leftrightarrow M\left(OH_2\right)_{(s)} \quad - H_2AsO_{4(s)}^- \quad (14)$$

Where; $M(OH)_{(s)}$ stand for metallic hydroxy group of the powdered eggshell, $MHASO_{4(s)}$ and $MASO_{4(s)}$ are the inner sphere complex compounds and $M(OH_2^+) - H_2AsO_4(s)$ is the outer sphere complex arsenic compound.

e) **Precipitation and ion exchange reactions of Arsenic with other metals:** Based on the elemental composition and the pollutant present: the following reactions and mechanisms are expected for the adsorption of arsenic on powdered eggshell (Flores-Canoa et a1., 2013; Adekunbi et al., 2023) as follows (Equations 15 to 17):

i. Precipitation

$$\equiv\left[Ca-OH\right]_{(s)}+H_2AsO_4^- \longrightarrow \equiv Ca-OAsO_3H+OH^- \tag{15}$$

$$\equiv\left[Fe-OH\right]_{(s)}+H_2AsO_4^- \longrightarrow \equiv Fe-OAsO_3H+OH^- \tag{16}$$

$$\equiv\left[Al-OH\right]_{(s)}+H_2AsO_4^- \longrightarrow \equiv Al-OAsO_3H+OH^- \tag{17}$$

ii. Ion exchange (equation 18 to 21):

$$CaCO_{3(s)}+H_2AsO_4^- \longrightarrow Ca-OAsO_3H+HCO_3^- \tag{18}$$

$$Al\left[OH\right]_{2(s)}+H_2AsO_4^- \longrightarrow Al-OAsO_3H+H_2O \tag{19}$$

$$Fe\left[OH\right]_{2(s)}+H_2AsO_4^- \longrightarrow Fe-OAsO_3H+H_2O \tag{20}$$

$$Ca\left[OH\right]_{2(s)}+H_2AsO_4^- \longrightarrow Ca-OAsO_3H+H_2O \tag{21}$$

f) **Surface acid- base, mononuclear and binuclear reactions of Arsenic:** Based on the elemental composition the following reactions and mechanisms are expected for the adsorption of arsenic on powdered eggshell (Namasivayam and Senthilkumar, 1998 Goldberg and Johnston, 2001; Alsina, et al., 2007; Chowdhury, 2017; He et al.,2019a and b; Wang et al.,2019 and Kim et al., 2020) as follows:

i. Surface acid -base reactions (equations 22 and 23)

$$SOH + H^{+} \rightleftharpoons SOH_2^{+} \tag{22}$$

$$SOH \rightleftharpoons SO^{-} + H^{+} \tag{23}$$

ii. Mononuclear arsenic (V) adsorption (equations 24 to 26):

$$SOH + H_3AsO_4 \rightleftharpoons SH_2AsO_4 + H_2O \tag{24}$$

$$SOH + H_3AsO_4 \rightleftharpoons SHAsO_4^{-} + H_2O + H^{+} \tag{25}$$

$$SOH + H_3AsO_4 \rightleftharpoons SAsO_4^{2-} + H_2O + 2H^{+} \tag{26}$$

iii. Binuclear arsenic (V) adsorption (equations 27 and 28):

$$2SOH + H_3AsO_4 \rightleftharpoons S_2HAsO_4 + 2H_2O \tag{27}$$

$$2SOH + H_3AsO_4 \rightleftharpoons S_2AsO_4^{-} + 2H_2O + H^{+} \tag{28}$$

Where; SOH stands for one reactive surface hydroxyl group bound to a surface metal ion of powdered eggshell. Figure 13a to 13e provide information and data on mechanism, affinity and structure of arsenic reduction and removal from aqueous solutions, which established some of the mechanisms of arsenic adsorption in aqueous solutions.

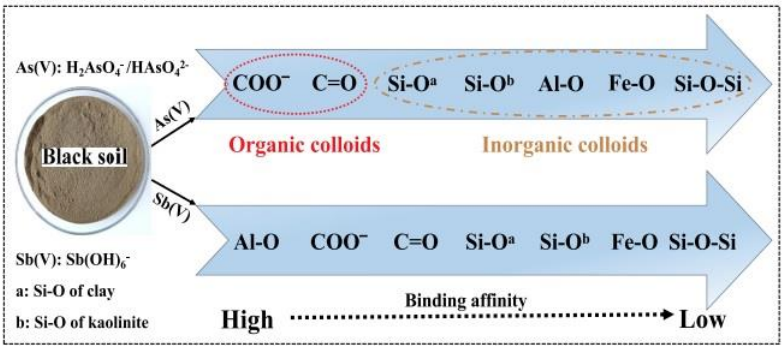


Figure 13a Affinity of arsenic adsorption in aqueous solutions in the presence of other pollutants (Source: Fan et al., 2020)

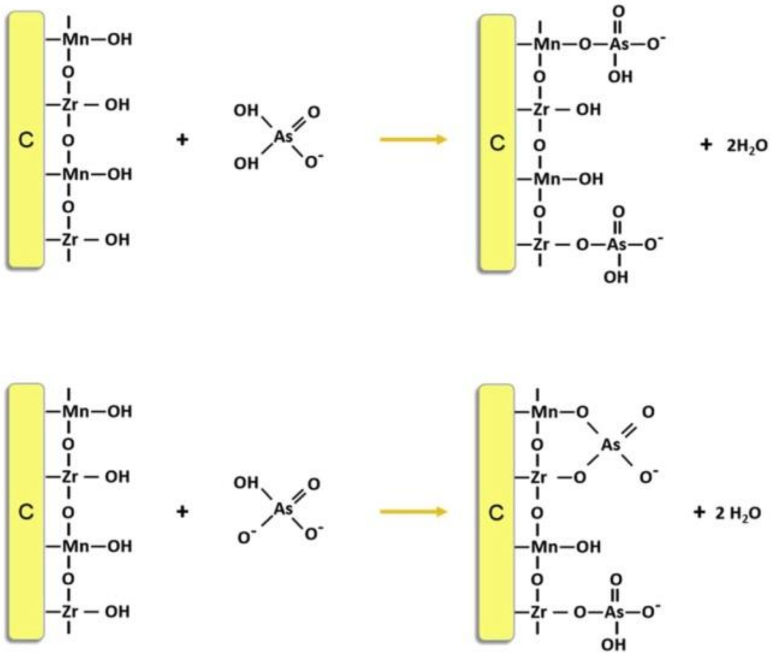


Figure 13b Mechanism diagram of arsenic adsorption in aqueous solutions in the presence of specific metals (Source: Yin et al., 2019)

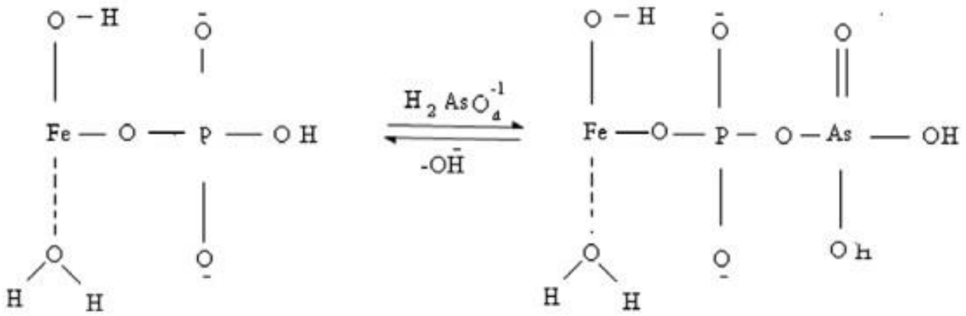


Figure 13c Mechanism diagram of Arsenic adsorption in aqueous solutions in the presence of phosphorus (Source: Hamayun et al., 2014)

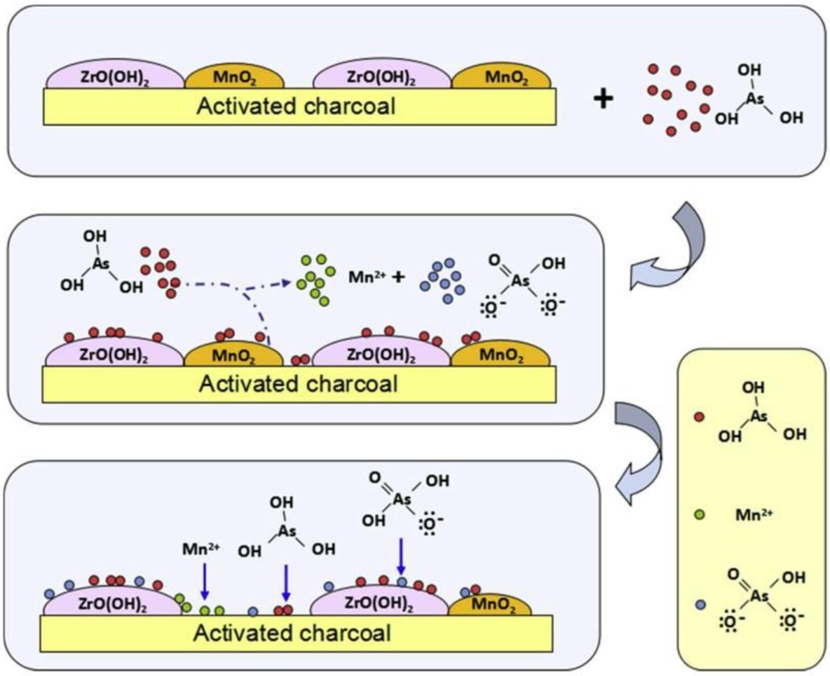


Figure 13d Mechanism diagram of arsenic adsorption by activated charcoal in aqueous solutions in the presence of selected metals (Source: Yin et al., 2019)

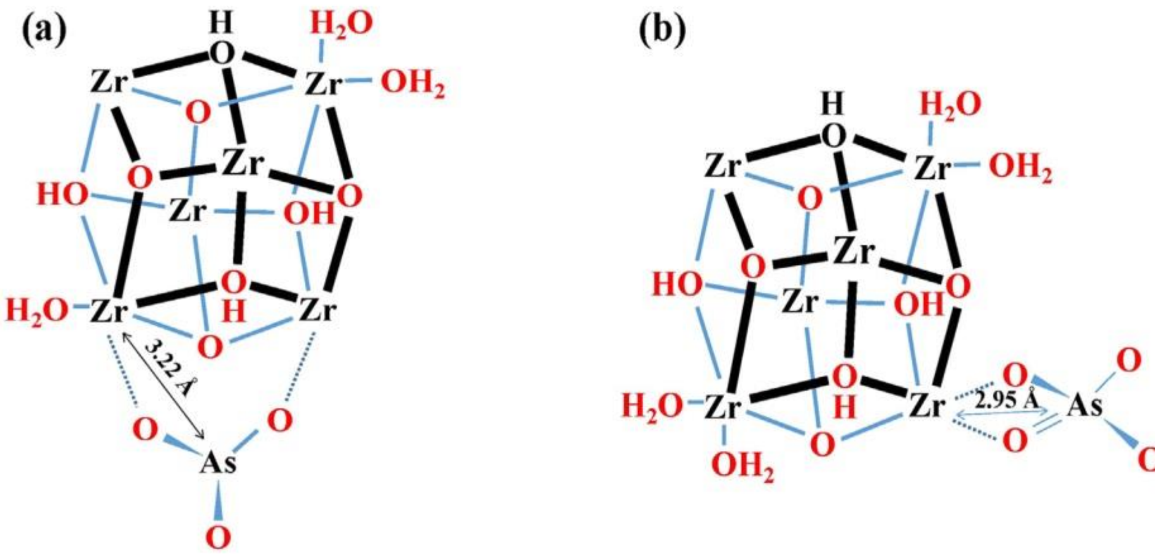


Figure 18e Binding mode and mechanism diagram of As adsorption in aqueous solutions in the presence of Zr (Source: He et al., 2019)

Conclusion

Based on the findings it can be concluded that the removal or reduction of arsenic by powdered eggshell is a function of several factors such as pH of the aqueous solution, the presence of hydroxyl groups, ion present in the solution, the nature of the aqueous solution, the composition of the aqueous solution is another vital factors. The mechanism of arsenic removal includes redox reactions, H-bond and surface complexation formations, electrostatic attraction, oxic and anoxic reactions.

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