New, Cheap and Efficient Synthetic Zeolite-X Decontaminant Agent from Fly Ash for Heavy Metal Toxicity

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ABSTRACT

The study aimed to synthesize and characterize a zeolite type X from recycling fly ash by hydrothermal treatment in the presence of sodium hydroxide and used it as decontaminant agent to remove some heavy metals (Zn^{+2}, Pb^{+2} and Cu^{+2}) from standard aqueous solution by adsorption process.

The prepared zeolite from fly ash by hydrothermal process was successively analyzed and characterized by X-ray Diffraction (XRD) and Fourier transfer infra-red (FTIRs) spectroscopy. Atomic absorption was used to determine the adsorption kinetic isotherm profile for the synthetic Zeolite-X, whilst the order of reaction was determined by application of Langmuir and Freundlich isotherm models.

The results showed that, the produced yield of Zeolite-X (Potassium Sodium Aluminum Silicate, Chemical formula: ($K_{57}Na_{42}(Al_{96} Si_{96} O_{38}$) was (74.8%).

The kinetic isotherm studies showed time-dependent heterogenous adsorption profile following Freundlich isotherm model with first order kinetic reaction.

Finally, we concluded that, the amount of Zeolite-X produced by hydrothermal process from Sudanese fly ash was found to be greater than others and was useful as a very sensitive and efficient synthetic decontaminant for elimination of heavy metals from aqueous solutions in very low concentrations.

The preferable heterogeneous Freundlich isotherm model was more applicable for this synthetic Zeolite-X than the homogenous Langmuir model. It was strongly recommended to use Zeolite X in industrial areas as well as areas sufferings form water pollution by heavy metals.

Keywords: Zeolite; Fly ash; Kinetic; Heavy metal; Decontaminant; Isotherm
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INTRODUCTION

Zeolites are microporous crystalline aluminosilicates, composed of TO_4 tetrahedral (T=Si, Al) with oxygen atoms connecting neighboring tetrahedral combination of TO_4 (T=Si) units in this fashion leads to completely uncharged solid siliceous structure (SiO_2) [1]. Upon incorporation of Al^{+3} into the silica framework, the [+3] charges on the Al^{+3} in line with [+4] of silica and [-8] of oxygen makes the framework negatively charged, and requires the

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presence of extra framework inorganic and organic cations within the structure to keep the overall framework neutral [2].

The zeolite composition can be best described as having three components which are: (Mm^+) is extra framework cations, ($Si1-n$, ALn and O_2) is framework and (nH_2O) was adsorbed phase. The extra framework cations are ion exchangeable and give rise to the rich ion-exchange chemistry of these materials [3]. The novelty of zeolites stems from their microporosity and is a result of the topology of the framework [4]. The amount of Al^{+3} within the framework can vary over a wide range, with ($Si/Al=1$: l), the completely siliceous form being polymorphs of SiO_2. Lowenstein proposed that, the low limit of $Si/Al=1$ of a zeolite framework arises because placement of adjacent AlO_3 tetrahedral is not favored, because of electrostatic repulsions between the negative charges [4]. The framework composition depends on the synthesis conditions, post synthesis modifications that insert Si^{+4} or Al^{+3} into the framework. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increases [3].

Zeolites are synthetized by a hydrothermal process with a silica and alumina reagents (fly ash) and for higher Si/Al ratio zeolites, organic molecules as structure-directing agents [5]. The role of inorganic metal cations such as Na^+ or K^+ is quite profound, the complexity of the process, including the presence of numerous soluble species, an amorphous phase, polymerization and depolymerization reactions, makes the synthesis susceptible to physical effects such as stirring, aging, and order of reagent addition [6]. Several independent processes are occurring in the medium, including nucleation (rate-limiting step) of various structures, crystallization as well as dissolution of metastable phases. It is commonly observed that, the conversion of the composition (gel or solution) to crystals is quite rapid once the crystallization process gets started [6].

A number of studies proposed different methods for synthesizing zeolites from fly ash by hydrothermal alkaline conversion [7-9]. The classical alkaline conversion uses open or closed hydrothermal systems with different activation solution/fly ash ratios NaOH or KOH solutions, at atmospheric and water vapor pressures from 80 to 200 C for 3 to 48 h have been used to synthesize up to 15 different zeolites from the same fly ash [10].

The zeolite contents of the resulting material varied widely (20 to 65%), depending on the activation conditions. The method has been improved by introducing an alkaline fusion stage prior to the conventional synthesis [11] and microwave [12] to reduce the reaction time. A two stage synthesis procedure enabled the production of>90% pure zeolite material from high-Si fly ash extracts. Moreover, a zeolitic material with lower purity is also obtained from the residue resulting from this Si-extraction. All these different processes resulted in the synthesis of high purity zeolite with low-silica sodium and potassium [13].

Nowadays, removing toxic heavy metal contaminants from aqueous waste streams is one of the greatest matters of interest for environmentalists due to its impact on human health and surroundings [14]. The toxic metals existing in high concentrations must be effectively removed from the waste waters by totally unknown very complex adsorption process.

Adsorption isotherms are mathematical models that describe the distribution of the adsorbates' specie among liquid and solid phases, based on a set of assumptions that are related to the heterogeneity/homogeneity of the solid surface, the type of coverage and the possibility of interaction between the adsorbates' species.

Adsorption equilibrium data were analyzed using the Freundlich, and Langmuir. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation commonly represented as: ($qe=kfce1/n$) and can be expressed in its linear form as: ($Ln\ qe=Lnkf+1 \backslash n\ Ln\ Ce$), where Ce (mg/L) is the equilibrium concentration and qe (mg/g) is the amount of adsorbed metal ion per unit mass of the adsorbent. The constant n is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface [15]. KF (L/g) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent. The Freundlich exponent, n, should have values lying in the range of 1 to 10 for classification as favorable adsorption form [15]. The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the sorbent surface.

The Langmuir model assumes that, uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir equation may be written as: ($qe=qm\ kL\ Ce/(1+kL\ Ce)$) and can be expressed in its linear form as: ($Ce/qe=1/qm\ KL+Ce/qm$), where qe is the amount adsorbed (mg/g), Ce is the equilibrium concentration of the metal ion (mg/L), qm (mg/g) is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites and KL (L/mg) is the Langmuir constant related to the energy of adsorption [16].

Zinc and lead are classified as strongly hydrating cations that are mostly toxic to some vertebrates, causing kidney and blood disorders in addition to other negative symptoms. These ions are mostly discharged by certain industries into rivers, lakes, seas and oceans causing serious contamination [17]. The lead ions cause poisoning and affect

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gastrointestinal track, or nervous system, this encouraged research into using low-cost adsorbent materials to purify water contaminated with metals [18].

This study was set out to synthesize and characterize a simple, cheap adsorbent agent (Zeolite) from fly ash and use it as efficient decontaminant agent to remove some heavy metals (Zn^{+2}, Pb^{+2} and Cu^{+2}) from standard aqueous solution by adsorption process.

MATERIALS AND METHODS

Preparation of the Crude Material

A-The fine powder of fly ash was obtained as a waste product from Garri's station (Khartoum Thermal Station for Electricity Production) that resulted from combustion of petroleum cook in, then its content was analyzed by X-ray fluorescence (XRF).

B-Standard aqueous salts solutions of heavy metals; (Pb^{+2}) (lead acetate trihydrate: M. wt: 379.34), Cu^{+2} (Copper (11) sulphate-pentahydrate M. wt: 249.68) and Zn^{+2} (Zinc sulphate M. wt: 278.45) were prepared with a concentration of (100 ppm).

C-Sodium hydroxide as crystal powder and Hydrochloric acid (conc., 90%) were used.

Synthesis of Zeolite-X from Fly Ash

Fly ash samples were screened through a BSS Tyler sieve of 80-mesh size to eliminate larger particles. Then the burnt carbon (4–6%) and other volatile materials present in the fly ash were removed by calcination in an oven at 800 ($\pm$10)$^{\circ}$C for 2 hours.

Fly ash samples were activated by treating with hydrochloric acid to increase its content, dealuminate (Increasing thermal stability and acidity of the zeolite) and reduce the iron content. A mixture of sodium hydroxide and fly ash (calcined and HCl treated) in (1:1.5) ratio, was melted and fused in a stainless steel tray at different temperatures ranging from 500–650°C for 1 hour. The sodium hydroxide added to the fly ash not only works as an activator, but also adjusts the sodium content in the starting material. Mullet and a-quartz present in the fly ash were the sources of aluminum and silicon respectively for zeolite formation. The resultant fused mixture was cooled to room temperature, grounded and added to water in a ratio of (10 gm fly ash/100 ml water). The slurry obtained was agitated mechanically at 90°C for 6 hours. The resultant precipitate was then filtered, washed with distilled water to remove excess sodium hydroxide, dried and weighted in grams, then the yield percentage was calculated as follow: [37.4/50 * 100%=74.8%]. The synthesis method was adopted according to the Keka's method [19].

Characterization of Prepared Zeolite

A-The X-ray diffraction (XRD) methods were used for characterizing the obtained synthetic zeolite, using a Philips X-ray diffractometer (Philips BW1710). Operating conditions involved the use of Co Ka radiation at 4 kV and 30 mA. The sample was scanned from 10-50° (2q, where q is the angle of diffraction). Various crystalline phases present in the samples were identified with the help of JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compound.

B-The Fourier transform infrared spectrophotometer (FT-IR) spectrum was used to investigate the characteristics of the prepared zeolite such as structural features and acidity. The functional groups of zeolite were tested using Fourier transform infrared spectrometry (FT-IR) (ECTORUKER, Germany) in the region of (4000-400) cm^{-1} wavenumbers. The analysis of the prepared zeolite samples was performed with a Nicolet Magna spectrometer with a DTG SBr detector and KBr as beam splitter with 100 scans for wave number range of 400-4000 cm^{-1}.

The Decontamination of Heavy Metal and their Kinetic Isotherm Profile

The kinetic isotherm studies regarding the effect of the contact time on the adsorption were carried out for constant initial concentrations (100 ppm) for the three heavy metals; Pb(II), Zn(II) and Cu(II) ions on synthetic zeolite. Batch mode experiments were performed in 100 ml beakers by addition of desired amount of zeolite (1 g/L) to 50 ml of standard aqueous solutions of heavy metals. In all experiments, the beakers were shaken at 100 rpm on the mechanical shaker for predetermined equilibrium time intervals of 30, 60, 90, 120 and 180 minutes at room temperatures. After agitation, the zeolite was separated by filtration using filter papers and some aliquots of filtrate in the supernatant were analyzed using atomic adsorption spectrophotometer (AAS). The amount of metal ion adsorbed on the zeolite was calculated by the following equation: % removal=(Ci - Ce)/Ci * 100

Where Ci=Concentration before adsorption, Ce=Concentration after adsorption [20].

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Application of Adsorption Isotherms Models for Reaction Order Determination

a) Freundlich isotherms expression: The linear form of the Freundlich model was applied to estimate the adsorption intensity of the sorbet on the sorbent surface. The experimental data at equilibrium from the batch sorption study of the three metal ions on zeolite were plotted logarithmically using the linear Freundlich isotherm equation and the useful parameters were estimated and used. The Freundlich equation was used as: lnqe=lnkf+1\n lnce.

Where Ce (mg/L) is the equilibrium concentration, qe (mg/g) is the amount adsorbed metal ion per unit mass of the adsorbent. The constant n is the Freundlich equation exponent and KF (L/g) is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent.

b) The Langmuir isotherms expression: The linear form of the Langmuir model was applied to estimate the adsorption intensity of the sorbet on the sorbent surface. The experimental data at equilibrium from the batch sorption study of the three metal ions on zeolite were plotted logarithmically using the linear Langmuir isotherm equation and the useful parameters were estimated and used. The Langmuir equation was used as: Ce/qe=1/(kLqm)+ce/qm, where qe is the amount adsorbed (mg/g), Ce is the equilibrium concentration of the metal ion (mg/L), qm (mg/g) is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites and KL (L/mg) is the Langmuir constant related to the energy of adsorption. The plots of specific sorption (Ce/qe) against the equilibrium concentration (Ce) for Pb(II), Zn(II) and Cu(II) as well as the linear isotherm parameters; qm, KL and the coefficient of determinations were manipulated into suitable statistical data.

Statistical Analysis

All results were analyzed using GraphPad prism 0.5 program and expressed as mean ± standard error of mean. The simple linear regression was applied to plot the correlation of all models and to estimate the Correlation coefficient (fitting goodness) and the slope (relation direction), besides, the two-tailed unpaired t-test was also used to compare the findings. The level of significance was set at $p \leq 0.05$ compared to the control group.

<div align="center">

RESULTS

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The Synthesis of Zeolite Results

Our synthesis by hydrothermal process produced (74.8%) yield of Zeolitic material, with empirical formula $(Al_{96}K_{57}.44Na_{42}.76O_{384}Si_{96})$ and density (g/cm^3): 1.58.

Characterization of Zeolite Prepared from Fly Ash

The X-ray diffraction (XRD) patterns of synthetized Zeolite powder showed (54.5%) of potassium sodium tecto alumnosilicate peak at position (6.1) within the spectrum, (25.1%) aluminum oxide position (35.1) and (20.4%) silica oxide-alpha position (26.6) as shown in Figure 1.
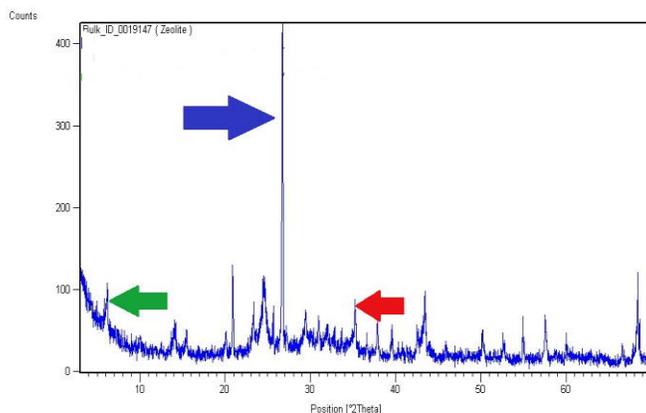

Figure 1: The X-ray diffraction (XRD) patterns of synthetized Zeolite powder from fly ash, showed different positions of main functional groups; Aluminum oxide (Red arrow), Potassium Sodium Tecto Aluminsilicate (Green arrow) and Silicon oxide-alpha (Blue arrow) in relation to the density of powder and comparable to the standard values of Zeolite Atlas

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On the other hand, the Fourier transform infrared spectrophotometer (FT-IR) spectrum of the prepared zeolite, showed mainly 8 absorption bands observed around 3475.4 cm^{-1}, 1649 cm^{-1}, 1469 cm^{-1}, 979 cm^{-1}, 734 cm^{-1}, 656 cm^{-1}, 563 cm^{-1} and 447 cm^{-1} (Figure 2).
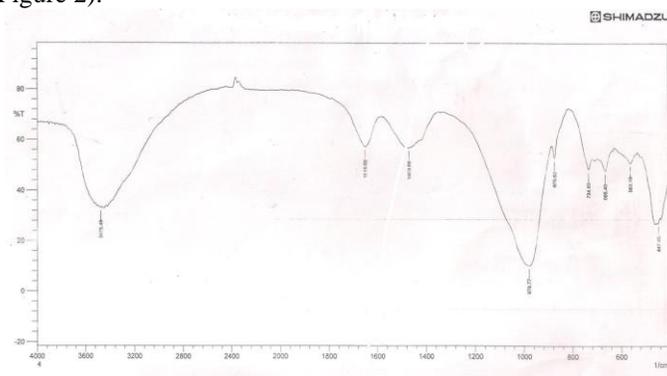

Figure 2: The Fourier transforms infrared spectrophotometer (FT-IR) patterns of Synthetized Zeolite prepared from fly ash, the spectrum showed the Zeolite main 8 absorption bands observed at different positions

The Adsorption Kinetic Isotherm Profile Results

The kinetic isotherm results using atomic absorption photometer of main heavy metal ions adsorbed on zeolite showed no adsorption at the beginning and then followed by gradual time-dependent phase (Figure 3).
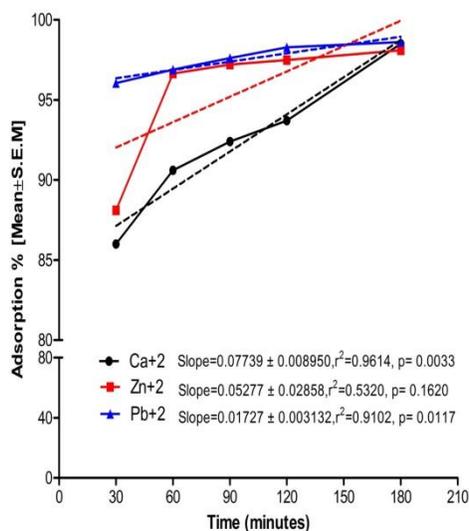

Figure 3: The kinetic isotherm effect of contact time on the adsorption rate (%) of heavy metals (Zn^{+2}, Cu^{+2} and Pb^{+2}) from prepared aqueous solution by the synthetic Zeolite-X. The adsorption rate was done by atomic absorption spectrophotometer, whilst data presented were means of triplet measures for five different time intervals

Application of Adsorption Isotherms Models for Reaction Order Determination

Application of Freundlich isotherm model on the three heavy metals adsorption by synthetic Zeolite, showed good fittings (r^2=0.97, 0.96 and 0.87) for Pb^{+2}, Zn^{+2} and Cu^{+2} respectively, with negative slopes as shown in Figure 4.

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4A

$r^2 = 0.8715, p = 0.0204$
Slope = -0.05658 ± 0.01254

4B

$r^2 = 0.9638, p = 0.0030$
Slope = -0.05945 ± 0.006655

4C

$r^2 = 0.9728, p = 0.0019$
Slope = -0.02470 ± 0.002386

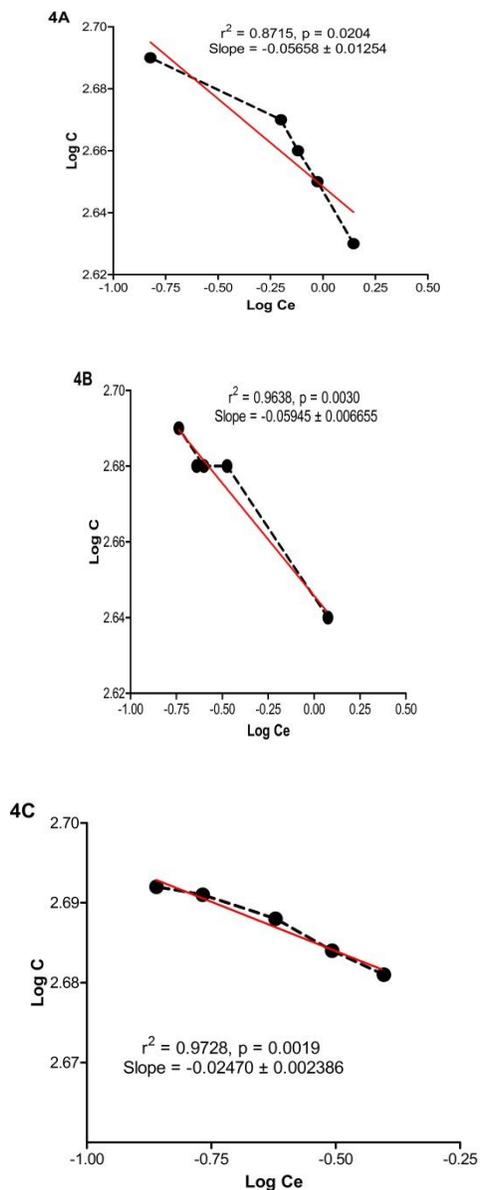**Figure 4: The linear regression of the Freundlich isotherm for Cu (A), Zn (B) and Pb, (C) with level of fitting goodness (r^2) and the slope (Mean ± SEM) and its level of significant difference (p-value) between the two lines**

On the other hand, Langmuir isotherm model showed various levels of fitting (r^2=0.89, 0.49 and 0.23) for Pb^{+2}, Zn^{+2} and Cu^{+2} respectively, with negative slopes as shown in Figure 5.
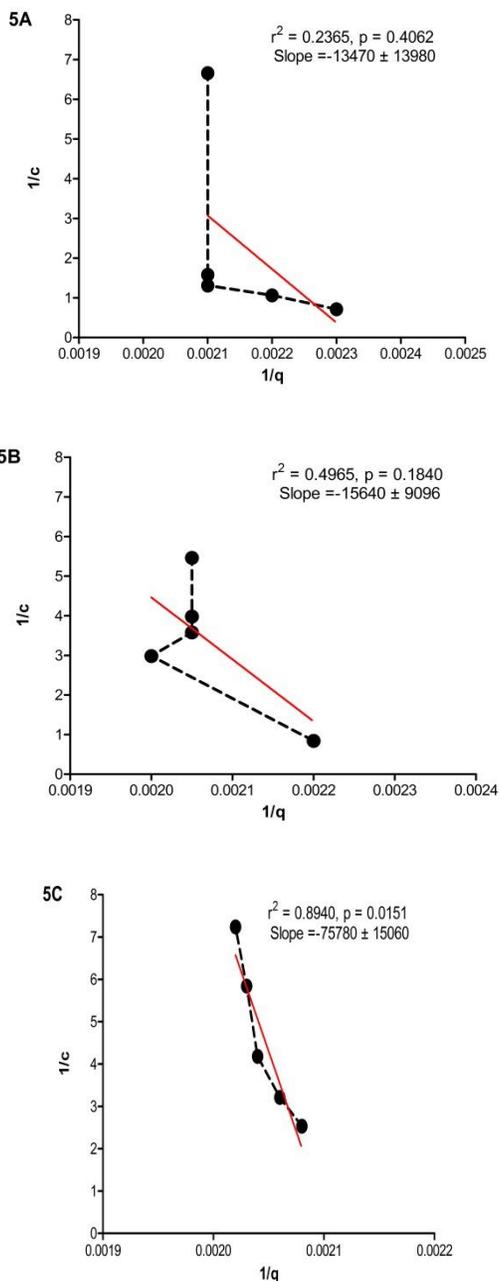
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Figure 5: The linear regression of the Langmuir isotherm for Cu (A), Zn (B) and Pb, (C) with level of fitting goodness (r²) and the slope (Mean ± SEM) and its level of significant difference (p-value) between the two lines

DISCUSSION

The presence of heavy metals in streams and lakes has been responsible for several types of health problems for animals, plants and human beings and their removal is of great interest using an ion exchanger with high selectively such as zeolitic material for these metals.

Our results revealed the production of 74.8% Zeolite by hydrothermal process. This means that, the yielded amount was greater than the expected percentage which ranged (20-65%). These findings are in line with literature information.

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The XRD showed three main peaks for the synthetic zeolite, which can be taken as an evidence for its type to be X-type according to the reference atlas and these findings, agree with who reported the zeolite –X peaks locations within the XRD spectrum.

Moreover, the Fourier transform infrared spectrophotometer (FT-IR) was used to determine its acidity and to confirm the characteristic adsorption bonds of the synthetic zeolite, where 8 absorption bands were observed. The band at 3475.4 cm^{-1} is attributed to OH stretching of H_2O forming hydrogen bonds, the bands at 979 cm^{-1} and 734 cm^{-1} are attributed to Si-O stretching vibration of Si-O-Si, and Si-O-Al respectively and the band at 447 cm^{-1} is assigned to be O-Si-O bending. This is typically as mentioned by [21].

The kinetic isotherm results revealed that, the adsorbed concentrations are zero at the beginning, then within a short period of time they vary considerably and further they ended up with a very gradual and quite narrow variation range. The initial rapid phase is due to the presence of large number of vacant sites, leading to increase in concentration gradient between adsorbate in solution and the adsorbent surface. As time proceeds, this concentration is reduced due to the accumulation of metal concentrations on the vacant sites, leading to decrease in gradient adsorption rate and these contradict with [20].

Contact time is an important parameter, because this factor determines the adsorption kinetics of an adsorbate at a given initial concentration of the adsorbate. In the case of concentration of 100 ppm, the time to reach equilibrium is 180 minutes. It also showed that, increase in initial metals ion concentrations increase the amount of metal ions uptake per unit weight of zeolite (mg/g), as it was expected, this indicates the high efficiency of the synthetic zeolite in removing the toxic heavy metals from the aqueous solution even in very low concentration of heavy metals. This is unlike the literature data which showed that, other zeolites only remove the heavy metal from the solution with normal or high concentrations.

The order of adsorption of heavy metals ions on zeolite was $Pb^{+2}>Zn^{+2}>Cu^{+2}$. This means that, the synthetic zeolite adsorbs the three main metals with various degrees, but with highest affinity to the Pb ion, whilst another study does not include Pb^{+2} [7].

To determine the order of synthetic zeolite adsorption kinetic reaction, two famous isotherm models were used; Freundlich and Langmuir, where the former showed good fittings (r^2=0.97, 0.96 and 0.87), whilst the later showed various levels of fitting (r^2=0.89, 0.49 and 0.23) and both with negative slopes, because the Langmuir model assumes that, uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions, in contrast with the Freundlich equation which is based on adsorption on a heterogeneous surface, which was more applicable for our case.

CONCLUSION

Finally, we can conclude that, the amount of zeolite produced by hydrothermal process from Sudanese fly ash was found to be greater than others.

The type of zeolite prepared from fly ash by recycling was Zeolite-X, (Potassium Sodium Aluminum Silicate) with Chemical formula: $(K_{57}Na_{42}(Al_{96}Si_{96}O_{38})$.

This synthesized zeolite is useful as a very sensitive and efficient synthetic decontaminant for elimination of heavy metals from aqueous solutions in very low concentrations.

The preferable heterogeneous Freundlich isotherm model was more applicable for this synthetic Zeolite-X than the homogenous Langmuir model.

It is strongly recommended to use Zeolite X in industrial areas as well as some rural areas in Sudan which suffer from water pollution by heavy metals.

In adsorption isotherm, the effect of contact time of adsorbent doses on the removal of heavy metal ions; Cu, Zn and Pb, a minimum of 180 minutes is recommended to keep the test running.

Application of the two common adsorption isotherm models; Langmuir and Freundlich revealed that, the synthetic Zeolite-X rate of adsorption is first order kinetic reaction with heterogeneous surface adsorption phenomenon.

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