Zeolite modified with copper oxide and iron oxide for lead and arsenic adsorption from aqueous solutions
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ABSTRACT
How to completely remove toxic metals from water is still a serious challenge, and is the mission that faces researchers and scientists today. In this work, zeolite/copper oxide (CuO) and zeolite/iron oxide (Fe₃O₄) nanocomposites (NCs) were prepared via a co-precipitation method. Several techniques were used for characterization of the prepared NCs including UV-visible, powder X-ray diffraction, N₂ adsorption for determining the specific surface areas (Brunauer–Emmett–Teller (BET)) and pore volumes. The morphology was investigated by field emission scanning electron microscopy. The batch adsorption experiment process was used to study the applicability of the prepared NCs to removing lead (Pb) and arsenic (As) from aqueous solutions. The effects of the adsorbent dosage, pH, initial metal concentration and contact time on the adsorption process were investigated. The obtained results revealed that in 40 minutes 0.15 g of prepared zeolite/Fe₃O₄ (NCs) was able to remove 97.2% of Pb and 96.8% of As from 100 mg/L aqua solutions at a pH of between 4 and 6. The Langmuir isotherm model showed higher correlation coefficients and provided better agreement with the experimental data. The adsorption kinetic is a chemi-physisorption process that follows the pseudo second-order kinetic model.

INTRODUCTION
Today the world community faces a serious problem: in addition to the poor water quality in a vast region of the world, it is reported that the world’s population is expected to increase in the coming two decades. Coupled with the rapid population increase, the demand for clean water will significantly increase by about seven-fold (Naseem & Tahir 2001; UNDP 2006). According to the report issued by the Environmental Protection Agency (US EPA) in the United States, lead (Pb) and arsenic (As) are the most toxic metals (US EPA 2015). The World Health Organization classified lead and arsenic as group one carcinogenic elements (Ali & Aboul-Enein 2002; Ali 2010; Ali et al. 2011). Such metals cause many human ailments and diseases including kidney disease, reproductive and central nervous system, liver and brain damage (Tangahu et al. 2011).

Thus, there is an urgent need to remove these toxic metals to protect people and for a healthier environment. To date, several treatment methods and techniques have been addressed for removal of these toxic metals from the water system. Among these techniques, adsorption has been recognized as the most appropriate and effective technique for toxic metal removal from water (Fu & Wang 2011). So far, several adsorbents have been developed including clay minerals (Abollino et al. 2005), chitosan (Gamage & Shahidi 2007), carbon nanotubes (Li et al. 2005), biosorbents (Park et al. 2006), activated carbon (Patnukao et al. 2008; Saleh 2015a, 2015b, 2016; Saleh & Al-Saadi 2015) and zeolite (Shaheen et al. 2012). Metal oxide nanoparticles (NPs) are classified as promising and desirable sorption materials for toxic metal removal from water systems in terms of their high selectivity and capacity, consequently providing efficient removal of these metals to meet strict regulations (Hua et al. 2012; Saleh et al. 2015). This is mainly due to their high surface area, high activity and large space for
the development of physical and chemical interchanges, reactions, etc. (Uheida et al. 2006). Surface modifications of metal oxide NPs with organic and inorganic materials provide a hybrid material with higher efficiency and capacity due to the additional properties that have been introduced by the organic and inorganic attachments, such as prevention of the agglomeration, stabilization of the NP, prevention of oxidation process, and provision of more functional groups and more reaction sites especially for removing toxic metals from the environment (Faraji et al. 2013). On the other hand, zeolites are considered to be promising and important hosts and stabilizers due to their unique features, such as porous structure, high ion exchange capacity, high surface area, hydrophilicity and easily tunable chemical properties, eco-friendly nature and high thermal stability (Xu & Ni 2013).

In this work, copper oxide (CuO) and iron oxide (Fe₃O₄) NP-based zeolites were prepared via a co-precipitation method as hybrid nanocomposite (NC) adsorbents to enhance the adsorption efficiency for the removal of lead and arsenic from a water solution. The prepared NCs were characterized using various techniques: UV-visible, powder X-ray diffraction (PXRD), N₂ adsorption for determining the specific surface areas (Brunauer–Emmett–Teller (BET)) and pore volumes. The surface morphology was observed by field emission scanning electron microscopy (FESEM).

MATERIALS AND METHODS

Materials

A synthetic zeolite powder forms a crystalline structure in sodium form, having an effective pore opening of 4 angstroms with average particle size being <45 μm obtained from Sigma-Aldrich (St Louis, MO, USA), copper (II) nitrate (Cu(NO₃)₂·3H₂O (99%)) was provided by Fisher brand (Hong Kong), and sodium hydroxide (NaOH (99%)) from R&M Chemical, UK. Lead nitrate (Pb(NO₃)₂ (99%)) and sodium hydrogen arsenate (Na₃HASO₄·7H₂O) were supplied by Fluka and Alpha Aesar (a Johnson Matthey company), respectively. Iron (III) chloride (FeCl₃·6H₂O (99%)) and iron sulphate (FeSO₄) were supplied by Acros Organic (USA) and Sigma-Aldrich respectively. Reagents used in this work were in analytical grades and used as received. Safety precautions in dealing with chemicals and process were considered (Saleh 2014).

Preparation of zeolite/CuO NCs

With some modifications for methodology described previously (Vijaikumar et al. 2008), zeolite/CuO NCs were prepared as shown in Figure 1. In brief, an amount of zeolite (5 g) was dispersed into 100 mL deionized water (DIW) in a 250 mL round bottom flask. An amount of copper nitrate (Cu(NO₃)₂·3H₂O), (1.2 g) was added to the suspension. The suspension (flask content) was stirred at 80 °C for 5 h for ion exchange between Cu²⁺ and Na⁺ exchangeable sites in zeolite (Figure 1). For precipitation of the CuO, 1 M solution of sodium hydroxide was added to the suspension until pH = 11–12 and the color changed from blue to dark blue to black. After 2 hours, the product (zeolite/CuO NCs) was filtered, washed extensively with deionized water and dried overnight at 110 °C.

Preparation of zeolite/Fe₃O₄ NCs

Zeolite/Fe₃O₄ NCs were prepared according to the previously described methodology (Attia et al. 2015) with some modifications. In brief, certain amounts of FeCl₃·6H₂O and FeSO₄ with a molar ratio of 2:1 were added to the solution contain (5 g) zeolite and dispersed into 100 mL deionized water (DIW). The suspension was stirred for 5 hours, thereafter NaOH (5 M) was added dropwise to the suspension being stirred until the color changed to black (Figure 2) and the slurry was then stirred for an additional hour. The formed black product was filtered, washed extensively with deionized water, and dried overnight at 110 °C. The samples were used without any further centrifuging and calcination.

CHARACTERIZATION OF ZEOLITE/CUO NCs AND ZEOLITE/Fe₃O₄ NCs

UV-visible absorbance was performed on powder samples using a UV-3600 Shimadzu.

The crystalline structures of the prepared NCs were investigated using PXRD with the Shimadzu XRD-6000 instrument in the wide angle range of 2θ (5–80°) at a scan speed of
4 °/min⁻¹, anode material Cu, current 30 mA, voltage 30 kV, specimen length 10 mm, receiving slit size 0.30 mm, measurement temperature 25 °C and wavelength 1.54 Å.

Nitrogen sorption isotherms were achieved using a Quantachrome AS1 Win™ (version 2.01) instrument at: bath temperature (77.3 K), outgas time: 12.0 hours, outgas temp: 300.0 °C, analysis time: 519.0 min and cell stem diameter (d): 4.00 mm, to determine the (BET) surface area and pore size distribution. To study the surface morphology of the prepared NCs, FESEM was used.

The arsenic and lead content in the solutions before and after the adsorption process were analyzed using flame
emission atomic absorption spectroscopy (AAS) (Thermo Scientific, S series Spectrometer: S Series GE712405 v1.27). This was achieved under the following conditions and parameters: first, spectrometer parameters, wavelength 193.7 and 217.0 nm and bandpass 0.5 nm; second, flame parameters; flame types N$_2$O-C$_2$H$_2$ and Air-C$_2$H$_2$, fuel flow: 4.2 and 1.1 L/min, burner height: 11.0 and 7.0 mm for arsenic and lead detection, respectively.

**Adsorption experiments**

**Preparation of lead (II) and arsenic (V) solution**

Two stock solutions (1,000 mg/L), Pb (II) and As (V) were prepared. The appropriate amounts of lead nitrate (Pb(NO$_3$)$_2$) and sodium hydrogen arsenate (Na$_2$HAsO$_4$·7H$_2$O) were dissolved separately in 1 L of deionized water. From the stock solutions, diluted solutions with predetermined concentrations of Pb (II) and As (V) were prepared.

**Batch adsorption experiments**

Adsorption experiments were carried out at room pressure and temperature using a batch equilibration method; thus, we could study the effect of several parameters that affect the sorption process including initial metal concentrations, initial pH, contact time and the amount of (NCs) adsorbent.

In the adsorption process, an amount of NCs adsorbent ranging from 0.05 to 0.2 g was added to 50 mL of Pb (II) and As (V) solutions separately, with the initial ion concentration ($C_0$) ranging between 20 and 100 mg/L. The initial pH of the solution was adjusted from 2 to 6 using 0.01 M of HNO$_3$. The contents of the solution were stirred until equilibrium at room temperature. Aliquots were taken from the system at different time intervals and analyzed using AAS. Each experiment was carried out three times for optimum accuracy of the data.

The adsorption capacity ($q_e$, mg/g) at equilibrium, was calculated using the following equation:

\[ q_e = \frac{(C_0 - C_e) V}{w} \]

where $C_0$ (mg/L) and $C_e$ (mg/L) are the lead and arsenic concentrations contained in the initial solution and at equilibrium, respectively; $V$ (L) is the volume of the water solution, and $w$ represents the amount of the adsorbent in grams.

The percentage removal of Pb (II) and As (V) is calculated by the following equation:

\[ \text{Removal} \% = \left( \frac{(C_o - C_e)}{C_o} \right) \times 100, \]

where $C_o$ and $C_e$ are the lead and arsenic concentrations at an initial concentration (mg/L), and at equilibrium, respectively.

**Adsorption isotherms**

Langmuir and Freundlich isotherm models, which correspond to homogeneous and heterogeneous adsorbent surfaces respectively, were used to analyze the obtained adsorption equilibrium data for adsorption of lead and arsenic onto zeolite/CuO NCs and zeolite/Fe$_3$O$_4$ NCs. The aim of the adsorption isotherm is to study the relation between the adsorbed amount at the interface and the adsorbate concentration in the bulk (Hameed et al. 2008). In this work, the adsorption isotherm of the toxic metals onto 0.15 g prepared NCs was carried out at five different As and Pb initial concentrations (20, 40, 60, 80, 100 mg/L) at pH 4, then samples were collected after 40 minutes to determine the As and Pb concentrations by AAS.

**Adsorption kinetics**

The adsorption kinetics of lead and arsenic onto zeolite/CuO NCs and zeolite/Fe$_3$O$_4$ NCs were analyzed by pseudo first- and second-order models. The agreement between the model’s predicted values and experimental data were expressed by the correlation coefficients ($R^2$). The model with a relatively high correlation coefficient value is fit for describing the adsorption kinetics process. The same process for adsorption equilibrium, detailed above, was used for the kinetic study. Namely, contact time has a remarkable effect on the adsorption kinetics of As and Pb from the
aqueous solutions. Thus, the kinetics of adsorption of these toxic metals by the prepared NCs were done at an initial As and Pb concentration of 100 mg/L, pH 4, and an adsorbent (NCs) amount of 0.15 g, and samples were collected at different time intervals for As and Pb analysis.

RESULT AND DISCUSSION

Characterization

The UV-vis absorption spectra in the solid form of zeolite/Fe3O4 and zeolite/CuO NCs were recorded and are shown in Figure 3. Both NCs display a wide absorption range between 200 and 800 nm, which could be attributed to the characteristic absorption of Fe3O4 and CuO, and the peaks' intensity decreases with an increase in the wavelength. Compared to the CuO and Fe3O4 bulk materials, the prepared NCs show a blue shift, which means that the particle sizes are reduced (Saleh 2014b; Behera et al. 2012; Naika et al. 2015).

The diffraction patterns of zeolite/CuO NCs and zeolite/Fe3O4 are presented in Figure 4. Figure 4(c) and 4(d) show the peak lists of CuO and Fe3O4, which are in accordance with Ref Cod 98-005-3116 and 98-001-2051 respectively. The other peaks in the XRD patterns (Figure 4(a) and 4(b)) are attributed to the pure zeolite according to the Ref Cod 01-087-1619. The particle sizes of the prepared CuO and Fe3O4 in the NCs are calculated by the Debye–Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where $k = 0.94$ is a coefficient, $(\lambda) = 0.15418 \text{ nm}$ is the X-ray wavelength, $\beta$ is the full-width half maximum of the sample and $\theta$ is the diffracting angle. The average particle diameters were 6.2 and 8.6 nm for CuO and Fe3O4 respectively.

The prepared NCs were further studied by nitrogen adsorption–desorption to determine the surface area. Hysteresis loops type H 3, according to the IUPAC classification (Lian et al. 2010), are present at higher pressure, meaning that mesoporous structures were generated by the accumulation of the metal oxides onto zeolite, which improves the structure porosity (Figure 5). Moreover, zeolite/Fe3O4 NCs exhibited a higher BET specific surface than zeolite/CuO NCs, as shown in Table 1.

The FESEM for the prepared NCs (Figures 6(a) and 6(b)) showed granules and particles on the surface of the typical cubic structure of the zeolite, indicating the formation of CuO and Fe3O4 NPs on the surface of the zeolite without a change in the zeolite structure. Figures 6(c) and 6(d) exhibit the porous layer that formed onto the surface of the
zeolite, which confirms the results obtained by XRD and nitrogen adsorption–desorption.

Adsorption efficiency

Under the optimum adsorption parameters (initial concentration 100 ppm of the metal solutions, dosage 0.15 g, pH 4, contact time 40 min) the removal of Pb and As by zeolite/CuO NCs, zeolite/Fe3O4 NCs, and commercial synthetic zeolite adsorbents was performed and the results are shown in Figure 7. Both NCs show the highly efficient removal of toxic metal from water compared to the zeolite with the percentage of removal (51.6, 82.8, and 97.2%) for Pb and (32.2, 81.7, 96.8%) for As by zeolite, zeolite/CuO NCs, and zeolite/Fe3O4 NCs, respectively.

Zeolite/Fe3O4 NCs exhibits higher removal efficiency for Pb and As, which could be attributed to a larger specific area, more active sites being available, and high porosity (Padervand & Reza Gholami 2013). In addition to the role of functional groups that were introduced to the surface of the zeolite by CuO and Fe3O4, there are two important factors that could explain the mechanism of removal of Pb and As by the prepared NCs: the metal ions moved through the channels of the crystal lattice or through the pores of the zeolite/CuO NCs and zeolite/Fe3O4 NCs mass. The other important factor is the ion exchange reaction between the protons on the surface NCs and the metal ions (Erdem et al. 2004; Li et al. 2006; Sheela et al. 2012).

Effect of adsorbent dosage

The effect of the NCs adsorbent dosage on the Pb (II) and arsenic (V) removal efficiency is illustrated in Figure 8. The increase in the adsorbent dosage from 0.01 to 0.15 g resulted in an increase in adsorption of the percentage of lead and arsenic from 30.6 to 83.7% and from 29.2 to 81.3% by zeolite/CuO NCs, and from 43.5 to 97.2% and from 56.2 to 96.8% by zeolite/Fe3O4 NCs, respectively. The increase in adsorption capacity is due to the larger surface area and greater number of adsorption sites available that were introduced by increasing the number of adsorbent particles, resulting in more metals being attached with the weight of adsorbent increasing (Mahdavi et al. 2013), whereas the decrease in the percentage of adsorption with a higher adsorbent dosage of 0.2 g for both metals may be due to the decrease of NCs adsorbent/surface area related to the aggregation of high adsorbent dose, or the insufficiency of metal ions in solution compared to the available binding sites, and interference between high adsorbed dose and binding sites (Rawajfih & Nsour 2008).

Effect of initial metal ion concentration

The adsorption of lead and arsenic was carried out at initial concentrations ranging from 20 to 100 mg/L. Figure 9 illustrates that the initial Pb and As concentrations do not show a remarkable effect on the removal efficiency at the range studied. The small decrease in the percentage of removal at higher concentrations could be attributed to the limited number of active sites of the NCs adsorbent, and the excess Pb and As, which compete for the available active sites, which become more saturated with an increase in the concentration of metal ions (Müller et al. 1985).

Table 1 | BET surface area, pore radius, and pore volume analysis

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area m²/g</th>
<th>Pore radius Å</th>
<th>Pore volume cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite/CuO NCs</td>
<td>15.028</td>
<td>28.21</td>
<td>0.035</td>
</tr>
<tr>
<td>Zeolite/Fe3O4 NCs</td>
<td>32.25</td>
<td>21.57</td>
<td>0.061</td>
</tr>
</tbody>
</table>

Figure 5 | Nitrogen adsorption/desorption isotherms: (a) zeolite/CuO NCs and (b) zeolite/Fe3O4 NCs at (77.3 K).
Effect of pH on the adsorption efficiency

The pH of the solution is an important factor in the adsorption process of metals on the adsorbent. The effect of pH on the adsorption of Pb and As ions on prepared NCs was investigated within a pH ranging from 2 to 6, as depicted in Figure 10, due to the chemical precipitation of metal hydroxides that occurs at higher pH values (Mahdavi et al. 2015). A noticeable increase in percentage adsorption of Pb and As is observed with increases in pH from 2 to 4 (Figure 10) due to the presence of the acidity medium (H⁺) in the solution, which competes with Pb (II) and As (V) for active sites on the adsorbent’s surface (Jiang et al. 2013); thus lesser adsorption was observed at lower pH. Another factor that might be playing an important role is the electrostatic interaction between the positively toxic metals’ cation charges and the oxygen, which negatively charges on the surface of the NCs. Maximum removal efficiency reached 97.5% for Pb (II) and 92.4% for As (V) at a pH of 4–6.

In order to determine the optimum pH range for this resin in Pb (II) and As (V) adsorption, the speciation over the entire pH range has to be taken into consideration.
Studies have identified three forms of lead species: Pb$^{2+}$, Pb(OH)$^+$, and Pb(OH)$_2$ in the pH range 2.0–8.0. The distribution of these species, as calculated by MINEQL software, shows that Pb$^{2+}$ is the preponderant species at pH between 1 and 6 and that its hydrolysis to Pb(OH)$^+$ and Pb(OH)$_2$ starts as the pH increases, while Pb(OH)$_2$ dominates at a pH higher than 6.0 (Schecher 2001). Under low pH, competition ensued between H$^+$ and Pb$^{2+}$, and on the other hand, the functional groups on the surface of the NCs are in protonated forms that do not favor coordination with Pb$^{2+}$ species; they are repelled by the electrostatic force. Thus, the Pb$^{2+}$ absorption capacity of the NCs is decreased (Liu et al. 2011). As the pH is increased, this competition reduces and the functional groups on the NCs become less protonated, thereby making them more available for coordination with Pb$^{2+}$. This accounts for the increased percentage removal that peaked at pH 6.0. Beyond pH 6.0, there is deprotonation as basicity increases, and the functional groups are in anionic forms that should encourage greater coordination with Pb$^{2+}$. However, this did not increase the percent Pb$^{2+}$ removal, as the lead is now being hydrolysed into Pb(OH)$^+$ and Pb(OH)$_2$, thereby reducing the amount of free Pb$^{2+}$ available for complexation. On the other hand, the literature reported that in the pH range 2–9, arsenic (V) is present as H$_2$AsO$_4^-$ and HAsO$_4^{2-}$ anionic form, thus these species could be adsorbed by NCs either through surface complexation or ion exchange chemical interactions (Han et al. 2013). The noticeable differences in adsorption efficiency between zeolite/CuO NCs and zeolite/Fe$_3$O$_4$
NCs could be attributed to the BET surface area and the number of functional groups available on the surface.

### Effect of contact time

The obtained results for the effect of varying contact time from 10 to 60 minutes are depicted in Figure 11. With increasing contact time, the amount of Pb (II) and As (V) adsorbed increased as the number of available adsorption sites decreased. The extent of lead and arsenic adsorbed by NCs was found to increase with increasing the contact time reach to the adsorption equilibrium at 40 min with adsorption efficiency 98 and 92.8% for zeolite/Fe₃O₄ NCs (Figure 11).

During the initial adsorption stage, more numbers of vacant surface sites are available while, after a lapse of time, the vacant surface sites almost got saturated with Pb (II) and As (V) and it would be difficult to be occupied due to the repulsive forces between the bulk phases and the solute molecules on the solid (Al Othman et al. 2015). As a result, the adsorption rate process slows down during the latter period.

### Adsorption isotherms

In the present work, the adsorption equilibrium data were fitted using Langmuir and Freundlich models for the investigation of the distribution of lead Pb (II) and arsenic (V) between the solid phases (NCs) and the bulk solution containing Pb and As at equilibrium. The Langmuir model is an empirical model based on the assumption that the
adsorption takes place on the surface of the adsorbent where the uniform energy sites. On the other hand, the Freundlich model assumes that, due to the diversity of adsorption sites, multilayer adsorption is formed.

**Langmuir isotherms**

The Langmuir equation governs the amount of lead Pb (II) and arsenic (V) adsorbed, and its linear equation is given by the following equation:

\[
\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}
\]

where \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of lead Pb (II) and arsenic (V) in the solution, \( q_e \) (mg g\(^{-1}\)) is the amount adsorbed at equilibrium, \( b \), and \( q_m \) (mg g\(^{-1}\)) is the Langmuir constant related to the energy of adsorption and maximum monolayer capacity (adsorption efficiency) respectively.

Figure 12 shows the plot \( C_e/q_e \) verse \( C_e \) and the values \( q_m \) and \( b \) are presented in Table 2. The amount adsorbed at equilibrium \( q_e \) (mg g\(^{-1}\)) by zeolite/Fe\(_3\)O\(_4\) NCs is quite higher than \( q_e \) of zeolite/CuO NCs for both toxic metals, which is in agreement with the results obtained above.

The separation factor \( R_L \) was calculated to confirm the favorability of the adsorption process (Hall et al. 1966):

\[
R_L = \frac{1}{1 + bC_o}
\]

where \( b \) (L/mg) is the Langmuir constant and \( C_o \) is the highest initial concentration of Pb (II) and As (V) (mg/L). The results represented in Figure 13 show the value of \( R_L \) between 0 and 1, which indicate that the adsorption of lead Pb (II) and arsenic (V) onto the prepared NCs is a favorable process.

**Freundlich isotherm**

The Freundlich isotherm model is expressed by the following equation:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

Table 2 | Parameters of adsorption isotherm model for adsorption of lead Pb (II) and arsenic (V) onto zeolite/CuO NCs and zeolite/Fe\(_3\)O\(_4\) NCs

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Metal ion</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( q_m ) (mg/g)</td>
<td>( b )</td>
</tr>
<tr>
<td>Zeolite/CuO NCs</td>
<td>Pb (II)</td>
<td>45.45</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>Arsenic (V)</td>
<td>44.8</td>
<td>0.048</td>
</tr>
<tr>
<td>Zeolite/Fe(_3)O(_4) NCs</td>
<td>Pb (II)</td>
<td>50</td>
<td>0.259</td>
</tr>
<tr>
<td></td>
<td>Arsenic (V)</td>
<td>47.4</td>
<td>0.15</td>
</tr>
</tbody>
</table>
where $K_f$ (mg/g) is the Freundlich constant related to the adsorption capacity of NCs adsorbents, which is calculated from the intercept, and $n$ is the Freundlich constant related to the adsorption intensity, where $1/n$ (g/L), which can be calculated from the slope, is giving an indication of how favorable the adsorption process is (Poots et al. 1978).

The plot of $\ln (q_e)$ against $\ln (C_e)$ is shown in Figure 14. The values of $K_f$ and $n$ were calculated from the intercepts and slopes and are listed in Table 2.

According to the results obtained and represented in Table 2, the $R^2$ values of the Langmuir isotherm model are higher than the Freundlich isotherm model, indicating that the experimental data fit more with the Langmuir isotherm model.

Table 3 demonstrates the $q_m$ (mg/g) calculated from the Langmuir isotherm for As and Pb adsorption by the present prepared NCs and the other reported adsorbents in the literature. From the table, it is clear that the prepared zeolite/Fe$_3$O$_4$ and zeolite/CuO NCs are very applicable and useful materials for efficient lead and arsenic removal from aqueous solutions.

**Adsorption kinetics**

The adsorption kinetics were modeled by pseudo first- and second-order models.

**Pseudo first-order**

The equation pseudo first-order, which describes the initial stage of the adsorption process, was given by the following
equation (Lagergren 1898): 

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

where \(q_e\) and \(q_t\) (mg/g) represent the amounts of lead and arsenic adsorbed at equilibrium and time \(t\) (min), respectively; and \(k_1\) (min\(^{-1}\)) is the rate constant of the Lagergren-first-order kinetics model.

The values of \(k_1\), calculated from the slope, and \(q_e\), were calculated from the intercept of the plot of \(\ln (q_e - q_t)\) versus \(t\) (Figure 15). Table 4 shows the correlation coefficient \(R^2\) of the pseudo first-order model is lower than the pseudo second-order model; moreover, the calculated \(q_e\) is lower than the experimental values.

**Pseudo second-order**

The following equation expresses the pseudo second-order kinetics (McKay & Ho 1999):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \(k_2\) (g/(mg min)) is the adsorption rate constant of the pseudo second-order model.
The values of $k_2$ and $q_e$ can be obtained from the intercept and slope respectively (Figure 16). Table 4 depicts the maximum amount adsorbed ($q_e$), the values of the rate constants ($k_2$) and the correlation coefficients ($R^2$). The pseudo second-order model is based on the assumption that the rate-limiting step may be chemisorption, which involves valence forces by sharing, or electron exchange between the adsorbate and the adsorbent (Wang & Wang 2008).

Based on the results obtained from these models, which are included in Table 4, the pseudo second-order model has the higher correlation coefficient ($R^2$) and the accordance between the experimental adsorption capacities $q_e$ and the adsorption capacities $q_e$ calculated from this model indicates that the pseudo second-order model is well suited for describing the adsorption of Pb and As onto zeolite/CuO NCs and zeolite/Fe$_3$O$_4$ NCs.

**CONCLUSIONS**

Zeolite/metal oxides NCs containing CuO and Fe$_3$O$_4$ with a diameter of less than 10 nm were prepared and confirmed by characterization techniques. FESEM confirmed the presence of the CuO and Fe$_3$O$_4$ porous layer onto the surface of the zeolite. At room ambient conditions, the prepared NCs showed significant adsorption efficiency, which reached 97.2% and 83.7% of Pb and 96.8 and 81.3% of As by zeolite/Fe$_3$O$_4$ NCs and zeolite/CuO NCs, respectively, at a pH between 4 and 6 over 40 minutes. The significant differences in adsorption efficiency between zeolite/CuO NCs and zeolite/Fe$_3$O$_4$ NCs are mainly due to the large zeolite/Fe$_3$O$_4$ NCs BET surface area and the amount of functional groups that are available on the surface. The adsorption isotherm data fitted well with the Langmuir isotherm model, while the kinetic study experimental data of lead and adsorption onto prepared NCs gave better correlation with the pseudo second-order kinetic model.

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