Removal of Arsenic in River Water Samples Obtained From A Minning Community in Ghana Using Laboratory Synthesized Zeolites

Bright Kwakye-Awuah[#1], Linus Labik[#2], Isaac Nkrumah[#3] and Craig Williams[#4]

#1Department of Physics (Materials Science Group), Kwame Nkrumah University of Science and Technology, Kumasi, Ghana Tel: +233 322 060 299, Email: bkwakye-awuah.cos@knust.edu.gh

#2 Department of Physics (Materials Science Group), Kwame Nkrumah University of Science and Technology, Kumasi, Ghana, Email: inkrumah.sci@knust.edu.gh, Tel: +233 322 060 299

#3Department of Physics (Materials Science Group), KNUST, Kumasi, Ghana

#4 Research Centre in Applied Science, University of Wolverhampton, WV1 1LY, United Kingdom, Email: c.williams@wlv.ac.uk, Tel: +44 1902 322 159

ABSTRACT

The removal performance of arsenic was investigated by adsorption process on Linde Type X (LTX), Low–Silica Type X and Linde Type A (LTA) zeolites. The zeolites were hydrothermally synthesized in the laboratory at 100 ± 1 $^{\circ}$C. The synthesized zeolites were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier-Transformed Infra-red spectroscopy and Thermogravimetric analysis (TGA). The removal capacity of arsenic, known to be a hazardous contaminant in drinking water that causes arsenical dermatitis and skin cancer was evaluated by adding 1.5 g of zeolites to 100 ml of wastewater. Removal efficiencies for arsenic removal after treating for 30 minutes with adsorbents ranged between 67.86–81.35 % for LTX, 67.86–86.31 % for LSX and 71.87–96.00 % for LTA. Langmuir and Freundlich isotherms were used in analyzing results obtained from experimental studies. It was concluded that the synthesized zeolites were efficient in removing arsenic contaminated water samples. The concentrations of arsenic obtained after treatment were below the minimum contaminant levels as stipulated by the Ghana EPA.

Key words: Arsenic, Linde Type A, Linde Type X, Low-Silica Type X, Treatment, Wastewater, Zeolites

Corresponding Author: Bright Kwakye-Awuah

INTRODUCTION

Arsenic occurs in many minerals, usually in conjunction with sulphur and other metals, and also as a pure elemental crystal or allotropes. Arsenic is a chemical element with the symbol As, atomic number 33 and relative atomic mass 74.92. In groundwater, arsenic combines with oxygen to form inorganic pentavalent arsenate and trivalent arsenite. Unlike other heavy metalloids and oxyanion-forming elements, arsenic can be mobilized under a wide range of oxidizing and reducing conditions at the pH values typically found in groundwaters (pH 6.5-8.5). Arsenic has been found to have four main chemical forms having oxidation states, -3, 0, +3, and +5, but in natural water its predominant forms are inorganic oxyanions of trivalent arseniteAs^{3+} or pentavalent arsenate As^{5+}[1, 15, 16].The toxicity of different arsenic species varies in the order arsenite> arsenate >monomethylarsonate>dimethylarsinate. Trivalent arsenic is about 60 times more toxic than arsenic in the oxidized pentavalent state, and inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds [1]. The organic forms of arsenic are found mostly in surface waters or in areas severely affected by industrial pollution. In general, ground waters exhibit higher concentrations of arsenic species that are more toxic than those found in surface waters. It has been found that when river water – a primary source of drinking water – is polluted by industrial or mining effluents, or by geothermal waste, the arsenic concentration increases [4, 11 – 14]. Their presence in streams and lakes has been responsible for the several types of health problems in animals and human beings [12, 13]In Ghana, many communities depend on rivers for their economic and social activities. The presence of arsenic in rivers is responsible for the causes of skin cancer and other related skin problems such as arsenical dermatitis. Other effects include enlargement of the liver, heart diseases, internal cancers and neurological effects [15 – 20]. Over 300,000 people die of arsenic related diseases worldwide every year [14, 15, 17 – 19]. In recent years zeolites have been used for the removal of heavy metal ions in both drinking and wastewater. Zeolites are crystalline hydrated aluminosilicates whose framework structure consists of cavities or pores that are occupied by cations or water molecules. Both the cation and the water molecule have considerable freedom of movements and this permits ion exchange and reversible dehydration [3, 5 – 10]. The zeolite structure is made up of a central atom commonly silicon or aluminum surrounded by four oxygen atoms. The loosely-bound nature of extra-framework metal ions means that they are often readily exchanged for other types of metal ions when in aqueous solution.In this work zeolite types LTA, LTX and LSX were synthesized in the laboratory and water samples from River Nyam in the Ashanti Region of Ghana were exposed the zeolites and the removal efficiencies of arsenic (As^{3+}) in the samples were investigated.

MATERIALS AND METHODS

Materials

Sodium hydroxide pellets, sodium aluminate powder and sodium metasilicate were purchased from Sigma Aldrich, UK. Nitric acid was purchased from Fischer Scientific, UK whilst distilled water was obtained from the Water Research Laboratory, Kwame Nkrumah University of Science and Technology (KNUST), Kumasi, Ghana. Zeolite types LTA, LTX and LSX were synthesized in the Water Research Laboratory, KNUST. Wastewater samples were collected

from the River Nyam, in the Obuasi Municipality in the Ashanti Region of Ghana and preserved with 0.1 M HNO_3.

Synthesis of zeolites

Linde Type A was synthesized following the method described by Kwakye-Awuah et al. [5, 10]. The batch composition for the synthesis is given by:

$3.165Na_2O: Al_2O_3: 1.926 SiO_2: 128H_2O$.

0.723 g of sodium hydroxide (Aldrich Chemicals, UK) was dissolved in 80 ml of distilled water. The solution was divided into two equal halves and each transferred into plastic beakers. 0.258 g of sodium aluminate (Sigma-Aldrich, UK) was added to the first halve with continuous stirring until a homogeneous solution was obtained. 15.48 g of disodium metasilicate (Aldrich, UK) was added to other half while mixing until the gel was homogenized. The two samples were mixed quickly and the mixture was again stirred continuously until a homogeneous solution was obtained. The gel was poured into PTFE-vessels and sealed with aluminium foils, with each vessel containing about 10 g of the gel. The bottles were put into an electric oven at a temperature of 100 ^{o}C for 4 hours. The reaction in the PTFE bottles was quenched by running cold water on the vessels after they were removed from the oven until they were cooled to room temperature. The synthesized samples were filtered using a vacuum funnel and Whatman No. 45 filter paper. The powder samples obtained were washed copiously with distilled water until pH of filtrate was less than 9. Following overnight drying of the powdered zeolite at 100 ^{o}C in an electrical oven, the zeolite was crushed into uniform powder with pestle and mortar and stored in a plastic bag.

Linde Type X was synthesised following the method described by Kwakye-Awuah et al. [5, 6, 8, 9]. The batch composition for the synthesis is given by:

$18Na_2O: Al_2O_3: 4SiO_2: 325H_2O$.

100 g of sodium hydroxide was dissolved in 100 g of distilled water. 97.5 g of alumina powder was added to sodium hydroxide solution while stirring until a homogeneous solution was obtained and allowed to cool. 202.5 g of distilled water was then added to the cooled solution. 219.7 g of sodium silicate was then added to form a gel and stirred for about 30 minutes continuously until a homogeneous gel was obtained. The gel was poured into PTFE-vessels and sealed with aluminium foils, with each vessel containing about 10 g of the gel. The bottles were put into an electric oven at a temperature of 100 ^{o}C for 8 hours. The reaction in the PTFE bottles was quenched by running cold water on the vessels after they were removed from the oven until they were cooled to room temperature. The synthesized samples were filtered using a vacuum funnel and Whatman No 45 filter paper. The powder samples obtained were washed copiously with distilled water until pH of filtrate was less than 10. Following overnight drying of the powdered zeolite at 100 ^{o}C in an electrical oven, the zeolite was crushed into uniform powder with pestle and mortar and stored in a plastic bag.

Low–Silica Type X synthesised following the method given by Khemthong et al. [2] with some modifications. The batch composition used in the synthesis is given by:

5.5Na$_2$O: 1.65K$_2$O: Al$_2$O$_3$: 2.2SiO$_2$: 122H$_2$O

22.37 g of sodium aluminate is added to 30 g of distilled water and stirred until all the sodium aluminate was dissolved. In another plastic beaker, 70 g of water was added to 21.53 g of potassium hydroxide and 31.09 g of sodium hydroxide. The mixture was stirred until dissolved. The first solution was then added to the second solution. The solution was then added to 71.8 g of distilled water and 46 g of sodium silicate solution to form a gel. The mixture was stirred until a homogeneous solution was obtained. The gel was poured into PTFE-vessels and sealed with aluminium foils, with each vessel containing about 10 g of the gel. The bottles were put into an electric oven at a temperature of 100 ^{o}C for 5 hours. The synthesized samples were diluted with distilled water and filtered using a vacuum funnel and Whatman No. 45 filter paper. The powder samples obtained were washed copiously with 600 ml of 0.01 N NaOH. Following overnight drying of the powdered zeolite at 100 ^{o}C in an electrical oven, the zeolite was crushed into uniform powder with pestle and mortar and stored in a plastic bag.

Characterization

The characterizations of the zeolites were done in the UK at Wolverhampton University. Characterization of the zeolites included Scanning Electron Microscopy (SEM) to confirm phase purity and structural morphology, Fourier Transform Infra-Red (FTIR) to determine the structural characterization of the zeolite, X-ray Diffraction (XRD) to monitor crystallization and purity of the product.

Batch sorption studies

The raw wastewater samples were collected every month for 5 months. The pH and conductivity measurements were taken before and after treatment with each zeolite. Batch kinetics was utilized to study ion exchange processes. An equal volume of 100 ml of water samples were measured into conical flasks and 1.5 g of zeolites was added to each flask resulting in a zeolite to water ratio of 1.5 g zeolite: 100 mlof wastewater sample. The flasks were placed on a rotary shaker at an average speed of 200 rpm at room temperature. Time intervals were 30 minutes. The zeolite was then separated from the supernatant at the required time. Each sample was filtered using Whatman Filter paper No. 1. The concentration of arsenic in the water samples from River Nyam before and after addition of zeolites were determined by ICP-OES (SGS LaboratoryServices, Tema, Ghana). Where necessary, samples were

RESULTS AND DISCUSSION

Characterization of Zeolite

Scanning Electron Microscopy (SEM), showed that zeolite LTX was octahedral in shape whilst LTA and LSX were found to be cubic as shown Figure 1(a - c)
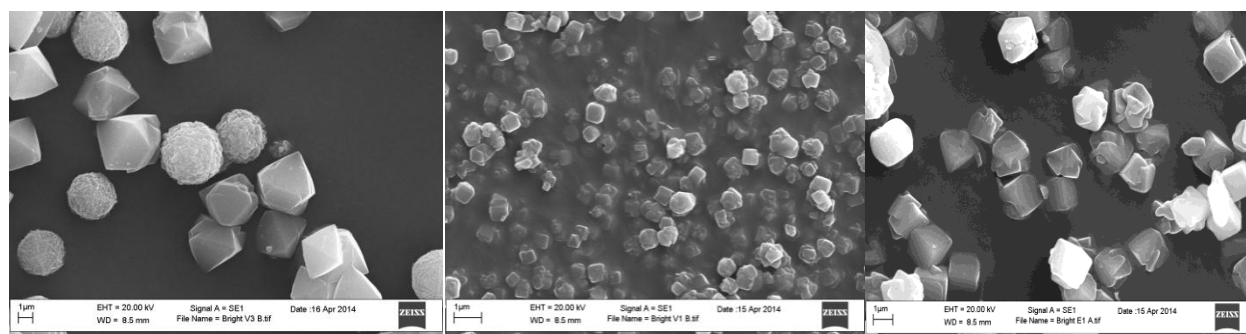

Fig 1:SEM Micrographs of zeolite types (a): LTX, (b): LTA and (c) LSX

X- Ray powder diffraction is an integral tool used in determining the crystal properties as well phase purity of the synthesized zeolite. The XRD pattern of zeolite X samples must in accord with the ICCD standard reference pattern in order to be validated as an as-synthesized zeolite. The first three peaks for zeolite LTX appeared at 5.1, 9.0 and 10.1° and shows no impurity phases as given by Figure 2(a – c). For zeolite LTA and LSX, the first three peaks were at 7.5, 10.0 and 12.5 $^{\circ}$ and 6.0, 10.0 and 12.0 $^{\circ}$ respectively.This is in agreement with work done by Kwakye-Awuah et al. (2008a).
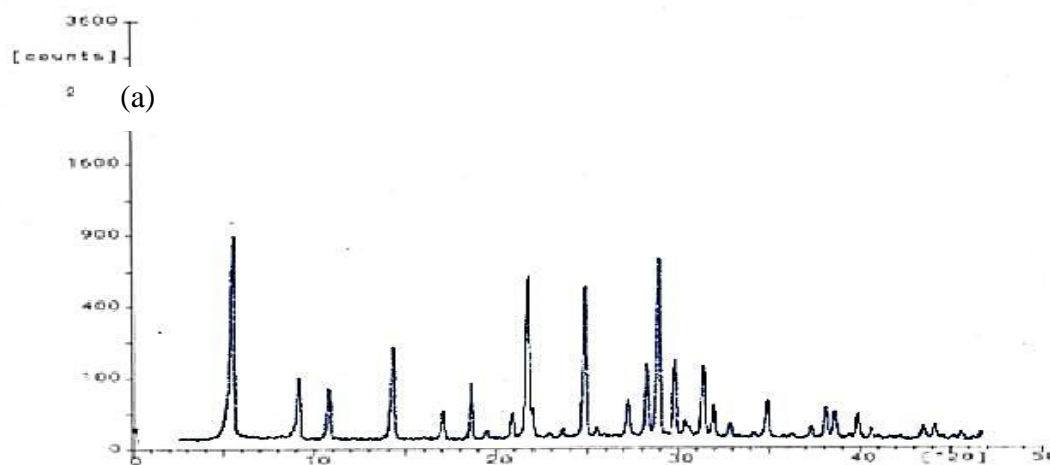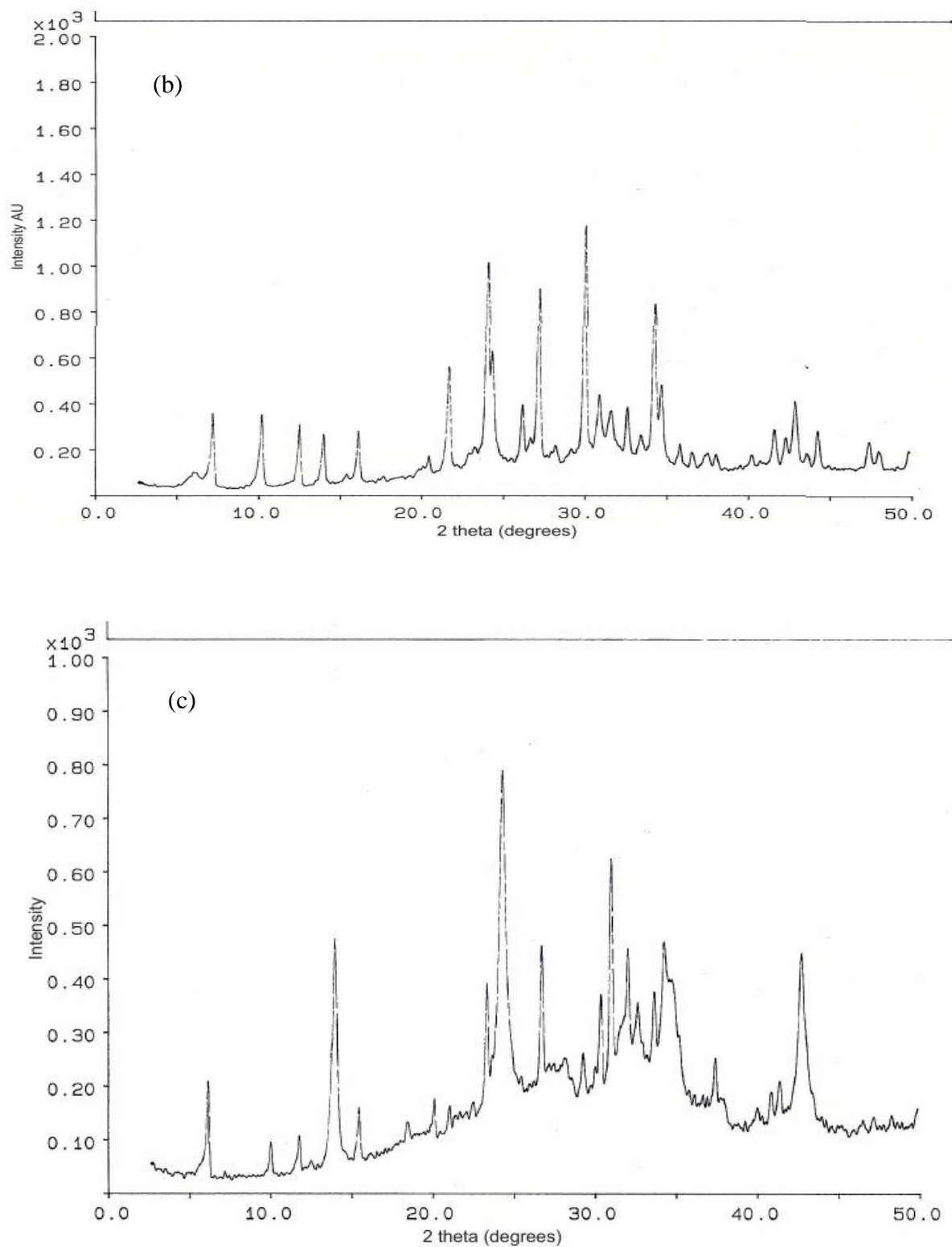
Fig 2: XRD spectra obtained for zeolite type (a): LTX, (b): LTA and (c): LSX

The general infrared assignments in Structural characterisation of the zeolite was done by FTIR to confirm the formation of the zeolite. Figure 3 shows the characteristic peaks obtained for the zeolites LTX, LTA and LSX after FTIR analysis. For zeolite LTX the spectrum exhibited at 1426 cm^{-1} and 968 cm^{-1}. Vibrations associated with double rings of the external T–O linkages occurred at 638 cm^{-1}. Assymmetric stretching due to the internal vibrations of the framework tetrahedra occurred at 968 cm^{-1} and the band at 426 cm^{-1}. For zeolite LTA, the band attributed to the overlapping of the asymmetric vibrations of Si–O (bridging) and Si–O (non-bridging) bonds occurred at 971 cm^{-1}. Vibrations associated with double rings occurred at 558 cm^{-1} and 519 cm^{-1} whilst the band at 442 cm^{-1} is the vibrations due to the bending of the T–O tetrahedra. According [3], the two most intense bands of zeolites usually occur at 860–1230 cm^{-1} and 420–500 cm^{-1} this agrees with the FTIR spectrum of the synthesized zeolite in this study. The absorbance band in between the wave numbers 980–1320 cm^{-1} in the spectra represents the presence of substituted Al atoms in the tetrahedral forms of the silica frameworks [3, 5, 8, 10]. T–O bending also occurred at 426 cm^{-1} for LTX, 423 cm^{-1} and 442 cm^{-1} for LTA. For LSX, a large band was observed at 962 cm^{-1} which can be attributed to the overlapping of the asymmetric vibrations of Si–O (bridging) and Si–O^{-} (non-bridging) bonds. Vibrations associated with double rings occurred at 615 cm^{-1} and 548 cm^{-1}. Symmetric stretching associated with internal vibrations occurred at 664 cm^{-1} and the band at 423 cm^{-1} is assigned to the vibrations due to the bending of the T–O tetrahedra.
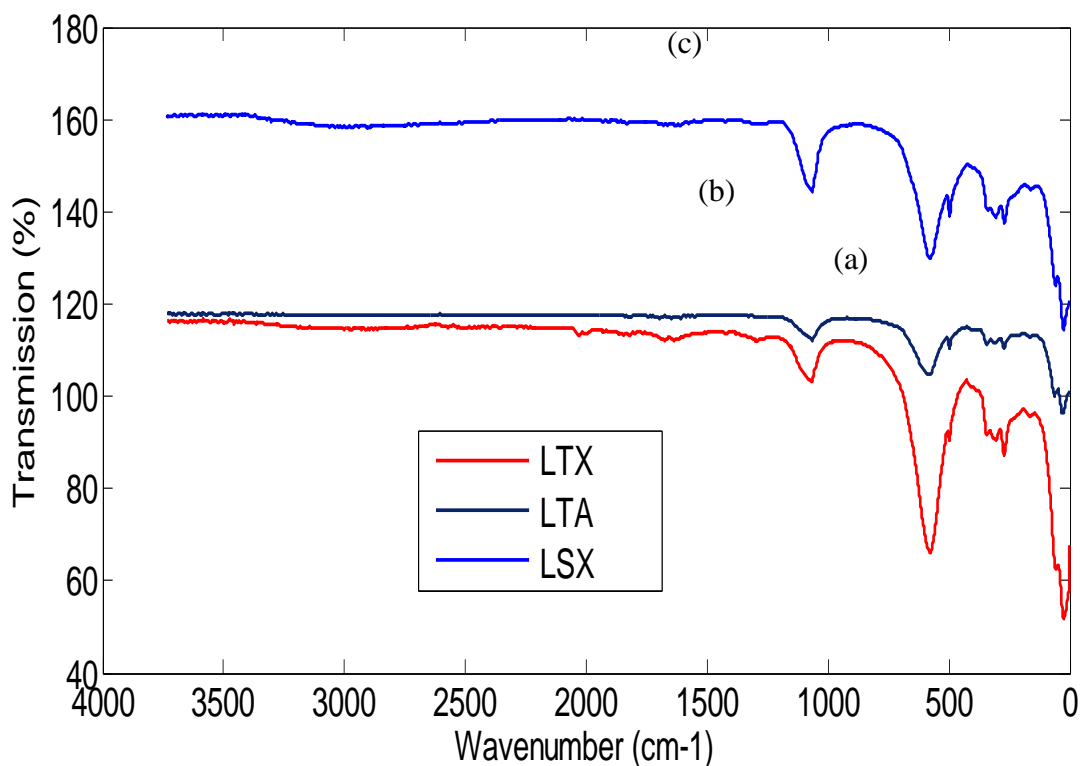

Fig 1: FTIR Spectra of (a): zeolite LTX, (b): zeolite LTA and (c): zeolite LSX

Table 1: Results showing initial concentrations, equilibrium concentrations, removal
efficiencies and sorption capacities of zeolite types LTX, LTA and LSX

| Zeolite Type	Water Sample #	Initial [As] (mg/l)	Equilibrium [As] (mg/l)	Removal Efficiency (%)	Equilibrium Sorption Capacity (mg/g)
LTX	1	0.15	0.028	81.33	8.13
	2	0.19	0.042	77.89	9.86
	3	0.28	0.090	67.86	12.67
	4	0.32	0.072	77.50	16.53
	5	0.20	0.062	69.00	9.20
LTA	1	0.15	0.006	85.33	9.60
	2	0.19	0.032	78.67	10.53
	3	0.28	0.050	82.14	15.33
	4	0.32	0.090	71.87	15.33
	5	0.20	0.032	84.00	11.20
LSX	1	0.15	0.022	96.00	8.53
	2	0.19	0.026	86.31	10.93
	3	0.28	0.090	67.86	12.67
	4	0.32	0.090	71.87	15.33
	5	0.20	0.032	84.00	11.20

Sorption isotherms were fitted with the Freundlich and Langmuir equations. The Freundlich
isotherm assumes a multilayer adsorption with interactions between ions and is expressed as
Kwakye-Awuah et al. [6]

$$q_e = k_F C_e^{\frac{1}{n}} (1)$$

Where q_e (mg/g) is the amount of arsenic ion adsorbed at equilibrium, k_F (measure of adsorption
capacity) and $\frac{1}{n}$ (measure of adsorption intensity) are Freundlich constants. Taking log on both
sides ofequation (1), we obtain:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e (2)$$

Values of C_e and k_F are calculated from a plot (Figure 4) of $\log q_e$ as ordinate and $\log C_e$ as
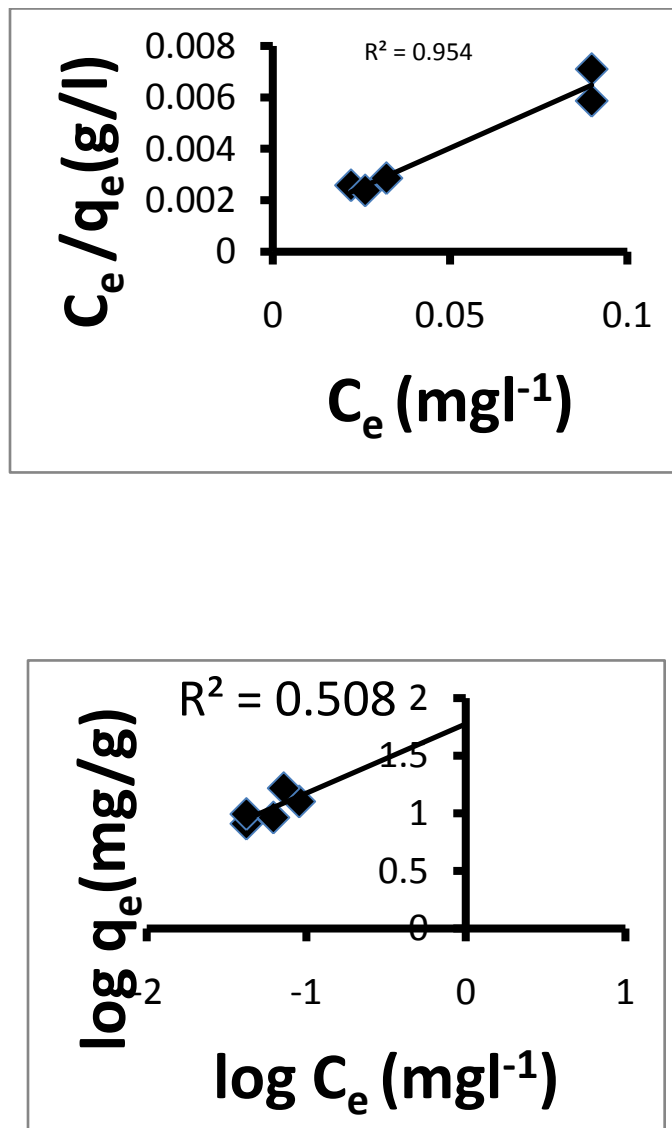abscissa
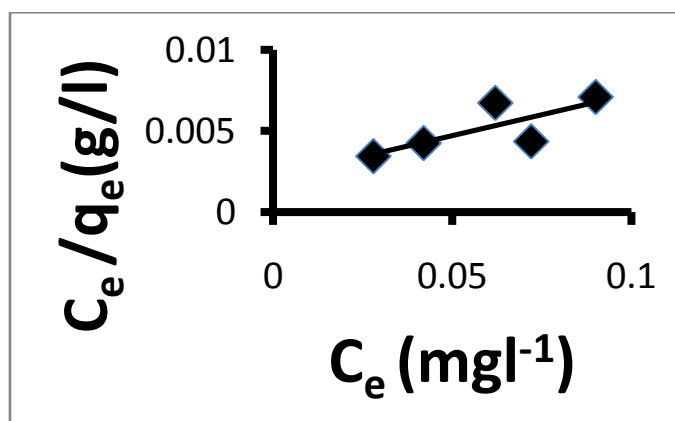
Fig 5: Graph obtained when sorption isotherms were fitted to the Langmuir equation for
(a): zeolite LTX, (b): zeolite LTA and (c): zeolite LSX.

Table 2: Isotherms equation coefficient extracted from the linearized curves for zeolite
LTX, LTA and LSX

	Langmuir model			Freundlich model			
Zeolite Type	$q_e(mg^{-1})$	$K_L(lmg^{-1})$	R^2	$1/n$	n	K_F (mgg^{-1})	R^2
LTX	19.6078	9.8039	0.594	0.601	1.7394	1.664	0.508
LSX	16.3934	$\times 10^3$	0.954	0.274	2.7582	3.650	0.771
LTA	14.0845	1.6393	0.936	0.073	6.5104	13.699	0.361

The Langmuir model yields a better fit ($R^2 = 0.594, 0.936, 0.954$) for zeolite LTX, LTA and LSX compared to the Freundlich model ($R^2 = 0.508, 0.361, 0.771$) for zeolite LTX, LTA and LSX respectively. The results were in agreement with that of removal of ammonium ions in mining wastewater [Kwakye-Awuah et al. [6]. For Freundlich parameter 1/n, a value of $\frac{1}{n}$between 0 and 1 indicate a favourable adsorption. Since the values of $\frac{1}{n}$ obtained in this study for all treatments were less than 1 it follows that the Freundlich adsorption conditions were favourable. High alumina zeolites have shown to have high exchange capacity in arsenic removal [4, 11, 13]. This may be due to a high concentration of terminol Al–OH species in low Si/Al ration zeolites which leads to a greater capacity for a ligand exchange reaction. The sorption data were fitted to the Langmuir and Freundlich equations, and the parameters for each model are given in Tables 2. For all cases, the Langmuir model represents a better fit to the experimental data than the Freundlich model and this was also observed in [1, 4, 12, 13]Furthermore, the results obtained in this study is in agreement with the R^2 obtained in the Freundlich plots.

LTX had an equilibrium sorption capacity (q_e of 19.6078 mgg[-1] and LSX and LTA had 16.3934 mgg[-1] and 14.6845 mgg[-1] respectively. This agrees with the removal efficiencies which makes LTA the best adsorbent since with the lowest q_e, thus, the volume of adsorbate required to form a monolayer on the adsorbent (LTA) was less than that of LTX and LSX. This confirms the relationship that the maximum adsorption capacity of an adsorbent is inversely proportional to its slope. Thus, the lower the slope or gradient of adsorption, the higher the adsorption capacity. The Freundlich isotherm, however, indicates that LTA had a very high adsorption capacity due to its low intercept and slope, thus confirming the relationship between adsorption capacity and gradient of adsorption. The adsorption intensity (1/n) gives an indication of the favourability of the adsorption. The high n values of LTA indicate a high favourability of adsorption by LTA. The World Health Organisation has set the minimum contaminant level for Arsenic as 0.01 mg/l [21]. Based on this it follows that only zeolite LTA was able to remove arsenic to such level (Table 1). However, it is possible that all the zeolite types could have removed almost all the arsenic if a second run of experiment was performed.

CONCLUSION

The removal of arsenic from rivers affected by mining activity in Ghana was successively investigated using zeolite types LTX, LTA and LSX. The sorption capacities of each zeolite were fitted with the Freundlich and Langmuir equations. Langmuir model gave a better fit in all cases as compared with the Freundlich model. However, the values of the Freundlich parameters indicate that the mechanism of arsenic removal can also be predicted by the Freundlich model. The high R^2 values obtained for zeolite type LTX and LSX with low R^2 value suggests that the mechanism of removal is dependent on the morphology of the zeolite

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