Preparation of Zeolite/Zinc Oxide Nanocomposites for toxic metals removal from water

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ABSTRACT

This research work has proposed preparation of Zeolite/Zinc Oxide Nanocomposite (Zeolite/ZnO NCs) by using a co-precipitation method. Then, the prepared Nanocomposite has been tested for adsorption of Lead Pb (II) and Arsenic As (V) from aqueous solution under the room pressure and temperature. After that, the prepared adsorbent has been studied by several techniques. For adsorption process; the effect of the adsorbent masses, contact time, pH and initial metals concentration as well as, the kinetics and isotherm for adsorption process have been investigated. The results revealed that; ZnO nanoparticles (NPs) with average diameter 4.5 nm have successfully been loaded into Zeolite. The optimum parameters for the removal of the toxic metals 93% and 89% of Pb (II) and As (V), respectively, in 100 mg/L aqua solutions were pH4, 0.15 g and 30 min. According to the obtained results; pseudo second-order kinetic and Langmuir isotherm model have higher correlation coefficients and provided a better agreement with the experimental data. The prepared sorbent showed an economical and effective way to remove the heavy toxic metals due to its ambient operation conditions, low-consumption energy and facile regeneration method.

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Introduction

Recently, nanomaterials are considered as the world most attractive materials due to their potential applications particularly for environmental challenges such as in water treatments [1]. Additionally, the use of nanostructured materials for water treatment processes is a reality and hot issue and thus there are long lists of nanomaterials in the markets [2]. In literature review, several studies have been addressed nanoparticles as efficient and effective adsorbents for removal of toxic metals from water systems. Among the available adsorbents, metal oxides nanoparticles (NPs) such as; titanium oxide, ferric oxide, magnesium oxide, alumina oxide, cesium oxide [3,4], manganese oxide [5], copper oxide, zinc oxide [6,7] and graphite oxide [8] which are classified as the promising and desirable sorption materials for toxic metals removal from aqua systems due to their high selectivity, capacity and efficiency to remove these metals to meet the strict regulations [9,10]. This is in addition to their high surface area, high activities caused by the size-quantization effect which means a large space for the development of physic and chemical interactions, reactions etc. [11–16]. Moreover, nanoparticles can penetrate into the contamination zone whereas microparticles cannot [16–18].

However, it is reported that, when the size of metal oxides decreases to nanometer range, the increased surface energy leads to their poor stability [19–23]. This would result in agglomeration of nanoparticles according to Van der Waals forces or other interactions. Thus, the effective surface area decreases and the high selectivity and capacity of these materials would be greatly decreased or even lost, as well as, they will have poor mechanic strength [24]. To improve the applicability of metal oxide nanoparticles for water treatment, nanocomposite (NCs) materials have emerged as suitable alternatives to overcome limitations of growth nanoparticles by employing porous supports materials of large area as a matrices or stabilizers to obtain hybrid nanocomposite adsorbents [25]. Among the various matrices, zeolites are considered to be promising hosts and stabilizers due to their unique features such as; large surface area, high ion exchange capacity,

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In the modern society, the lead (Pb) and Arsenic (As) in water are considered as the main source of contaminations which have fatal effects on the human health. Indeed, several human activities cause the contamination such as petroleum refining, mining operations, textile dyeing, glass industries and battery manufacture [28]. Ingestion of lead and arsenic in contaminated drinking water causes several diseases such as; kidney cancer, skin lungs, gastrointestinal disease, bone marrow disorder, cardiovascular diseases and so on [29]. Thus, World Health Organization (WHO, Geneva, Switzerland), Environmental Protection Agency (US-EPA, United States), [30,31] and Central Pollution Control Board (CPCB, India) [32,33] have fixed existing arsenic and lead in drinking water if any. However, the environmental researchers still try to decrease the existing contaminans in drinking water [34].

Based on that, this work suggested a co-precipitation method in order to combine zinc oxide nanoparticles with zeolite as hybrid nanocomposite adsorbents to enhance the adsorption efficiency for lead and arsenic removal from water solution. This method was used to load ZnO NPs into zeolite type A framework for preparing Zeolite/ZnO NCs without using a capping agent. Then the prepared NCs has been analyzed by using various techniques; N₂ adsorption for determining the specific surface areas (BET), pore volumes, Powder X-ray diffraction (PXRD) and Fourier transform infrared (FT-IR) spectroscopy. The morphology and particle’s size has been investigated by Field emission scanning electron microscopy (FE SEM) and Transmission electron microscopy (TEM), respectively. Flame emission atomic absorption spectroscopy (AAS) was used to analyze the lead and arsenic contents in the solutions before and after adsorption process, as well.

Materials and methods

In this work, all chemical materials were used without any further purification. A synthetic zeolite powder form type A crystalline structure in Sodium form, with average particle size <45 µm and effective pore opening of 4 Å purchased from Sigma-Aldrich (St Louis, MO, USA). Zinc acetate dihydrate (99.5%), Zn (Ac₂):2H₂O was supplied from Riendemann Schmidt., Sodium hydroxide NaOH of 99% from R&M Chemical United Kingdom. Lead nitrate Pb(NO₃)₂ (99%) and Sodium hydrogen arsenate Na₂HAsO₄·7H₂O were supplied from fluka and Alpha Aesar (Ajohnson Matthey company), respectively. For the experimental procedures, all the glassware used in this work were washed by fresh solution of Aqua regia then by deionized water, and dried in oven before used.

Preparation Zeolite/ZnO NCs

5 g of zeolite was dispersed into 100 ml deionized water (D.W) in a 250 ml round bottom flask volume. Equivalent amount of 5 wt % of ZnO:zeolite from Zn(AC₂):2H₂O was added to the suspension. The slurry was stirred under reflux reaction at 80 °C for 5 h for ion exchange and to get Zn⁺ exchanged zeolite. 0.1 M of NaOH was added to the suspension until pH11. After 2 h, the product was filtered and washed extensively by deionized water for removing the acetate residual before dried at 60 °C overnight. Lastly, the final product was calcined for 2 h at 450 °C. The process of formation Zeolite/ZnO NCs can be represented by the following schematicallly illustrated as flown in Fig. 1:

The chemical formula of Zeolite A is Na₃₂ [(AlO₂)₉ (SiO₂)₁₂]. 27H₂O. In an aqueous solution, ions can exchange into and out of the zeolite framework structure.
between 20 and 100 (mg/L). Initial pH of the solution adjusted from 2 to 6 using 0.01 M of HNO₃. The solution contents were stirred until equilibrium at room temperature. Aliquots were taken from the system at different time intervals and analyzed using atomic absorption spectroscopy.

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

\[
\text{Percentage removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

where \(C_0\) and \(C_e\) are the lead and arsenic initial concentration (mg/L), and concentration (mg/L) at equilibrium respectively.

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) is the initial concentration 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 \(w\) (gram) represents the weight of adsorbent.

**Adsorption kinetics**

The kinetics of lead and arsenic adsorption on Zeolite/ZnO NCs analyzed by pseudo first-order and pseudo-second-order models.

The agreement between the models predicted values and experimental data were expressed by the correlation coefficients \(R^2\). Model with relatively high correlation coefficients value is fit for describing the adsorption kinetics process.

**Adsorption isotherms**

The obtained adsorption equilibrium data for adsorption of lead and arsenic onto Zeolite/ZnO NCs were analyzed using Langmuir and Freundlich isotherm models, which correspond to homogenous and heterogeneous adsorbent surfaces, respectively.

**Regeneration experiment**

The desorption of Pb and As-loaded into Zeolite/ZnO NCs and regeneration the Zeolite/ZnO NCs adsorbent were performed three times to study the reusability of the prepared nanoadsorbent. In brief, after adsorption process the adsorbent was separated using filter papers. Then, the nanocomposites adsorbent with the adsorbed toxic metals were added into 20 ml of 0.005 M HNO₃ and stirred for 30 min to desorb the metal ions Pb (II) and As (V). Then, Zeolite/ZnO NCs adsorbent was separated using filter papers and washed three times by deionized water and dried at 70 °C overnight for reuse. This process was repeated three times.

**Results and discussion**

**Surface area and pore size**

Zeolite/ZnO NCs exhibited IV isotherm adsorption behavior due to the presence of zeolitic micropores [35], as well as mesopores formed by the aggregation of crystals (Fig. 2). The BET surface area increased from 4.3 m²/g for Zeolite to 17.31 m²/g for Zeolite/ZnO NCs (Table 1). The almost fourfold higher surface area of the prepared nanocomposite indicated that the ZnO NPs phases formed a porous layer on the surface and in the channel of the zeolite structural. Further, the formed ZnO NPs layer, with a large surface area, provides a large number of functional groups that enhance the adsorption process [36]. On the other hand, the average diameter decreased from 21.64 Å for zeolite to 11.1 Å Zeolite/ZnO NCs as a result of filling of these pores with ZnO nanoparticles [37].
related to the Zinc Oxide which were in accordance with ZnO (JCPDS:79-0205) [38], while some other ZnO peaks (Fig. 2C) at (010) at 31.72°, (013) at 62.801° and (112) at 67.863°, cannot be observed in the XRD pattern of Zeolite/ZnO NCs, meaning that; the ZnO NPs are confined inside the zeolite, the same reason was reported [39]. From XRD results; ZnO NPs were formed inside and outside of the zeolite framework, these results are in agreement with result obtained from N₂ sorption.

The average crystallite sizes of the prepared NCs calculated by Scherrer equation and found between 1 nm and 20 nm. Moreover, there are no other diffracting peaks appeared in the product except the diffraction peaks of Zeolite and ZnO NPs, which means the prepared product is pure.

**Fourier transform infrared**

Fig. 4 illustrates FT-IR spectra of zeolite type A and the prepared Zeolite/ZnO NCs. The vibration bands at 3349 cm⁻¹ and 1648 cm⁻¹ were assigned for O–H stretching due to the H₂O interporous structure of O–H stretching (H bonding). The band at 965 cm⁻¹ is due to the stretching vibration of Si–O, and the bands at 548–459 cm⁻¹ for Si–O–Si bending vibration [40].

In general, comparing between the FT-IR spectrum of sample containing zinc oxide nanoparticles (Fig. 4B) with pure zeolite spectrum we can conclude that; small decrease in the peaks intensity, broadening and shifting of the peak at 357 cm⁻¹ to 353 cm⁻¹ also evident for present of ZnO NPs and can be assigned to Zn–O bond in the ZnO NPs [41,42]. The decreasing in the peaks intensities and small blue shift in the positions of the peaks in FT-IR spectrum figures illustrated that; ZnO NPs were precipitated on the crystal structure in porous system of zeolite; these results are in agreement with pervious reported study [43].

**Morphology**

Fig. 5 demonstrates smooth surface and the typical structure for zeolite which is a cubic shape, while the surface of Zeolite/ZnO NCs (Fig. 4B) has granular shapes, indicating the present of ZnO NPs on the surface of zeolite.

Meanwhile, the cubic structure shape of the zeolite did not change when ZnO NPs formed on the zeolite; these confirm the results obtained from BET and XRD analyses. Fig. 6(A–B) show the TEM images of zeolite and Zeolite/ZnO NCs respectively. These two images demonstrate that zeolite which has smooth surface as shown in Fig. 5A, while in Fig. 5B there are some areas in white colour. This is due to the present of ZnO NPs attached in zeolite. Moreover, it is clear that the ZnO NPs are well distributed and there is no obvious agglomeration of ZnO NPs on the surface of the zeolite as shown in Fig. 6B. [38,44,45]. The mean grain size measured by image j program is estimated to be 4.3 nm.

**Adsorption studies**

Comparison of percentage adsorption between pure Zeolite and the prepared nanoadsorbents

Fig. 7 shows the percentage adsorption of Lead and Arsenic from aqua solution by pure Zeolite and the prepared nanoadsorbents under the same parameters (initial concentration 100 ppm of metals solutions, dosage 0.15 g, pH4, contact time 30 min). It is clear that, the prepared Zeolite/ZnO NCs adsorbant has noticeable higher percentage adsorption (92 and 85.7%) than pure zeolite (43.6 and 32.3%) for Lead and Arsenic respectively. This increment in the adsorption capacity for Zeolite/ZnO NCs adsorbent is attributed to the larger BET surface area and the chemical property of their surfaces such as the functional groups introduced by ZnO, which is corresponded to the previous studies [46].

Effect of pH

The pH level of the solution is an important factor in the adsorption process of metals on the adsorbent. Since the metal hydroxide chemical precipitation occurs at higher PH value [47], thus the effect of pH on the adsorption of Pb and As ions on Zeolite/ZnO NCs was investigated within pH range from 2 to 6 as depicted in (Fig. 8). It is obviously observed that there was noticeable increase in adsorption percentage of lead and arsenic with increase of pH from 2 to 4 (Fig. 8) due to the present the acidity medium (H⁺) in the solution which competes with Pb (II) and As (V) for active sites on the adsorbents surface thus lesser adsorption was observed [6]. Maximum removal efficiency reached 92.5% for Pb (II) and 85.4% for As (V) at pH between 4 and 6.

Effect of mass of adsorbent

The amounts of Pb (II) and Arsenic (V) adsorbed by different amount of Zeolite/ZnO NCs adsorbent are shown in (Fig. 9). The increase in adsorbent dosage from 0.01 to 0.15 g resulted in an increase in adsorptions percentage of lead and arsenic from 38.9 to 90.8% and from 52 to 85.5% respectively. The initial increase in adsorption capacity is attributed to the larger surface area and more adsorption sites that introduced by increasing the number of adsorbent particles results in more metals attached with the weight of adsorbent increasing [48]. On the other hand, the decrease in the percentage of adsorption with increasing the adsorbent dosage from 0.15 to 0.2 g for both metals may be due the aggregation of high adsorbent dose, as a result the surface area of the adsorbent will decrease, it may also due to either the insufficiency of metal ions in solution comparing to the available binding sites or interference between higher adsorbed dose and binding sites [49,50].

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. Figs. 10 shows that when increasing initial metals concentration the percentage of removal decreases from 97.8 to 89% and from 94.5 to 86% for Lead and Arsenic respectively. This decrease may due to the limited number of active sites of the Zeolite/ZnO NCs adsorbent which become more saturated with increasing the concentration of metal ion. On the other hand, there was an increase in adsorption capacity with increasing the initial Pb (II) and As (V) concentration in the range of concentrations studied (Fig. 11). The concentration of Pb (II) and As (V) at higher range led to continues of the adsorption
process because the active sites of Zeolite/ZnO NCs adsorbent were enclosed by much more metal ions and leading to higher amount of Pb (II) and As (V) that adsorbed from the aqua solution. Thus, the values of $q_e$ increase with increasing the initial metal ion concentrations ($C_0$).

The mechanism behind that could be explained by the adsorption process where the metal ions moved through channels of the crystal lattice or through the pores of Zeolite/ZnO NCs mass. The other important factor is ion exchange reaction between the protons on the surface Zeolite/ZnO NCs and the metal ions [7,51,52].

Effect of contact time

The extent of Lead and Arsenic removal by Zeolite/ZnO NCs was found to increase with increasing the contact time reach a maximum value after 30 min (Fig. 12). After that, it decreases with the increase in contact time which may be due to a desorption process. With increasing contact time, the amount Pb (II) and As (V) adsorbed increased as the number of available adsorption sites decreased.

During the initial adsorption stage, large 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 repulsive forces between the bulk phases and the solute molecules on the solid [53,54]. As a result, the adsorption rate process is slowing down during the later period.

Adsorption kinetics

For analysis of experimental kinetic data, two kinetic models were applied. Pseudo-first order kinetics which usually describes
the initial stage of the adsorption process and pseudo-second-order kinetics which gives good description of the whole adsorption process and based on the adsorption capacity [55].

**Pseudo-first-order**

The equation Pseudo-first-order was given by Lagergren [56].

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

where, \( q_e \) and \( q_t \) (mg/g) are the amounts of lead an 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.

\[ t = \frac{1}{k_1 q_e^2} \times \frac{t}{q} \]

The \( k_1 \) and \( q_e \) were calculated from the slope and intercept (Fig. 13). (Table 2) shows the correlation coefficient \( R^2 \) of the pseudo first order model is lower than the pseudo second order model, moreover, the calculated of \( q_e \) is lower than the experimental values, indicating that the adsorption of Lead Pb (II) and Arsenic (V) on Zeolite/ZnO NCs cannot be described by the pseudo first order kinetic.

**Pseudo-second-order**

The following equation expresses the pseudo-second-order kinetics [57].

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

![Fig. 7. Percentage of removal of Pb (II) and Arsenic (V) by Zeolite and Zeolite/ZnO NCs; 50 ml solution, pH 4, concentration 100 mg/L, adsorbent dose 0.15 g, and contact time 30 min.](image)

![Fig. 8. Effect of pH solution on the percentage adsorption of Pb (II) and Arsenic (V) by Zeolite/ZnO NCs; 50 ml solution, concentration 100 mg/L, adsorbent dose 0.15 g and contact time 30 min.](image)

![Fig. 9. Effect of adsorbent dosage on the percentage adsorption of Pb (II) and Arsenic (V) by Zeolite/ZnO NCs; 50 ml solution, concentration 100 mg/L, pH4 and contact time 30 min.](image)

![Fig. 10. Effect of initial Pb (II) and Arsenic (V) concentration on the percentage of adsorption by Zeolite/ZnO NCs; 50 ml solution, dosage 0.15 g, pH4 and contact time 30 min.](image)
409 \( k_2 \) (g/(mg min)) is the adsorption rate constant of pseudo-second-order model.

410 The \( q_e \) and \( k_2 \) can be obtained from the intercept and slope respectively (Fig. 14). Table 2 depicts the maximum amount adsorbed (\( q_e \)), 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 [58].

411 The higher correlation coefficient (\( R^2 \)) and the accordance between the experimental adsorption capacities \( q_e \) and the adsorption capacities \( q_e \) calculated from the pseudo second order model indicate that; pseudo second order model is more fit for describing the adsorption process.

412 Adsorption isotherms

413 In this work, the adsorption equilibrium data were fitted using Langmuir and Freundlich models for investigation of the adsorption of Lead Pb (II) and Arsenic (V) onto Zeolite/ZnO NCs. 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 the multilayer adsorption formed.

414 Langmuir isotherms

415 The Langmuir equation [59] governs the amount of Lead Pb (II) and Arsenic (V) adsorbed and its linear equation is given in the following equation:

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

where \( C_e \) (mg/L) is the equilibrium concentration of Lead Pb (II) and Arsenic (V) in the solution, \( q_e \) (mg/g) is the amount adsorbed at equilibrium, \( b \) and \( q_m \) (mg/g) is the Langmuir constant related to the energy of adsorption and maximum monolayer capacity (adsorption efficiency), respectively.

The values of \( 1/q_m \) and \( 1/bq_m \) can be calculated from slope and intercept of linear plots of \( C_e/q_e \) against \( C_e \) (Fig. 15).

The separation factor \( R_L \) was calculated to confirm the favorability of the adsorption process (Table 3) [60].

\[
R_L = \frac{1}{1 + bC_0}
\]

where \( b \) (L/mg) is Langmuir constant and \( C_0 \) is the highest initial concentration of Pb (II) and As (V) (mg/L). The results represented in (Table 3) show the values of RL between 0 and 1 which indicate that the adsorption of Lead Pb (II) and Arsenic (V) on Zeolite/ZnO NCs is a favorable process.
The Freundlich isotherm model describes the multilayer sorption and it is expressed by the following equation:

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

where \( K_f \) (mg/g) is Freundlich constant related to the adsorption capacity of Zeolite/ZnO NCs adsorbent and \( n \) is the Freundlich constant related to the adsorption intensity, where \( 1/n \) (g/L) giving an indication of how favorable the adsorption process [61].

By plotting a graph of \( \ln (q_e) \) against \( \ln (C_e) \) (Fig. 16) we can determine the \( K_f \) and \( n \) constants. The results represented in (Table 3) showed the \( n \) values are more than one which indicates that the adsorption process is desirable.

From the information represented in (Table 3) the \( R^2 \) values of Langmuir isotherm model is higher than the Freundlich isotherm model indicating that; the experimental data are well fit with the Langmuir isotherm model.

### Regeneration study

Reusability the adsorbents is an important issue in the economic development for adsorption process. The regeneration and
In this study, the obtained results suggest that Zeolite/ZnO NCs nano-adsorbent has a good reusability and stability as well as it is considered to be an efficient hybrid adsorbent for further practical applications.

Conclusions

In this study, Zeolite/ZnO NCs were carefully prepared and characterized. The prepared sample was examined for Lead (II) and Arsenic (V) removal from aqua solutions at ambient conditions in batch adsorption systems. pH4, 0.15 g and 30 min were the optimum parameters for removal 93% and 89% of Pb (II) and As (V) from 100 mg/L aqua solutions. Langmuir model provided a better fit for the two metal ions to the experimental data, while the adsorption kinetics demonstrated that; the adsorption mechanism followed the pseudo second-order. The obtained results revealed that the Zeolite/ZnO NCs adsorbent was found to have high adsorption capacity and it could be employed as an efficient and low-cost adsorbent for removal of heavy metals from water. Furthermore, it can be easily regenerated by 0.005 M HNO₃ and used for several cycles.

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