

Detoxification of lead and arsenic from galamsey polluted water using nano synthesized iron oxide from cupola furnace slag

John Ato Koomson^{a,*}, Bennetta Koomson^a, Clement Owusu^b, Frank Ofori Agyemang^a

^a Kwame Nkrumah University of Science and Technology, Ghana

^b University of Mines and Technology, Ghana

HIGHLIGHTS

- Cupola furnace slags are rich in iron oxides and can be recovered for various application.
- Magnetic separation and froth flotation were used to recover the iron oxides from the cupola furnace slag.
- The recovered iron oxides (Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, FeO_2H and $\gamma\text{-Fe}_2\text{O}_3$) were used for lead and arsenic adsorption.
- The iron oxides achieved high removal efficiency for the heavy metals (Pb and As).

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ABSTRACT

Drinking of water polluted with heavy metals is a means by which heavy metals bio accumulate in the human body. The rise in galamsey (illegal mining) activities in Ghana has resulted in heavy metal pollution in most water bodies in the country. Above the permissible limits, these metals cause health issues such as cancer, brain damage, kidney damage and other respiratory diseases. Hence, a smart solution to this menace is urgently needed. In this study, iron oxides were recovered from cupola furnace slag by magnetic separation and froth flotation. The recovered iron oxide was modified using electrospinning with the aid of polyvinyl alcohol after which it was calcined and used as adsorbent to detoxify lead and arsenic from two galamsey polluted water bodies in Obuasi, Ghana. Samples of the adsorbent were characterized using X-ray Fluorescence (XRF), X-ray Diffractometry (XRD), Fourier Transform Infrared Spectrometry (FTIR), Scanning Electron Microscopy (SEM) and Brunauer-Emmer-Teller (BET) method. The highest recovery for iron oxide using magnetic separation was 99.42% and that of froth flotation was 90.64%. The recovered iron oxide used as adsorbent was composed 53.04% iron oxide, with major phases like magnetite, hematite, goethite and quartz. Moreover, the surface functional group were determined to be Fe-O and OH. Also, the calcined nano fibres which were spherical in shape with rough surfaces had a specific surface area of $1.1331 \text{ m}^2/\text{g}$. The contaminated and detoxified water were also analyzed using Atomic absorption Spectroscopy (AAS). Both adsorbent (beneficiated iron oxide and calcined nano fibre) performed well in the adsorption process, with the recovered iron oxide having 97.33% maximum lead removal efficiency while an 81.00% maximum removal efficiency for arsenic. The calcined nano fibre had a maximum of 99.99% removal efficiency for lead and 88.40% maximum efficiency for arsenic. Additionally, the adsorption fits the Langmuirian isotherm model better than the Freundlich model, indicating mono layer coverage.

1. Introduction

The contamination of water bodies by heavy metals is a worldwide concern due to its effects on human health [1–4]. For instance, heavy metals exposure can lead to hypertension, decline in fertility, brain

damage, anemia, kidney damage and nervous system disorders [5–7]. Further, children who survive heavy metal poisoning are known to have behavioral disorders afterwards [8,9]. Additionally, it is important to mention that some of the aforementioned implications related to heavy metals exposure are irreversible.

* Corresponding author.

E-mail address: johnkoomson332@gmail.com (J.A. Koomson).

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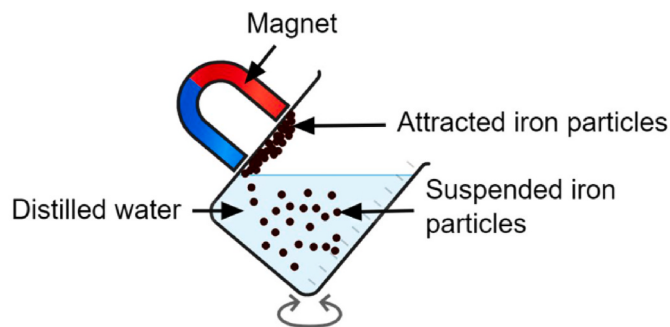


Fig. 1. Schematic diagram of magnetic separation.

In recent times, surface water, which is a major source of drinking water in many villages and towns in Ghana has experienced heavy metal contamination. This is due to the upsurge of illegal mining (popularly known as ‘*galamsey*’) activities [10,11]. Since large volumes of water is needed for washing the ores these mining activities are sited near water bodies, leading to the release of such heavy metals into water bodies. The release is as a result of heavy metals being associated with these ores. Arsenic for instance is associated with sulphide bearing minerals like arsenopyrite (FeAsS), Realgar (As_2S_2) and Orpiment (As_2S_3) [12].

Also, the annual ferrous slag production in Ghana stands at about 50 000 tons – a figure that keeps increasing with a significant rise in foundries across the country [13,14]. Ferrous slags generated in Ghana are mostly disposed in un-engineered landfills [14]. Characterization of typical ferrous slag samples from cupola furnace slags generated in Ghana gave the following compositions; CaO 4.19–5.97%, MgO 0.34–2.00%, Al_2O_3 6.10–18.16%, SiO_2 22.2–48.54%, Na_2O 4.88–15.90%, Fe_2O_3 3.67–19.26%, MnO 0.55–1.79% and K_2O 0.27–0.41% [13,14]. From the composition, it is obvious that iron oxide and silica are major constituents of steel slags found in Ghana.

Recovery of iron content in ferrous slag is a well-known technique [15]. [16] optimized the magnetic separation process and were able to recover up to 93.20 wt%, 92.48 wt% and 85.82 wt% for basic oxygen furnace slag (BOFS), desulfurization slag (DS) and iron ladle slag (ILS) respectively [14]. also worked on cupola furnace slag (CFS) at a particle size of 80% passing 75 μm , using magnetic separation. The recovery was 99.04%. Although flotation has not been used to concentrate ferrous slags, it has shown significant advantages like higher process selectivity and rates, as well as satisfactory results even when hard water is used for treating low grade ores containing iron-bearing silicates [17]. In this work, magnetic separation and froth flotation are used to recover iron oxide from cupola furnace slag.

Moreover, to improve the effectiveness of the recovered iron oxide for adsorption purposes, the iron oxides were electrospun into nano fibres. Nano-based adsorbents are a preferred choice in detoxifying heavy metals when paralleled with their bulk counterparts due to features such as small size, large surface area, easy separation of adsorbents from the system, ability to adsorb toxic substances by ion precipitation, ion exchange and its reusability (which leads to a decrease in the economic burden) [2,3]. Consequently, in the removal of heavy metals such as arsenic, chromium and lead from polluted water, magnetic nanoparticles like magnetite (Fe_3O_4) and hematite (Fe_2O_3) have been employed as nano-adsorbents [2,18].

This research work thus focuses on beneficiating iron oxides using froth flotation and magnetic separation and nano synthesising the iron oxides using electrospinning for subsequent arsenic and lead removal from *galamsey* polluted water. Additionally, properties like mineralogical, morphological and surface area of the recovered iron oxide and the electrospun fibres were compared.

2. Materials and methods

2.1. Sampling and sample preparation

2.1.1. Slag and water sample

Samples of cupola furnace slags were sourced from Suame Magazine (6.724229°, –1.625748°), located in Kumasi- Ghana. Using simple random sampling, slag samples were collected from different companies in the vicinity.

Water samples were collected at two river bodies from Obuasi- Ghana, namely; Kwabrafo River (6.19498°, –1.65252°) (less than 200 m from the *galamsey* site) and Jimi River (5.98043°, –1.7751°) (about 1 km from the *galamsey* site) during the dry season (December 2021). The samples were collected into plastic bottles, which had been adequately washed with detergents and rinsed several times with deionized water. The water samples upon collection were stored in a cool place (~20 °C) prior to subsequent laboratory works.

2.1.2. Cupola slag sample preparation (comminution of the sample)

Cupola furnace slag samples were crushed using a laboratory jaw crusher (KHD Humboldt Wedag AG, 9 857 655 054), and a metallic mortar and pestle were used to further reduce the size. The sample (about 3 kg) was then dry milled using a ball mill (15 kg charge steel balls, 73 rev/min) for 15 min to obtain the required feed size for subsequent characterization and beneficiation studies. The milled products were then screened into different size fractions (–150 + 90 μm , –90 + 45 μm and –45 μm) using test sieves. Representative samples of the respective size fractions were used for beneficiation processes. A loss on ignition test was carried out on the slag sample following ASTM D7348 – 13 to determine the organic matter content of the slag. Compared to others this method is a simple and cost effective method used to determine the amount of organic matter in the sample. Percentage loss on ignition was calculated using Equation (1). The result from this test was used to estimate the percentage of volatile matter in the crucible.

$$LOI = \frac{M_1 - M_2}{M_1} \times 100\% \quad (1)$$

LOI is the percentage loss on ignition (%).

M_1 is the mass of slag before ignition (g)

M_2 is the mass of slag after ignition (g)

2.2. Beneficiation

2.2.1. Magnetic separation of iron oxide from cupola furnace slag

Magnetic separation with a hand-held laboratory magnet was conducted using 10 g of the sample for each separation process. The sample was slurried to achieve 10% solid loading. The hand-held laboratory magnet with strength 111.5 mT tested using a hand held Digital Tesla-meter (Tunkia, TD8620), was used to separate the magnetic fraction from gangue. A schematic diagram of the process is shown in Fig. 1. Concentrates and tailings from the entire process were then oven dried at 100 °C for 1 h 30 min (Binder GmbH Bergstr. 14 D-78532 Tuttingen) before metal assay analysis. Results of recoveries were computed using Equation (2):

$$R = \frac{100c(f - t)}{f(c - t)} \quad (2)$$

Where.

R is the % Recovery (%)

c is the assay of concentrate (%)

f is the assay of feed (%)

t is the assay of tailings (%)

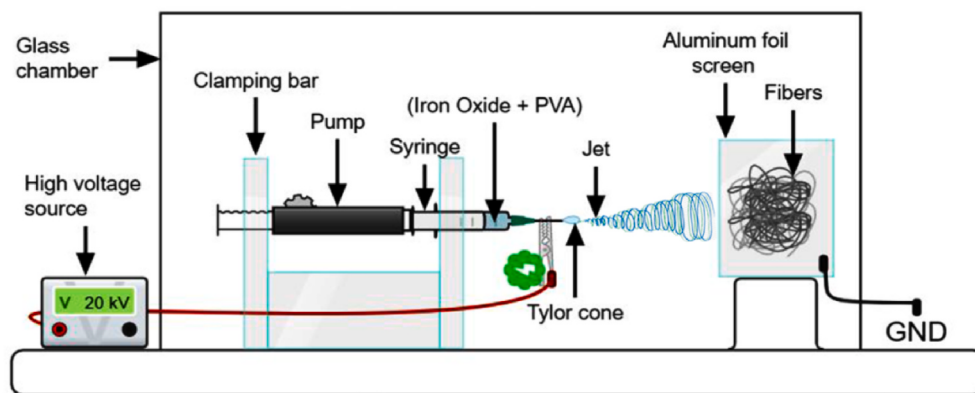


Fig. 2. Schematic diagram of electrospinning set – up.

Table 1

Initial concentration and pH values of samples.

Sample	Lead		Arsenic	
	Concentration (ppm)	pH	Concentration (ppm)	pH
Solution	10	3.30–3.32	10	2.63–2.73
Jimi	0.74	7.68–7.80	13.87	3.82–3.89
Kwabrafo	8.77	7.45–7.64	21.00	3.61–3.65

Table 2

Other metals present in River samples.

River	Zn	Cu	Cd
	Concentration (ppm)		
Jimi	0.031	0.016	0.126
Kwabrafo	0.110	0.039	0.122

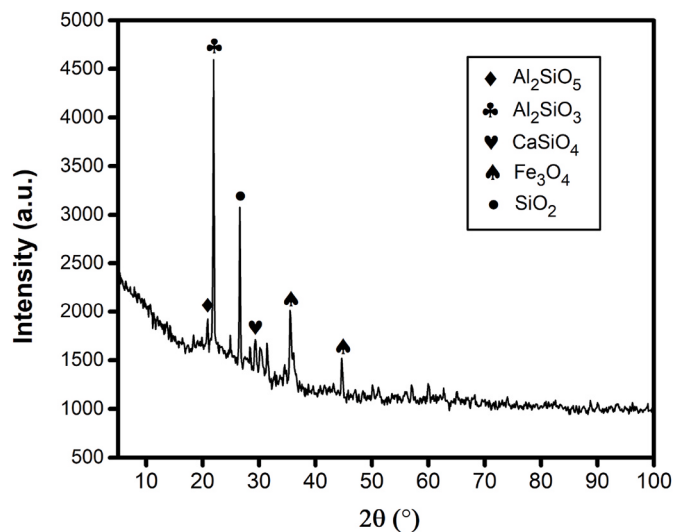


Fig. 4. XRD spectra of cupola furnace slag.

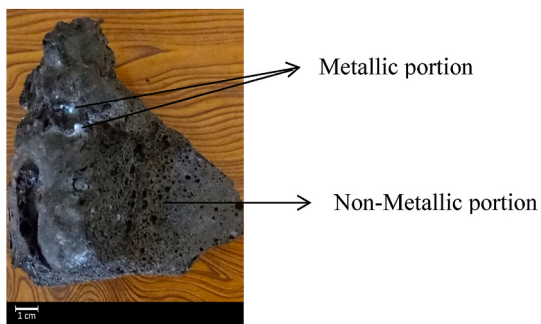


Fig. 3. Image of cupola furnace slag.

Table 3

Chemical composition of cupola furnace slag.

Chemical	Composition (wt%)
SiO ₂	54.44
Fe ₃ O ₄	22.85
MnO	4.40
Al ₂ O ₃	3.95
Others	2.66
CaO	2.067
P ₂ O ₅	0.45
TiO ₂	0.37
K ₂ O	0.36
SO ₃	0.064
LOI	–2.75

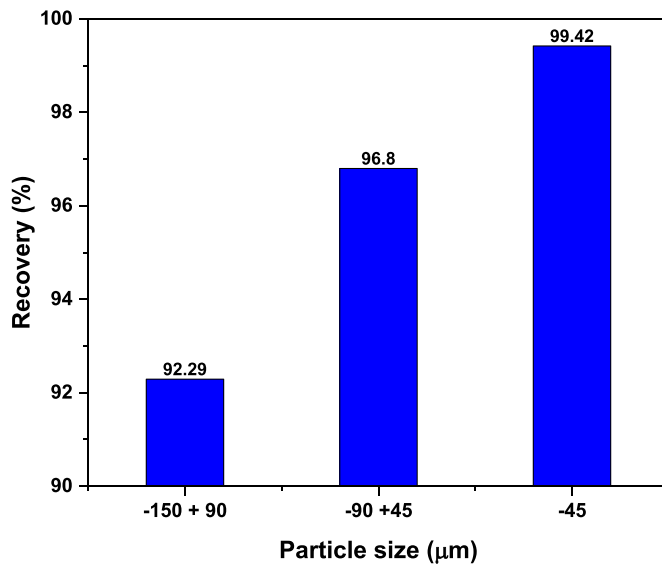


Fig. 5. Effect of particle size on iron oxide recovery.

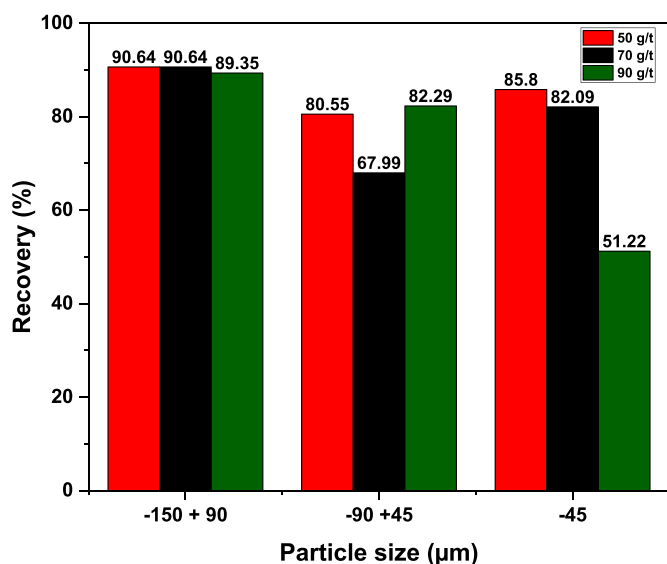


Fig. 6. Effect of particle size on iron oxide recovery.

2.2.2. Flotation of iron oxide from cupola furnace slag

Flotation tests were done using a Denver D12 Laboratory Machine. Two hundred grams (200 g) of the slag sample was used for each experiment. All experiments were conducted at the natural pH of the slags (8.12–8.30) to ascertain the floatability of slag in its natural state. The pulp density was 17%. The collector used was sodium oleate at dosages of 50 g/t, 70 g/t and 90 g/t. The frother used was 10 drops of

18% Nitrogen sulfide. The conditioning time for the pulp, frother and collector were 2 min, 2 min and 1 min respectively. The impeller speed was maintained at 1100 rpm for both conditioning and flotation. Deionized water was used in all the test work. Flotation time was 5 min and oxygen flow rate for all samples was 4–5 L/min.

The flotation products; concentrates and tailings were dried in an oven at 105 °C (Binder GmbH Bergstr. 14 D-78532 Tuttingen) and analyzed using XRF. Iron oxide recovery was determined using Equation (2).

2.3. Electrospinning of iron oxide nano fibres

About 3 g of polyvinyl alcohol (PVA) chips were dissolved in 30 mL of water. The mixture was stirred at 500 rpm (25 °C) for 1 h, the temperature was then raised to 95 °C for 2 h using stirring hotplate (Heidolph MR3001K, Germany). 0.24 g of iron oxide were dispersed in 5 mL distilled water. The iron oxide nanoparticles suspension, were then added to the as prepared PVA solution and stirred to obtain a homogeneous mixture before electrospinning.

Table 4

Chemical composition of the iron oxide.

Chemical	Composition (wt %)
Fe ₃ O ₄	53.04
SiO ₂	34.98
Others	5.21
MnO	2.79
Al ₂ O ₃	2.76
CaO	1.22

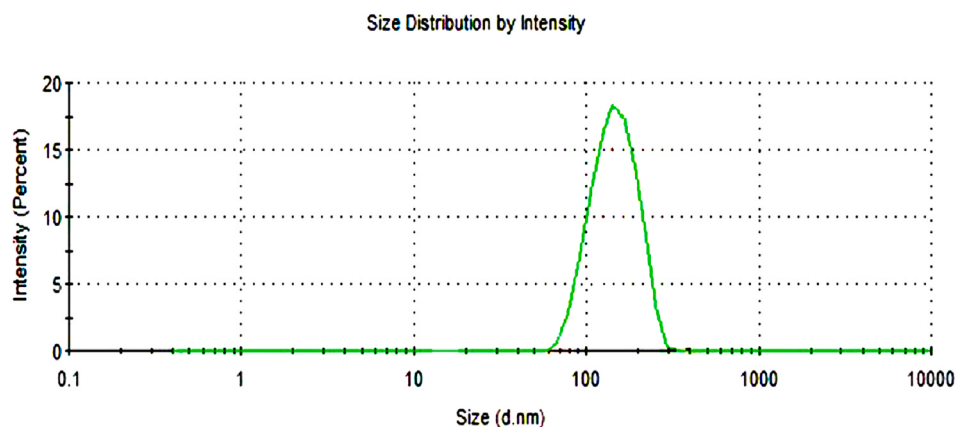


Fig. 7. Particle size Distribution of iron oxide nanoparticles.

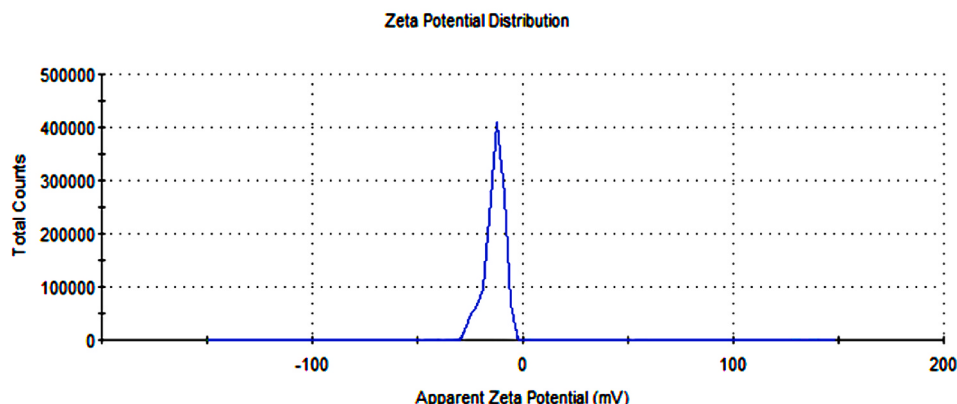


Fig. 8. Zeta Potential Distribution of iron oxide nanoparticles.

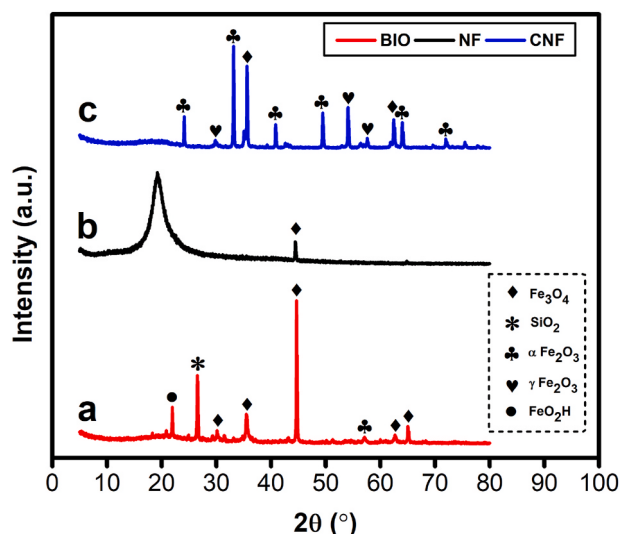


Fig. 9. XRD spectra of (a) beneficiated iron oxide (BIO) (b) iron oxide/PVA nano fibre (NF) and (c) calcined nano fibre (CNF).

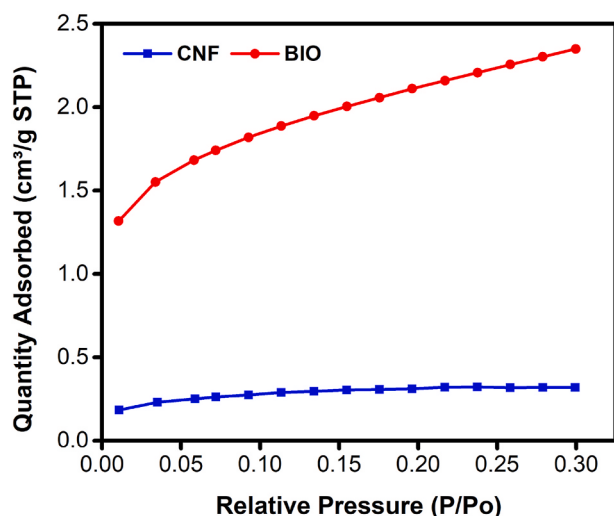


Fig. 10. Adsorption isotherm of adsorbents.

The electrospinning set up consisted of a syringe pump, a DC voltage source (NanoNC) and a stationary collector. The solution was electrospun using 20 kV at a flow rate of 0.5 mL/h and a 15 cm distance between collector and injector. The nano fibres were collected on a cleaned aluminum foil. The fibres were removed and dried at 105 °C for 10 min. After drying, it was calcined at 600 °C for 2 h. Set up for the electrospinning process is shown in Fig. 2.

2.4. Physical, chemical and mineralogical characterization of adsorbent

To determine the chemical composition of the beneficiated iron oxide (BIO), representative sample was analyzed using a hand-held portable X-ray fluorescence spectroscopy gun (XRF- Spectro X-LAB 2000). Particle size distribution of iron oxides was analyzed to determine the size range prior to the electrospinning process. The particle size distribution and zeta potential of the iron oxide sample were determined using the Dynamic Light Scattering (DLS) procedure with a Malvern Zetasizer Nano ZS ZEN 3600. Mineralogical composition of adsorbents were determined using a Bruker X-ray diffractometer (Advance D8) operated at 40 kV and 40 mA with Cu K α radiation of a wavelength, $\lambda = 0.1541$ nm. Scanning was performed for 2θ values between 10° and 80° at a step size of 0.02°/min. To obtain data on the surface functional groups of the adsorbents, spectra of the samples were acquired using a Bruker Platinum ATR spectrometer. The characterization was done by taking readings from 400 cm^{-1} to 4000 cm^{-1} . Surface area measurements were carried out by nitrogen adsorption conducted at room temperature on a Micromeritics TriStar II 320. Surface morphology of adsorbents was done using A JSM-6390 Scanning Electron Microscope at an acceleration voltage of 20 kV.

2.5. Batch adsorption experiment

Arsenic (As^{3+}) and lead (Pb^{2+}) concentrations of 10 ppm each were prepared from 1000 ppm stock solution. All reagents used were of acceptable commercial grade (source: inorganic ventures). The batch adsorption experiments were done by adding 1 mg and 2 mg of

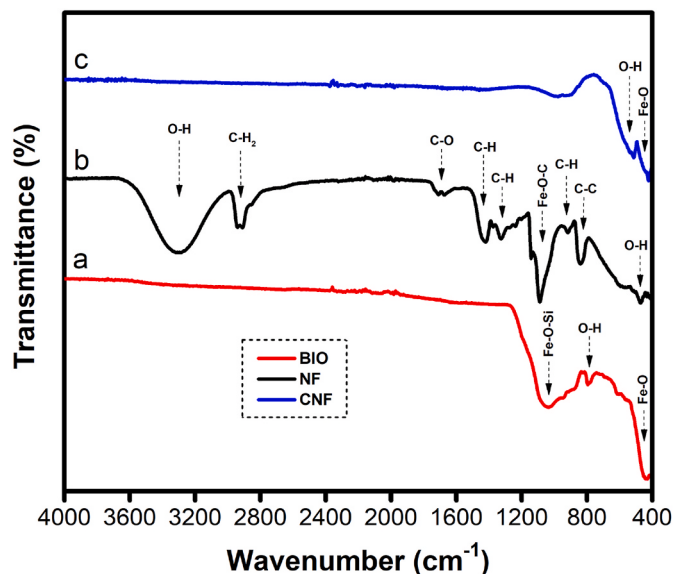


Fig. 12. FTIR of (a) beneficiated iron oxide (b) iron oxide/PVA nano fibre and (c) calcined nano fibre.

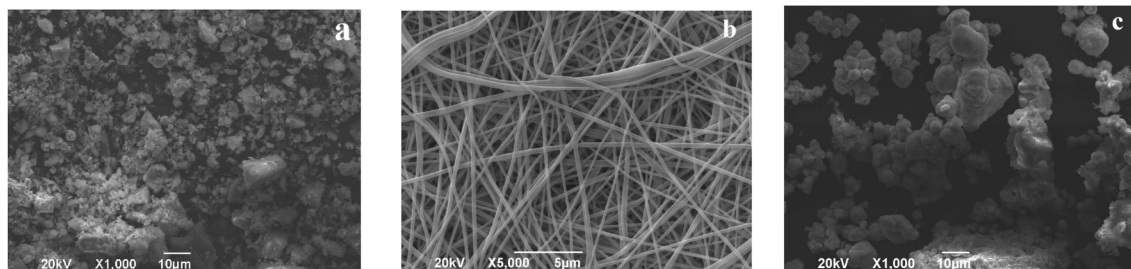


Fig. 11. SEM images of (a) beneficiated iron oxide (b) iron oxide/PVA nano fibre (c) calcined nano fibre.

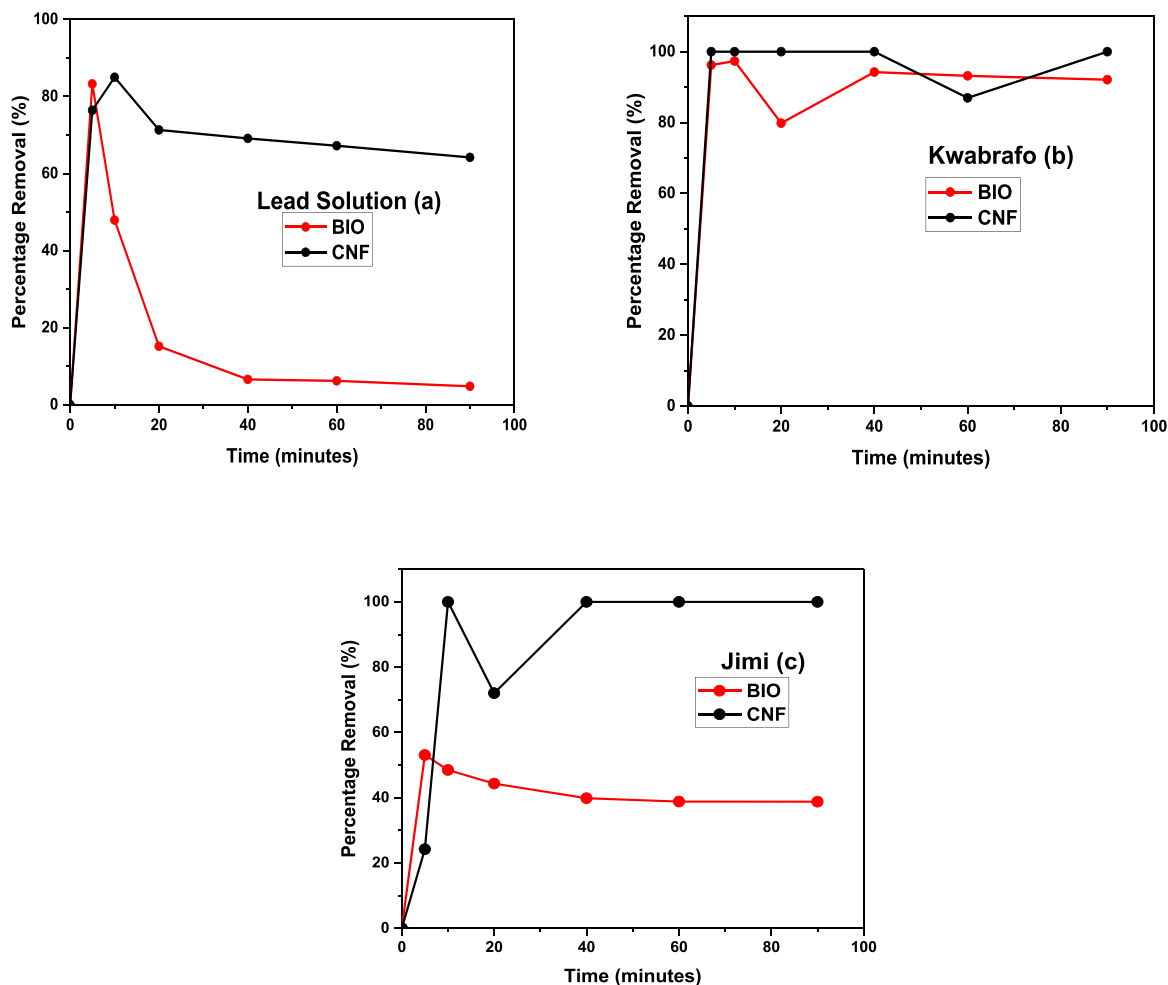


Fig. 13. Effect of contact time on lead adsorption: (a) lead solution (b), Kwabrafo River (c) Jimi River.

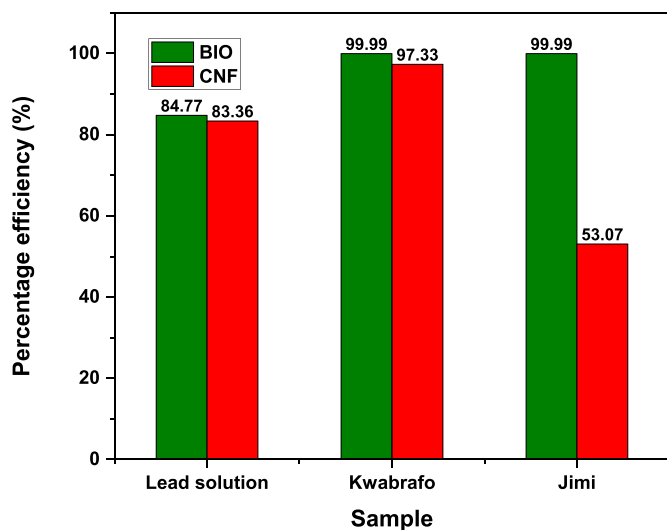


Fig. 14. Effect of adsorbent type on lead adsorption.

adsorbents into 40 mL of the lead solution and 30 mL of arsenic solution. The tubes were mounted onto a rotary suspension mixer at a constant speed of 80 rpm. All experiments were done at 1 atm and 20 °C.

Afterwards, the centrifuge tubes were removed at different time interval for analysis. The same procedure was repeated for the galamsey polluted water from Jimi and Kwabrafo. The adsorption efficiency was calculated using Equation (3). The initial concentrations and chosen pH of the samples used for adsorption is shown in Table 1. Table 2 shows other heavy metals present in the river samples.

$$AE = \frac{C_i - C_f}{C_i} \times 100\% \quad (3)$$

Where,

AE is the adsorption efficiency (%)

C_i is initial concentration of metal ion (ppm)

C_f is the residual final concentration of metal ion (ppm)

2.6. Adsorption isotherm and other related parameters

The amount of solute adsorbed per unit weight of adsorbent at equilibrium was calculated using equation (4).

$$q_e = \frac{(c_i - c_e)V}{m} \quad (4)$$

Where,

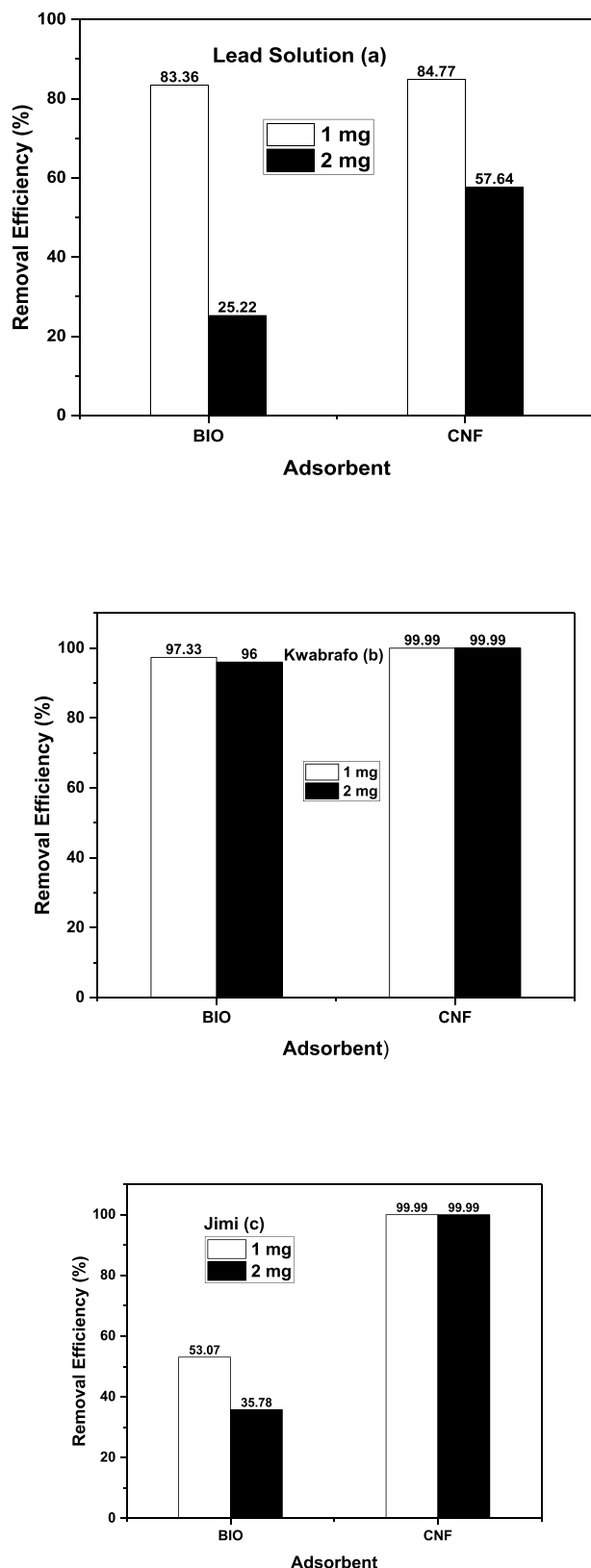


Fig. 15. Effect of adsorbent dosage on lead adsorption: (a) lead solution (b) Kwabrafo River (c) Jimi River.

q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g).

C_e is the equilibrium concentration of solute in solution (mg/L).

m is the mass of adsorbent (g)

V is the volume of solution (L)

Adsorption data was fitted to linearized form of Freundlich and Langmuir isotherm models using equations (5) and (6) respectively.

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad (5)$$

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e} \quad (6)$$

Where.

K_f is the Freundlich adsorption constant

n is the empirical constant

q_{max} is the maximum adsorption capacity of adsorbent (mg/g).

b is the Langmuir constant (L/mg).

The separation factor which determines the favourability of adsorption in the Langmuir model was calculated using equation (7).

$$R_L = \frac{1}{1 + bC_i} \quad (7)$$

Where.

R_L is the separation factor

3. Results and discussion

3.1. Characterization of slag

3.1.1. Physical characteristics

Fig. 3 is an image of cupola furnace slag used in this work. It can be noticed from the image that the slag has black to dark blue colour which is similar to that realized by Ref. [13]. The metallic parts are lustrous while the non-metallic portions are dim. It is observed that the inefficiency of the melting process leads to portions of the free metals ending in with the slag phase. Portions of the metal are free while others were bonded to the slag. Commintion was therefore needed to separate as much as possible the other components from the iron oxide for maximum recovery.

3.1.2. Chemical composition of slag

The result of the chemical and mineralogical composition of the slag is presented in Table 3. The result shows the presence of major oxides; SiO_2 (54.44 wt %) and Fe_3O_4 (22.85 wt %). Minor oxides like Al_2O_3 , and MnO were also noticed.

This composition agrees with the assertion that even without slag forming additives, the slag formed by a cupola furnace is composed of Al_2O_3 , SiO_2 , and oxides of manganese and iron [19]. It is also realized that K_2O , CaO and TiO_2 are in trace amounts. The iron oxide content is high enough to be beneficiated using magnetic separation and froth flotation. The Loss on ignition for the sample was found to be negative, indicating that elements in the sample can undergo oxidation. For instance, magnetite can undergo oxidation to form maghemite ($\gamma\text{-Fe}_2\text{O}_3$) [14].

3.1.3. Mineralogical composition of slag

The result of the mineralogical composition of the slag is presented in Fig. 4. The major phases present in the slag include magnetite (Fe_3O_4), Quartz (SiO_2), Kaynite (Al_2SiO_5) and Calcium Silicate (CaSiO_4). These phases represent uniform compositions and properties in the slag.

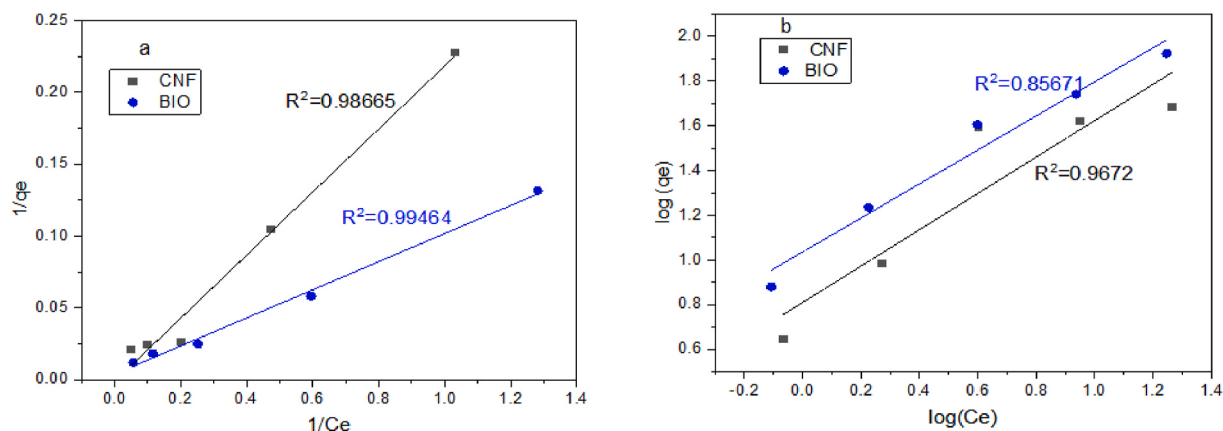


Fig. 16. Isotherm model plots for lead adsorption (a) Langmuir (b) Freundlich.

Table 5

Isotherm models' parameters for adsorption of lead unto adsorbents.

Isotherm	Langmuir				Freundlich	
	b (L/mg)	q _{max} (mg/g)	R _L (min)	R _L (max)	n	K _f
BIO	0.0389	264.4672	0.9625	0.562	1.314	10.88
CNF	0.0293	155.039	0.9715	0.631	1.230	6.47

3.2. Beneficiation

3.2.1. Magnetic separation of iron oxide from cupola furnace slag sample

The results of wet low intensity magnetic separation are presented in Fig. 5. It can be noticed that from a feed grade of 22.85%, the particle size ranges; $-150 + 90 \mu\text{m}$, $-90 + 45 \mu\text{m}$ and $-45 \mu\text{m}$ had recoveries of 92.29%, 96.8% and 99.45% respectively, revealing that the process was effective. Evidently, reduction in particle size of the slag leads to higher recoveries; this can be associated with the liberation of iron oxide from gangue minerals in the slag for finer particles. When iron oxides are liberated from gangue minerals, they become available for magnetic attraction, leading to higher recovery values. Coarser particles exhibit a net low susceptibility value due to the presence of impurities which are bonded to the iron oxide surface leading to low recovery values [14].

3.2.2. Froth flotation of iron oxide from cupola furnace slag

Fig. 6 shows result obtained from the flotation process applied in the work. Flotation of iron ores are characterized by different complex interaction at the surface of both gangue and mineral of interest. Generally, higher recovery values were noticed, however, the grade of

these products were low. It can be inferred that generally higher collector dosage led to a reduction in the recovery of iron oxide. For instance, for the particle size below $45 \mu\text{m}$, recovery values of 85.8%, 82.09% and 51.22% were obtained for collector dosages of 50 g/t, 70 g/t and 90 g/t.

It can be observed that the particles size range of $-150 + 90 \mu\text{m}$ gave the highest recovery. This is attributed to true flotation as opposed to particle entrainment which was responsible for the floating iron oxide particles at certain dosages in the lower particle size range.

The effect of collector dosage on recovery is seen to be very minimal on particle size between $-150 + 90 \mu\text{m}$, with recovery values of approximately 90%. For particle size between $-90 + 45 \mu\text{m}$, a discrepancy was noticed at collector dosage 70 g/t, where a recovery value of 67.99% was obtained. This observation could be attributed to either iron oxide particles floating due to particle entrainment or the presence of Ca^{2+} ions [20] from the slag sample which can get adsorbed to the fine iron oxide particles and join the froth.

3.3. Characterization of adsorbents

3.3.1. Particle size distribution and zeta potential of beneficiated iron oxide (BIO)

Fig. 7 is the particle size distribution of the iron oxide particles used for the nano fibre synthesis. The results obtained show that the particles were between the 100–1000 nm range, and the average particle size being 284.5 nm. This particle size range can be effectively used for nano fibre synthesis.

Fig. 8 presents result of the zeta potential of the beneficiated iron oxide. The results revealed that the average zeta potential of the iron

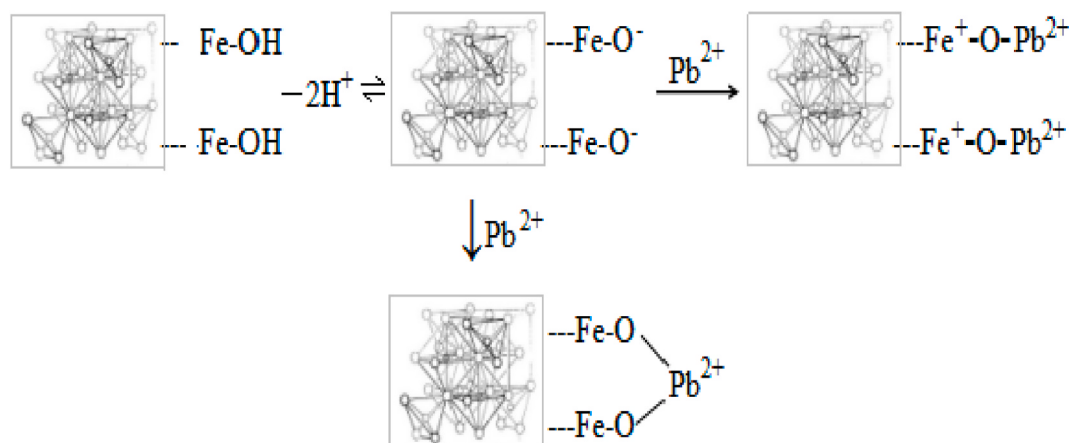


Fig. 17. Adsorption mechanism of lead on iron oxide nanoparticles [35].

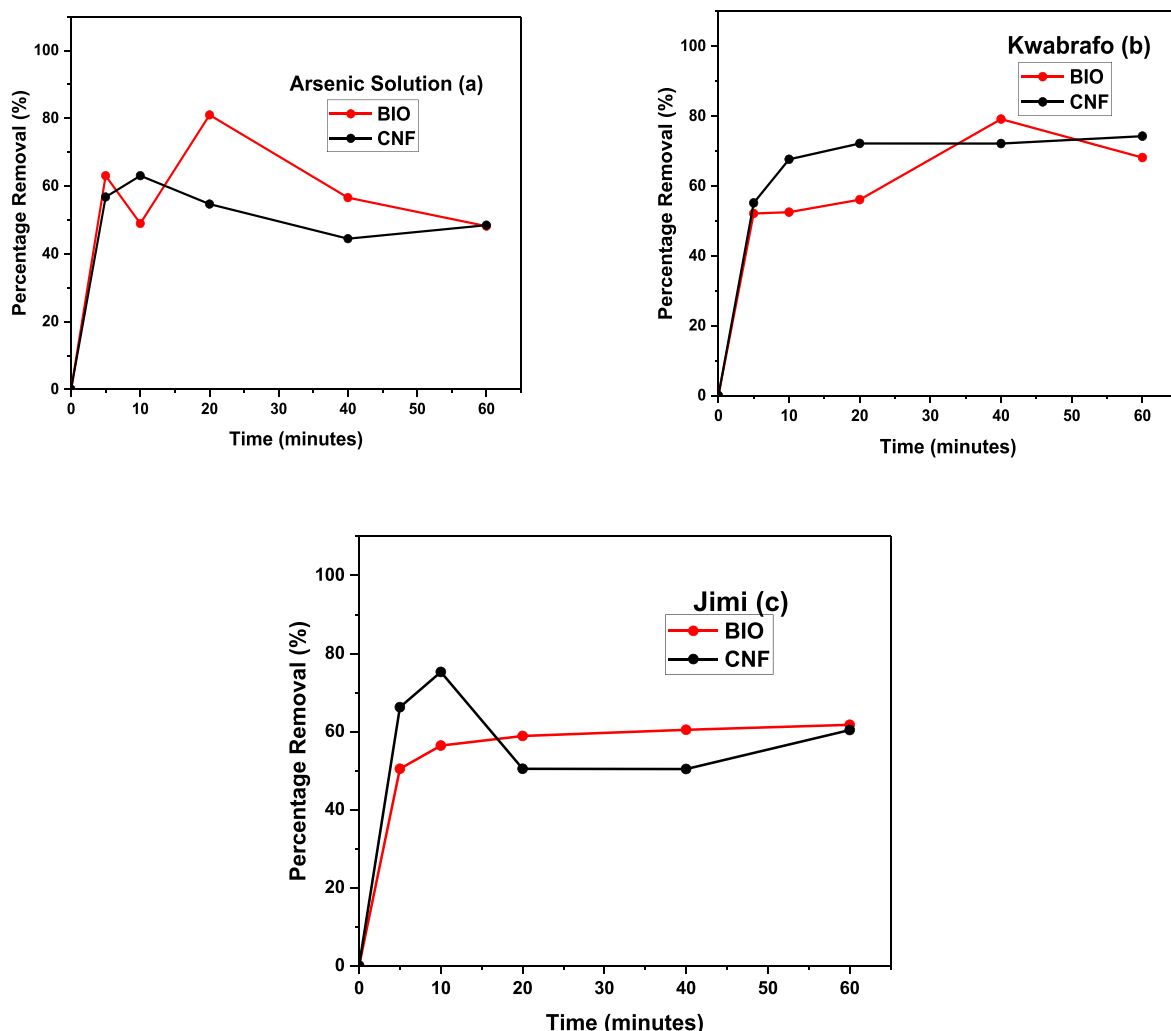


Fig. 18. Effects of contact time on arsenic adsorption: (a) arsenic solution, (b) Kwabrafo River, (c) Jimi River.

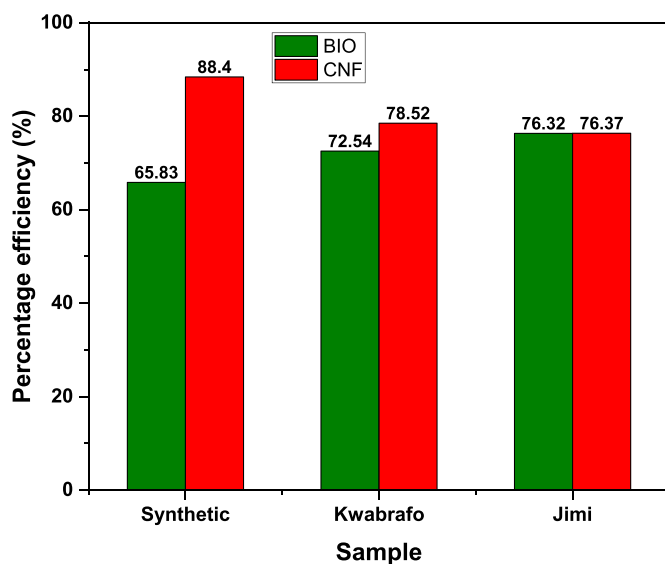


Fig. 19. Effect of adsorbent type on arsenic adsorption.

oxide used for synthesis was -10.7 mV, similar to value obtained by Ref. [21]. A zeta potential value above 30 mV (absolute) is a sign of an electrically stable suspension, this value suggests that a suspension of the iron oxide will be unstable and a possible agglomeration [22]. this results in colloidal particles becoming heavier and falling during adsorption, and consequently easily separable from the liquid phase. However, it will also lower the specific surface area and hence adsorption efficiency.

3.3.2. Chemical composition of beneficiated iron oxide

Table 4 presents the chemical composition of the beneficiated iron oxide sample employed in the adsorption. Apparently, the sample is composed majorly of iron oxide. From an initial iron oxide composition of 22.85% , it was upgraded to 53.04% . Other compounds such as Al_2O_3 , SiO_2 and MnO are also present due to their high composition in the slag sample.

3.3.3. Mineralogical composition of adsorbents

The iron oxide/PVA nano fibre (NF) show two main peaks: a broad peak at 19.2 and a peak at 44.4 . The broad peak at a 2θ value of 19.2 shows the semi-crystalline nature of the polymer used (PVA) and also the presence of large number of hydroxyl ($-\text{OH}$) groups in the PVA act as chelating sites for the metal cation in a definite pattern. The peak at 44.4 represents magnetite (Fe_3O_4). The low concentration of iron oxide

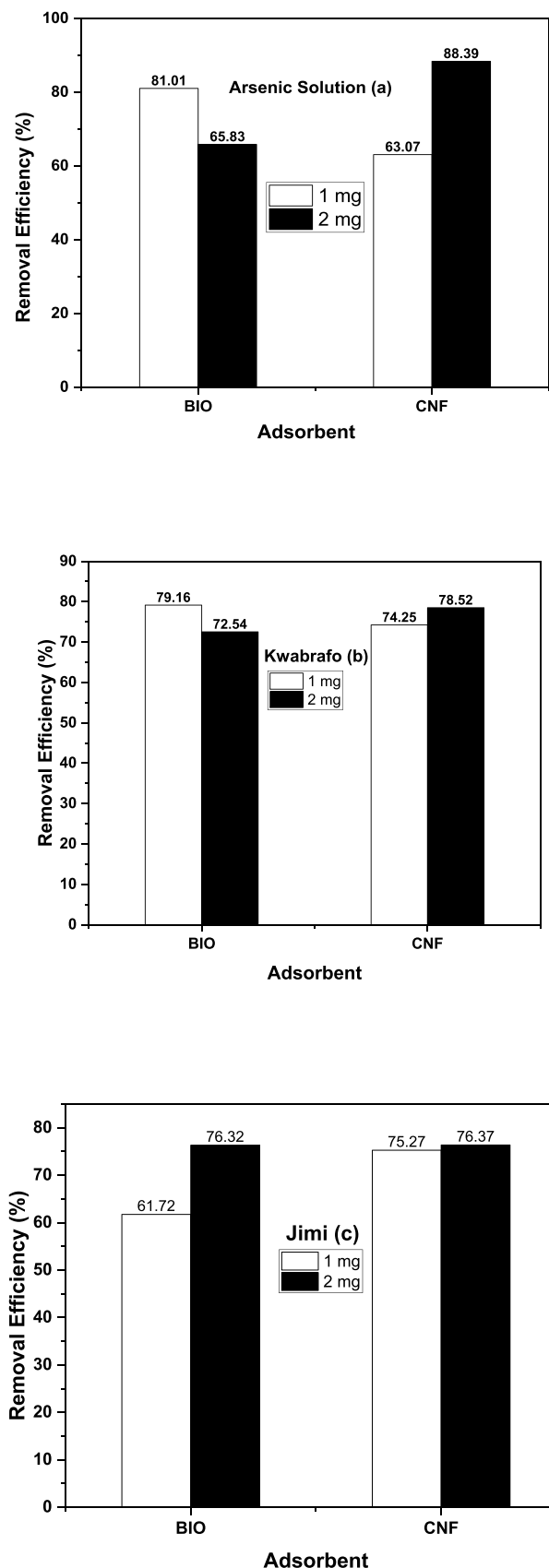


Fig. 20. Effect of adsorbent dosage on arsenic adsorption: (a) arsenic solution (b) Kwabrafo River, (c) Jimi River.

resulted in the amorphous patterns with diffraction lines [25].

The calcined nano fibre (CNF) had phases similar to the recovered iron oxide. However, it was observed that some phases have undergone phase transformation due to the high temperature the sample was subjected to. For instance, at a temperature between 300 and 425 °C, magnetite can transform to maghemite. Furthermore, transformation of magnetite to hematite can occur at 600 °C [26,27], hence, the observed phase transformations due to calcination.

Fig. 9 presents result of the mineralogical composition of the adsorbents used in this work. The patterns were within the interval of 10 ° to 80 °. The main peaks observed indicate the presence of magnetite, hematite goethite (FeO₂H) and quartz in the beneficiated iron oxide (BIO). The presence of the quartz phase is due to its relatively large amount in the slag sample. Intense and sharp peaks represent well crystalline nature of the iron oxide nanoparticles [23] while reduction in peak intensities represent amorphous nature [24].

3.3.4. Surface area of adsorbents

Fig. 10 is the nitrogen adsorption isotherm of the adsorbents used in the work. The BIO sample corresponds to the Type I isotherm. Type I isotherm is characterized by mono layer coverage explained by Langmuir isotherm. This indicates the presence of micro pores which fill at very low relative pressure with a steep uptake [28]. The graph not leveling off indicates the presence of appreciable amount of mesopores. The measured specific surface area value for the sample is 7.4972 m²/g.

The CNF corresponds to the Type I isotherm. This isotherm type is characterized by mono layer coverage and also shows the presence of micro pores. Micro pores fill at very low relative pressure with a steep uptake [28]. The value of the specific surface area was measured to be 1.1331 m²/g.

3.3.5. Morphology of adsorbents

Fig. 11 presents results of SEM image of adsorbents used and the electrospun nano fibre. The beneficiated iron oxide is irregularly shaped. Also, particles have agglomerated, this can be attributed to electrostatic interaction between the surfaces of the particles which causes particles to be attracted to each other [29]. The electrospun fibre is shown to be cylindrical, continuous, randomly oriented and homogenous with average diameter 319 nm. Additionally, the fibre does not show any major defect. The calcined fibres are mostly spherical in shape with rough surfaces which are good properties for adsorption purposes [30].

3.4. Batch adsorption

3.4.1. Fourier transform infrared spectroscopy (FTIR)

Fig. 12 presents the surface functional groups of the adsorbents used in this work. The major peaks at 429 cm⁻¹, 795 cm⁻¹ and 1035 cm⁻¹ represent Fe–O stretching [31] which also confirms the presence of magnetite, OH bond and Fe–O–Si stretching vibration [31] respectively. Also, the band at 3306 cm⁻¹ indicates the presence of an OH absorption stretching bond, 2935 cm⁻¹ and 2905 cm⁻¹ represents asymmetric and stretching and symmetric stretching of CH₂ respectively. The peak on 1710 cm⁻¹–1692 cm⁻¹ represent C=O (carbonyl stretching). The peak at 1426 cm⁻¹ and 1327 cm⁻¹ are CH bending vibrations of CH₂ and CH deformation vibrations [32,33]. The peak at 1085 cm⁻¹ is attributed Fe–O–C bond and further confirming PVA and Fe₃O₄ interaction [34]. The peaks at 916 cm⁻¹ is attributed to CH₂ rocking and the peak at 839 cm⁻¹ is assigned to C–C stretching vibration [32].

Adsorption of both lead and Arsenic can be achieved using hydroxyl functional group [14,35]. Hence peaks at 429 cm⁻¹ and 795 cm⁻¹ will enhance the adsorption abilities of the adsorbents.

3.4.2. Lead adsorption

3.4.2.1. Effect of contact time. The effect of contact time on the

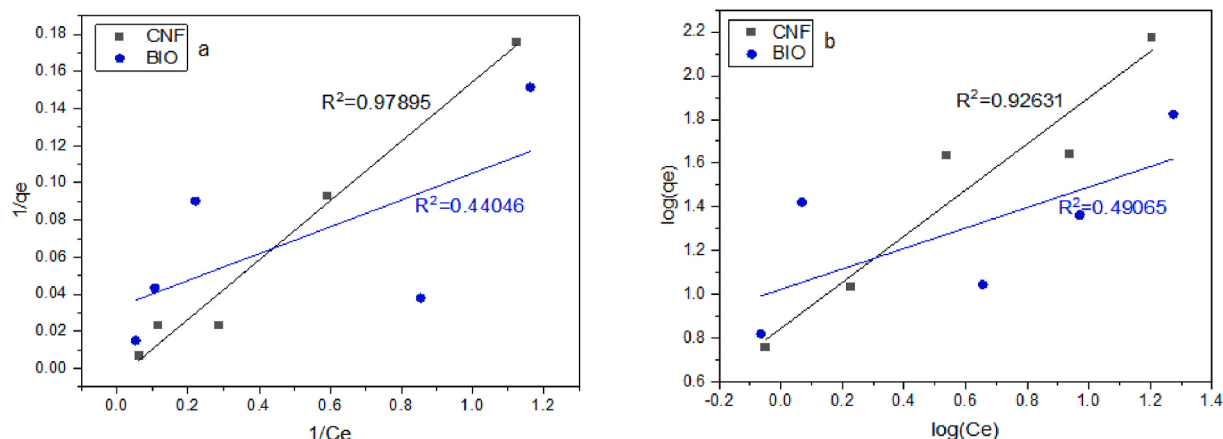


Fig. 21. Isotherm model plots for arsenic adsorption (a) Langmuir (b) Freundlich.

Table 6

Isotherm models' parameters for adsorption of arsenic unto adsorbents.

Isotherm	Langmuir				Freundlich	
	b (L/mg)	q _{max} (mg/g)	R _L (min)	R _L (max)	n	K _f
BIO	0.455	30.395	0.6871	0.09891	2.37	10.55
CNF	0.0144	434.78	0.9858	0.7764	0.95	6.99

adsorption behaviour of the adsorbents (BIO and CNF) is shown in Fig. 13. From the graphs it is evident that for each sample trends are similar for both adsorbents.

For the lead solution, after 5 min of adsorption, BIO and CNF had lead removal values of 83.26% and 76.40% respectively. After another 5 min (10th minute) the BIO reduced to 47.90% while the CNF increased to 84.97%. After the 40th minute, both started equilibrating. Optimum time therefore, is 5 and 10 min respectively for the BIO and CNF respectively.

For the Kwabrafo river, at the 5th minute BIO and CNF had adsorbed 96.22% and 99.97% respectively. Beneficiated iron oxide however dropped at the 20th minute to 79.80 after which it then increased to values above 90% again. Desorption of lead could be attributed to the breaking of the bonds between adsorbent and the lead ions, leading to the ions going back to solution. Desorption of lead into solution could also be attributed to the effect of other ions present in the water. The CNF however, maintained values of 99.99% except for the 60th minute where it had a value of 86.95% removal. Optimum time therefore is 10 min for both adsorbents.

For the Jimi River, there was a quick uptake by the BIO at the 5th minute with value of 53.07% after which it desorbed and equilibrated by the 40th minute at values between 38.70 and 39.83%. The CNF increased and by the 10th minute maximum adsorption had been reached, there was however desorption at the 20th minute after which it increased again to 99.99%. The reduction experienced at the 20th minute could be attributed to interactions of the solution and adsorbent which resulted to lead ions desorbing from the adsorbent surface back into the solution. Optimum time therefore, is 5 and 10 min respectively for the BIO and CNF respectively.

The effect of contact time can therefore be seen to be dependent on the type of water sample. Also, maximum adsorption is generally attained within the first 10 min.

The graph also shows equilibrium is generally reached after the 40th minute. However, since maximum adsorption is within the 10 min, adsorbents should be separated from water samples just after 10 min.

3.4.2.2. Effect of adsorbent type. Fig. 14 shows the effect of adsorbent type on the adsorption efficiency. The result reveals that the CNF

performed better than the BIO for all samples compared. For instance, for both Kwabrafo and Jimi the CNF had removal efficiency of 99.99% while the BIO had 97.33% and 53.07% respectively. The low performance by the BIO in the Jimi River sample is possibly due to the effect of the other ions such as zinc, arsenic, copper and cadmium in the river which compete for active sites on the adsorbent. The results from both adsorbents reveals that enhancing the structure of the material through electrospinning enhances the performance of the iron oxide. Properties like good surface roughness and stability of particles in solution improves the performance of the nano fibre [22,30].

3.4.2.3. Effect of adsorbent dosage. The effect of adsorbent dosage on adsorption efficiency is shown in Fig. 15. The result shows that the amount of Lead adsorbed by the nano fibre is not significantly affected by the dosage of the CNF for the river bodies but conversely for the lead solution. A decrease was seen when the dosage was increased from 1 mg to 2 mg for the lead solution. The values obtained for these dosages were 84.97% and 57.64% respectively. However, for the BIO, adsorbent dosage affects the amount of lead adsorbed significantly. For the concentrate an increase in dosage led to a decrease in lead removal considerably. When 1 mg adsorbent was used maximum recoveries of 83.36%, 97.33% and 53.07% were obtained for Lead solution, Kwabrafo and Jimi respectively. While 35.78%, 96.00% and 25.22% were obtained for Jimi, Kwabrafo and lead solution respectively, when 2 mg adsorbent was employed. The decrease in the efficiency on increasing adsorbent can be attributed to the agglomeration of adsorbent which leads to a decrease in surface area and hence lowering the adsorption capacity [36].

3.4.2.4. Isotherms. Both BIO and CNF were fitted with both Langmuir and Freundlich isotherm plots. The graphs are shown in Fig. 16.

From the Langmuir isotherm plot, the maximum adsorption capacities were found to be 264.4672 mg/g and 155.039 mg/g for BIO and CNF respectively. Also, the Langmuir constants for the BIO and CNF were 0.0389 L/mg and 0.0293 L/mg respectively. The dimensionless separation factors for both adsorbents were within the ranges of 0 and 1, indicating adsorption is favourable [14].

The calculated Freundlich constant from the Freundlich isotherm plot were 6.469 and 10.88 for CNF and BIO respectively. The values of the empirical constant n were also found to be 1.2298 and 1.314 for CNF and BIO respectively.

The values of the R^2 show the adsorption fit both isotherms. However, the R^2 values obtained for Langmuir were higher than Freundlich indicating mono layer coverage of lead ions on the surface of iron oxide [4,7]. Values of constants and other parameters obtained for both isotherms are shown in Table 5.

3.4.2.5. Mechanism of adsorption. Fig. 17 shows the adsorption mechanism by iron oxide nanoparticles. The uptake of dissolved lead in solution by iron oxide is known to be influenced by protonation and deprotonation which is affected by changes in pH [35,37]. On a surface of magnetite for instance, Fe-O⁻ could be available, and this is known to easily bond with Pb²⁺ [35], and more effectively above the point of zero charge of the iron oxide [37]. At lower pH values, due to the presence of more H⁺ ions, adsorption capacity is lowered since there is more competition between H⁺ and Pb²⁺ for negatively charged surfaces. Increasing pH reduces the H⁺ ions in solution, hence leading to higher adsorption by iron oxide. At very high pH values however (far above 8) adsorption capacity is lowered [7] this is possibly due to the high concentration of OH⁻ ions leading to Pb²⁺ precipitation [38].

3.4.3. Arsenic adsorption

3.4.3.1. Effect of contact time. The effect of contact time on the adsorption of arsenic is shown in Fig. 18. From the results obtained, the effect of contact time on arsenic adsorption with time is described in two main ways. A gradual removal with time and equilibrating or a quick uptake at the initial stages, and continuous desorption and re-adsorption.

In the arsenic solution for example, BIO had an initial removal of 63.07% and then desorbed to 48.96 before reaching the highest removal of 81.01% on the 20th minute. After this desorption kept occurring. Meanwhile the CNF kept increasing till the 10 min, achieving a removal percentage of 63.07%. A gradual desorption was then observed.

For Kwabrafo both adsorbents kept adsorbing with time. The fibre had an initial arsenic removal of 55.14% and increased to 74.25% by the 60th minute, however between the 20th and 60th minutes only a 2% increment was noticed. Hence, 20 min is the optimum time for arsenic removal. The BIO on the other hand generally increased to the 40th minute, achieving 79.16% arsenic removal before reducing at the 60th minute to 68.12%.

For Jimi, it is observed that BIO had removal percentage increasing to 50.46% at the 5th minute, and then gradually till the 60th minute, where the removal percentage was 61.72%. The CNF increased to 75.27% on the 10th minute and then reduced drastically to 50.39% on the 40th minute before an increment to 61.37% at the 60th minute.

This observed trend can be attributed to the presence of more vacant sites at the early stages leading to high removal, with time adsorption is slowed due to competition of ion for the few vacant sites. In other instances, desorption occurs and then re-adsorption before equilibrium is achieved.

3.4.3.2. Effect of adsorbent type. Fig. 19 presents the effect of adsorbent type on the adsorption efficiency. From the results both adsorbents performed well in adsorbing arsenic from solution. It can be observed however that the CNF performed better than the BIO. The adsorption efficiencies for both adsorbents on the Jimi River sample is approximately equal. While the BIO had removal efficiencies of 65.83% and 72.54% for Arsenic solution and Kwabrafo River respectively, the CNF had efficiencies of 88.4% and 78.52%. The high efficiencies of the CNF are due to the change in the structure as seen by various characterizations which subsequently improved the properties like adsorbent's stability in solution and surface roughness. Also, the relatively low performance of the adsorbent on the river bodies compared to the synthetic sample is due to the presence of competing ions like zinc, copper, lead and cadmium in the river samples.

3.4.3.3. Effect of adsorbent dosage. Fig. 20 shows the effect of adsorbent dosage on adsorption efficiency. The influence of adsorbent dosage of the BIO is seen to be inversely related to removal efficiency of arsenic. For instance, for the lead solution BIO had efficiencies of 81.01% and 65.83 for 1 mg and 2 mg respectively. Only Jimi River showed a

different trend where efficiency values were 61.72% and 76.32%. The inverse relation experience by the concentrate is attributed to the tendency of the adsorbent agglomerating in solution [36] which leads to a reduction in surface area and subsequently removal efficiency.

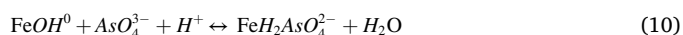
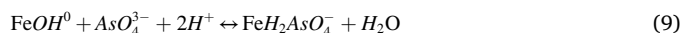
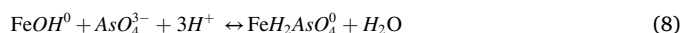
Increasing adsorbent increased the sites for adsorption [39] and hence adsorption efficiency. Increasing dosage from 1 mg to 2 mg for arsenic solution for instance, increased the maximum removal from 63.07 to 88.4%. The trend showed by CNF is due to its stability in solution.

3.4.3.4. Adsorption isotherm. Both BIO and CNF were fitted with the Langmuir isotherm and Freundlich plot. Fig. 21 is the results of graphs obtained.

The maximum adsorption capacities were found from the Langmuir plot to be 30.395 mg/g and 434.78 mg/g for BIO and CNF respectively. Also, the Langmuir constants were 0.455 L/mg and 0.0144 L/mg for BIO and CNF respectively. The dimensionless separation factors for both adsorbents were within the ranges of 0 and 1, indicating adsorption is favourable [14].

From the Freundlich isotherm plot, the values of the empirical constants *n* were found to be 0.95 and 2.37 for CNF and BIO respectively. Also, the Freundlich constants for BIO and CNF were 10.55 and 6.99 respectively. Values of constants and other parameters obtained for both isotherms are shown in Table 6.

3.4.3.5. Mechanism of adsorption. The adsorption of arsenic on iron oxide is influenced by the pH of the solution containing the arsenic ions. This is characterized by the presence of surface functional groups like FeOH²⁺, FeOH and FeO⁻. In solution Arsenic usually exists in the form H₂AsO₄⁻, hence in the acidic region adsorption is favoured. At lower pH values, more positive charges become available on the adsorbent surface hence attracting more arsenic ions, above the point of zero charge however, adsorption of arsenic is decreased as a result of the repulsive electrostatic effect [40]. Furthermore, the functional group of iron hydrides have double pairs of electrons with a hydrogen that dissociates, aiding the reaction between iron oxides and other ions in solution to form surface complexes [41] as shown in Equations (8)–(11).



4. Conclusion

In this research, the nano synthesis of iron oxides recovered from cupola furnace slag for heavy metal removal from *galamsey* polluted water was aimed at. From the results obtained, the following conclusions can be drawn; The slag used was a typical CFS. Major mineral phases found include magnetite, quartz, kaynite and calcium silicate confirming the presence of iron oxide which made up to 22.05% of the entire slag, a grade high enough for beneficiation. The results showed that reduction in particle size liberates the iron oxide for higher recovery. Recovery values of 92.29%, 96.8% and 99.45% for -150 + 90 μm, -90 + 45 μm and -45 μm respectively were obtained. The use of flotation for iron oxide recovery is also possible and yielded relatively high recoveries. This implies the over 50 000 tons of ferrous slags produced in Ghana can be put to good use by reclamation of iron content using magnetic separation or flotation. Moreover, electrospinning in tandem with calcination can be used to synthesize iron oxide nano fibres for adsorption purposes. Both adsorbent (beneficiated iron oxide and calcined nano fibre) are able to adsorb lead and arsenic from polluted water. The beneficiated iron oxide had maximum removal efficiency of

97.33% for lead and 81.00% for arsenic. While calcined nano fibre had maximum removal efficiency of 99.99% for lead and 88.4% for arsenic. The adsorption mechanism by the iron oxides is well described by the Langmuir isotherm model, indicating mono layer coverage. These results show the recovered iron oxides from ferrous slags can contribute significantly in solving the problem of heavy metal pollution by galvanic activities.

Credit author statement

John Ato Koomson: Obtained samples for the work. Performed sample preparation and experiments. Analyzed and interpreted data obtained. Drafted manuscript. And acquired Funding for the research. Bennetta Koomson: Devised the main conceptual idea of the research. Performed sample preparation and experiments. Analyzed results obtained. Reviewed manuscript. And acquired Funding for the research. Frank Agyemang: Obtained samples for the work. Analyzed results obtained. Reviewed manuscript. Clement Owusu: Performed sample preparation and experiments. Analyzed results obtained. Reviewed manuscript.

Declaration of competing interest

There is no conflict of interest of competing interest due to financial support or funding acquired.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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