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# Removal of lead ions from aqueous solutions by insolubilized Iraqi humic acid

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## ABSTRACT

Humic acid from Adhamiya clay soil was extracted and converted to insolubilized humic acid (INaHA). It was characterized by Fourier-transform infrared spectroscopy, elemental analysis, thermal gravimetric analysis, X-ray diffraction, differential scanning calorimetry, and scanning electron microscopy. Adsorption of Pb(II) ions by INaHA was studied using the batch technique at different temperatures (25.0°C, 35.0°C and 45.0°C) and at different pH values (3.0, 4.0 and 5.0), The solutions adjusted to pH 4 were found to be the optimum media for the removal Pb(II) ions. Pseudo-second-order kinetic model was used to understand the mechanism for adsorption, the maximum capacity of the uptake of lead ions was achieved after 24 h. The rate constant $k_2$ of the pseudo-second-order sorption was used to calculate the activation energy ($E_a$) of (20.26 kJ/mol), which gives evidence that the physisorption process took place. Isotherm equilibrium models were investigated, Langmuir, Freundlich and Dubinin–Radushkevich) were applied to the data acquired at different temperature values 25.0°C, 35.0°C and 45.0°C. It was found that the Langmuir isotherm is the best model to describe this adsorption depending on the $R^2$. The energy $E$ which is determined from the Dubinin–Radushkevich isotherm model was taken the range 1.16 to 1.03 kJ/mol. The experimental thermodynamic functions, $\Delta G°$, $\Delta H°$ and $\Delta S°$ are –4.5 kJ/mol, 9.23 kJ/mol and 46.13 J/mol.K, respectively. The %uptake of lead was determined using a continuous column experiment and was found to be 93.91%. The recovery of desorbed Pb(II) using 1 M of $HNO_3$ is higher than using 1 M of HCl.

*Keywords:* Insolubilized humic acid; Lead ions; Removal; Isotherm models; Kinetic models

## 1. Introduction

Water pollution is basically the degradation in water quality which is caused by the introduction of some toxic substances that changes the physical and chemical characteristics of water making it unfit for normal use. The solid, liquid or gaseous materials have different effects according to their amount and potential danger. These materials can be of a human origin when they are introduced by humans or a natural origin which is produced by the decomposition of organic debris, climate conditions, and erosion factors. [1]

The pollutants are divided into organic pollutants, biological pollutants and inorganic pollutants [2]. Many heavy metal ions have been discharged into the environment as industrial wastes causing serious soil and water pollution such as $Zn^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Cd^{2+}$, which are accumulated in organisms [3,4]. Among all heavy metal pollutants, lead is the most common and one of the most toxic, reaching water sources from various industrial activities such as mining, oil refining, metal plating and finishing, and battery manufacturing. The current maximum lead concentration limit, according to the US Environmental Protection Agency (EPA) for drinking water is 0.015 mg/L. Lead has no biological role in the human body and can be toxic even at a very low concentration in drinking water. Thus, the World Health Organization (WHO) has set the

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maximum permissible limit for Pb in drinking water to be 0.01 ppm (WHO) [5]. When lead concentrations become elevated, serious health problems can occur. Lead poisoning can cause kidney damage, anemia, and toxicity symptoms including impaired kidney function, hypertension, and headache [6,7]. Various technologies are employed for the removal of heavy metals from water including chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and adsorption [3].

Among these techniques, adsorption is the most effective method due to its cost-effective, versatile, and simple operation for removing trace levels of ions. There are many kinds of natural adsorbents such as clay, zeolite, and plants. The biopolymers derived from microbes are known to bind metals strongly, humic substances which are organic matter are widely used to make purification of waste-water because of its strength of binding with metal ions. Humic substances are divided into three fractions: humic acid (HA), fulvic acid, and humin. Humic acid soluble in alkaline solution and insoluble in acidic solutions has a high complexing ability with various heavy metal ions. However, it is difficult to use humic acid as adsorbent because of its high solubility in water above pH 3.5 [1].

In the present study, the HA was extracted from the soil brought from Iraq, the insolubilized form was prepared according to a method which described in previous reports [1,8], The main purpose of this study is to set up a suitable method for treatment of wastewater using low-cost purification adsorbent such as insolubilized HA from Iraq soil (INaHA) to remove inorganic pollutants such as lead ions Pb(II) from aqueous solutions. In order to study the adsorption mechanism between the Pb(II) ions and the INaHA, thermodynamic and kinetic data were investigated after the analysis of the experimental results. The adsorption isotherm models such as Langmuir, Freundlich and Dubinin–Radushkevich were applied to test the nature of this interaction between the lead ions and the surface of the solid adsorbent (INaHA), we used the experimental adsorption partition constant ($K_d$) to figure out thermodynamic parameters such as free energy ($\Delta G_{\text{ads}}$), enthalpy ($\Delta H_{\text{ads}}$), and entropy ($\Delta S_{\text{ads}}$) to understand the type of adsorption [9]. Kinetic models: pseudo-first-order and pseudo-second-order were investigated to understand the behavior of adsorption. This study is a part of a research program in which we try to investigate the removal of various contaminants using insolubilized HA. In all experiment the uptake of lead ions is calculated using the following equation:

$$q_t = \frac{\left(C_i - C_t\right) \times V}{m} \tag{1}$$

where $q_t$ is the metal uptake (mg/g), $C_i$ and $C_t$ are the initial and metal concentrations in solution (mg/L) at time $t$, respectively. $V$ is the solution volume (L), and $m$ is the mass of adsorbent (g) [9]. The distribution coefficient ($K_d$) (L/g) of lead ions between the aqueous phase and the solid phase can be directly obtained using Eq. (2) [9]:

$$K_d = \frac{q_e}{C_e} \tag{2}$$

where $q_e$ is the equilibrium amount of solute adsorbed per unit mass of adsorbent (mg g$^{-1}$) and $C_e$ is the equilibrium concentration of solute (mg/L).

### 1.1. Adsorption isotherm models and adsorption kinetics

The relationship between the solute which is the adsorbate and the solid surface of the adsorbent at equilibrium can be characterized by the adsorption isotherm models like Langmuir, Freundlich and Dubinin–Radushkevich. These models explained the distribution of the solute between the bulk solution and the solid. The equilibrium constants of these models are estimated at a fixed temperature. All the isotherm models have a relationship between the $q_e$ which is the equilibrium amount adsorbed per unit mass of adsorbent (mg/g) and $C_e$ is the equilibrium concentration of the adsorbate in solution (mg/L).

The Langmuir model simplest and generally used for the analysis of adsorption data, according to this model all adsorption sites has equal energy of adsorption, which implies a homogeneous surface. The adsorption capacity of the monolayer, $q_m$ (mg g$^{-1}$), and $K_L$ which is the Langmuir constant related to the energy and affinity of binding sites of adsorption (L mg$^{-1}$) are obtained from the linearized Langmuir equation as shown (Eq. (3)) [10,11].

$$\frac{1}{q_e} = \left(\frac{1}{\left(q_m K_L\right)}\right)\frac{1}{C_e} + \frac{1}{q_m} \tag{3}$$

The values of $q_m$ and $K_L$ can be determined from the slope and the intercept of the plot of the linear forms of the Langmuir equation. The behavior of the isotherm is described by $R_L$, this constant can be calculated using equation (4)

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

Unfavorable adsorption if ($R_L > 1$), linear adsorption if ($R_L = 1$), and favorable adsorption if ($0 < R_L < 1$), $C_0$ is the maximum initial concentration [9].

The Freundlich adsorption model can be used to fit non-ideal adsorption behavior in which the adsorption isotherm does not reach a plateau with an increasing concentration of solute. This occurs when multilayer is formed on heterogeneous surfaces with active sites with different energies.

The logarithmic linear form of the Freundlich equation is given as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

where $K_F$ is the Freundlich isotherm constant, and $n$ is the adsorption intensity. $K_F$ and $1/n$ could be calculated from the intercept and the slope, respectively. $K_F$ is related to the maximum adsorption capacity and also gives an idea about the extent of adsorption. The value of $n$ refers to the adsorption intensity and confirms the degree of favorability of the adsorption process, if the value of $n \geq 1.0$ is a favorable process, whereas if the value of $n \leq 1.0$ is an unfavorable process [12,13].

*Dubinin–Radushkevich model*. This isotherm is commonly used to describe the sorption isotherm of a single solute system, although this is analog to the Langmuir model, Dubinin–Radushkevich model is more general than Langmuir as it rejects the homogenous surface or constant adsorption potential. Dubinin–Radushkevich adsorption isotherm is applied to the sorption data based on the heterogeneous surface of the adsorbate in order to distinguish between chemical and physical adsorption and it is valid at low concentration ranges.

The linear (Dubinin–Radushkevich) model has the following expression:

$$\mathrm{Ln}\, q_e = \mathrm{Ln}\, q_{\mathrm{DR}} - \beta\varepsilon^2 \tag{6}$$

$$\varepsilon = RT\ \mathrm{Ln}\left(\frac{1+1}{C_e}\right) \tag{7}$$

where $R$ is the universal ideal gas constant (8.3145 J mol$^{-1}$ K$^{-1}$), and $T$ is the absolute temperature (Kelvin). The adsorption free energy ($E$), Eq. (12), is defined as the free energy change required for transferring one mole of ions from solution to the solid surface [12,13], this energy is calculated as follows:

$$E = \frac{1}{\left(2\beta\right)^{0.5}} \tag{8}$$

The $K_d$ parameters from Eq. (2) can be used to calculate thermodynamic parameters include $\Delta G°$ which is the free energy, using the following equation:

$$\Delta G° = -RT\ \ln K_d \tag{9}$$

where $\Delta H°$ and $\Delta S°$ can be estimated following equation:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

where $R$ is the universal ideal gas constant (8.3145 J mol$^{-1}$ K$^{-1}$) and $T$ is the temperature in Kelvin. If the plot of ln$K_d$ against $1/T$ gives a linear relationship, then $\Delta H°$ and $\Delta S°$ could be obtained from the slope and intercept, respectively [14].

Kinetic models are used in the literature to fit time-dependent adsorption data; pseudo-first-order, and pseudo-second-order. In our research, the pseudo-second-order is applied because our experimental results did not fit the pseudo-first-order. The rate of pseudo-second-order reaction is dependent on the amount of adsorbate on the surface of the adsorbent and the amount of adsorbate adsorbed. The sorption equilibrium ($q_e$) is a function of many parameters such as the temperature, the initial metal ion concentration.

The linearized pseudo-second-order equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

where $k_2$ is the second-order reaction constant (g mg$^{-1}$ min$^{-1}$), $q_e$ and $q_t$ are the amount of metal ions adsorbed per unit weight at equilibrium and $t$ is time, respectively. The $q_e$ and $k_2$ can be computed from the plot $t/q_t$ vs. $t$ which gives a straight line. The accuracy of this model can be tested by comparing the experimental $q_e$ values when $q_t$ reaches a plateau with the calculated value [15,16].

## 2. Experimental setup

### 2.1. Material and methods

All reagents used in this study were of analytical grade reagents. Sodium hydroxide from LOBA (India), hydrochloric acid 37% from S&C Chemicals Supply Co., (USA), nitric acid 69% from LabChem (USA), lead(II) nitrate from PRS PanReac (USA). The soil samples used in this study were collected from Adhamiya (SahatAntarmashatel) in the north-west of Baghdad City Center, (latitude: 33.37 and longitude: 44.37), the soil has a gray color.

The location from the GPS is (https://geographic.org/geographic_names/name.php?uni=-4379335&fid=3149&c=iraq/). All of the solid samples are stored in plastic specimen cups with a screw-on lid.

### 2.2. Extraction of the HA from Adhamiya soil

Soil samples were used from the O horizon of a clay soil from Adhamiya (SahatAntarmashatel) in the north-west of the Baghdad City Center. The soil samples were air-dried, crushed and homogenized prior to extraction. Humic acid was extracted from Adhamiya soil samples by the following procedure: 4.0 kg ± 0.1 g of soil was treated with 4.0 L of 0.1 M NaOH for 24 h at room temperature. The mixture was filtered through filter paper after that the supernatant was acidified using 37% w/w (12.5 M) HCl to pH = 1.5 and left at room temperature for 24 h. The resulting precipitate was rinsed many times with deionized water to remove chloride ions and was tested by the $AgNO_3$ (1.0 M) solution. The precipitate was dried at 95°C for 8 h and the resulting solid is 23.0000 ± 0.0001 g.

### 2.3. Preparation of insolubilized HA

The insolubilized HA was prepared as described in the previous reports [1,8]. The extracted HA from the Iraqi soil was calcinated at 330°C for 2.0 h, then it was treated with 1.0 M $NaNO_3$ solution for 48 h, and the obtained insolubilized sodium form (INaHA) was filtered and dried at 80°C for 24 h. The percentage yield for INaHA from soil according to this procedure was 0.45%, where the total number of grams that obtained from 4 kg, Adhamiya soil sample was 17.8000 ± 0.0001 g.

The characterization of (INaHA) was done using the following instruments: Fourier-transform infrared spectroscopy (FTIR) (Thermo Nicolet NEXUS 670 FTIR Spectrophotometer, USA). Elemental analyses (EuroVector 3000 Elemental Analyzer, Italy) and thermogravimetric analysis (TGA) (NETZSCH STA 409 PG/PC, Germany) with the thermal analyzer in the temperature range (0°C–1,000°C), at a heating rate of 20°C/min. Thermal stability and melting were carried by calorimetric analysis by NETZSCH differential scanning calorimeter (DSC) 204 F1, where the temperature range (0°C–500°C), and heating rate of 20°C/min. X-ray diffraction (XRD) (Philips X'Pert PW 3060, USA), operated at 45 kV and 40 mA. The shape with 3-dimensional (3D) and surface morphology of INaHA was examined with NCFL's FEI QUANTA 600 FEG scanning electron microscopy (SEM). Samples were shaken using a GFL-1083 thermostatic shaker.

### 2.4. Batch experiments

The removal of lead ions by INaHA was carried out using the batch method, 25.0 mL of 20 mg/L Pb(II) solution was contacted with 20 mg of INaHA, the experiments were done at different pH values which are 3.00, 4.00, and 5.00, the optimum pH value was applied in all other experiments. The effect of contact time was studied also by contacting 25.0 mL of 20 mg/L Pb(II) with 20 mg INaHA at different contact time intervals (0.08, 0.17, 0.25, 0.33, 0.42, 0.5, 1.0, 2.0, 4.0, 8.0 to 24.0 h). The influence of temperature on lead ion removal was investigated at different temperatures (25.0°C, 35.0°C and 45.0°C), all sample solutions were prepared with a concentration of 20 mg/L and contacted with 20 mg of INaHA at pH 4 and were shaken for 24 h and the optimum pH value was applied in all other experiments.

### 2.5. Equilibrium studies

All of the separate batch adsorption experiment was carried out at the optimum conditions: pH = 4, the equilibrium time is 24 h at an ionic strength of 0.1 M and using 20 mg of INaHA was carried out using exactly 25.0 mL of known initial concentration in the range of 5–20 mg/L of Pb(II) ions, all the samples were shaken at different temperature values (25.0°C, 35.0°C and 45.0°C).

### 2.6. Removal kinetic studies

All kinetic batch experiments were done by adding 20 mg of INaHA to 20 mg/L of Pb(II) at pH 4. Several experiments were done using the above conditions at different contact time intervals (0, 0.08, 0.17, 0.25, 0.33, 0.42, 0.5, 1.00, 2.00, 4.00, 8.00 to 24.00 h), each solution has separate interval time. These kinetic experiments were done at different temperature values which are (25.0°C, 35.0°C and 45.0°C).

### 2.7. Column reactor

A glass column of 20 cm length and 20 mm inner diameter was used in this experiment. The column was packed with 1.0 g INaHA then Pb(II) ions loaded on INaHA. 50.0 mL of 1,000 mg/L Pb(II) ions, at pH = 4.0 was passed through the column at a flow rate of 0.56 mL/min. The eluate was collected in 100.0 mL plastic specimen cups with screw lid, and the accumulated concentration of the metal ion unloaded was then determined by the atomic absorption spectrometer (AAS). The desorption of the Pb(II) ion was carried out using the same loaded column with Pb(II) ions using 50.0 mL of three eluting agents, 1.00 M $HNO_3$, 0.50 M $HNO_3$, and 1.00 M HCl were used separately, keeping the flow rate of elution at 0.56 mL/min. The concentration of Pb(II) ions in each eluate collected in five 10.0 mL portions, was determined by the atomic absorption spectrometer (AAS).

All of the experiments were duplicates and the average was used in the calculation and data analysis.

## 3. Results and discussion

Characteristics of adsorbent were done using FTIR spectroscopy, XRD, TGA, DSC and SEM.

### 3.1. FTIR spectroscopy

The FTIR a spectrum of INaHA is displayed in Fig. 1. It shows broad bands in the region from 3,200–3,700 $cm^{-1}$ due to –OH stretching. The two bands at 2,918 and 2,854 $cm^{-1}$ were assigned to (aliphatic –CH). The band at 1,634 $cm^{-1}$ was assigned to C=O stretching of ketones and quinones and C=C olefin group. The band at 1,404.66 $cm^{-1}$ was assigned to O–H deformation and asymmetric stretching of $COO^-$. The band at 1,036 $cm^{-1}$ was assigned to aliphatic C–O stretching, and the stretching and at 906 $cm^{-1}$ describe ring stretching, finally, the bands in region 488–530 $cm^{-1}$ describe aliphatic torsion.

### 3.2. XRD study

The diffractogram of INaHA is shown in Fig. 2, from the figure the solid adsorbent has amorphous nature due to the stacking of aromatic moieties, and polymers that formed through insolubilization. The XRD peaks at $2\theta$ = 19.94° and 20.82° are due to aliphatic or saturated rings, while $2\theta$ = 26.66° and 28.00° are due aromatic moiety, and finally, $2\theta$ = 34.92° indicates the existence of graphite-like layers. Both (XRD and IR) indicate high aromaticity [17].

### 3.3. Thermal properties

#### 3.3.1. Thermogravimetric analysis

The TGA curve of INaHA is illustrated in Fig. 3 shows the presence of three main stages of weight loss curves. The first stage represents a solvent loss it takes place around 110°C and it originates from the evaporation of the water contained in the INaHA itself. The second and third stages of the weight loss are attributed to the thermal degradation of INaHA at approximately 400°C and 1,000°C, respectively. The residual mass of the heating process at 998°C where 82.28% by sample mass is INaHA is a residual metal oxide.

#### 3.3.2. Differential scanning calorimetry

The Heat flow profiles of the input INaHA are shown in Fig. 4 using differential scanning calorimetry, the results indicated that heating temperature influence on INaHA is an endothermic transition with denaturation of chemical nature INaHA at $t$ = 110.7°C. It is due to water evaporation and decomposition aliphatic carbon decomposition [18].

#### 3.3.3. SEM analysis

The SEM micrographs of the INaHA are shown in Figs. 5a and b, respectively. As shown in Fig. 5a the surface

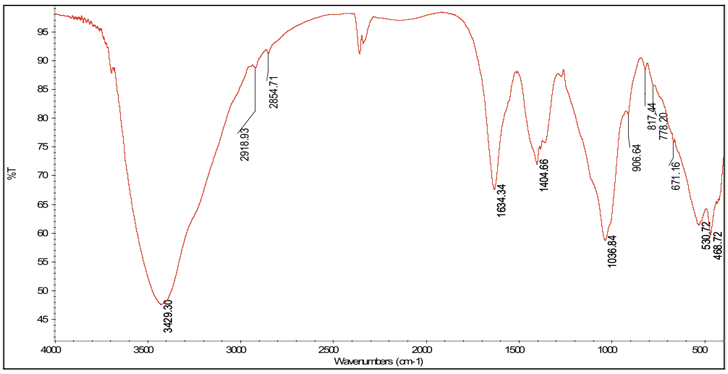

Fig. 1. FTIR spectrum for INaHA.

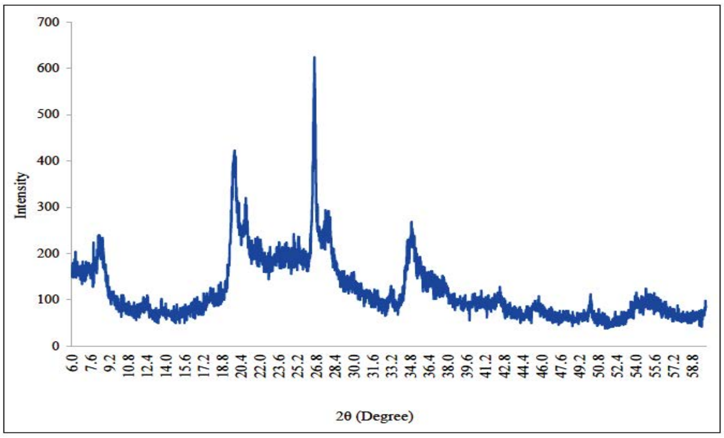

Fig. 2. Analysis of INaHA using XRD.

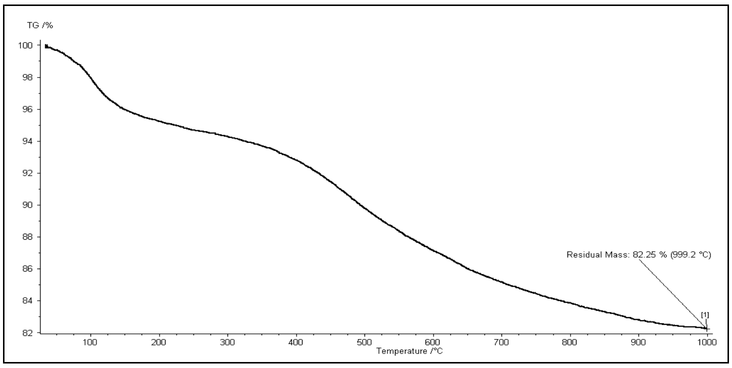

Fig. 3. Analysis of INaHA using TGA.

of INaHA shows numerous irregular particles shape and give a rough surface. While when Pb(II) ions are adsorbed on the INaHA surface, the particles of INaHA became finer and the surface much smoother as shown in Fig. 5b.

#### 3.3.4. Elemental analysis

Table 1 shows the percentages (%) of carbon, nitrogen, and hydrogen in INaHA. The low % C is due to the decarboxylation of humic acid and extensive decomposition of aliphatic structures under the calcination process. In addition, the presence of sodium (INaHA) may lead to a decrease in the % C. The (C/H) mole ratio was low (0–35), and this indicates the high hydrogen content compare to C and high saturation in the HA after heating.

## 4. Batch experiments

### 4.1. Effect of contact time

The effect of contact time on lead ions uptake using INaHA was studied at different temperature values 25.0°C,

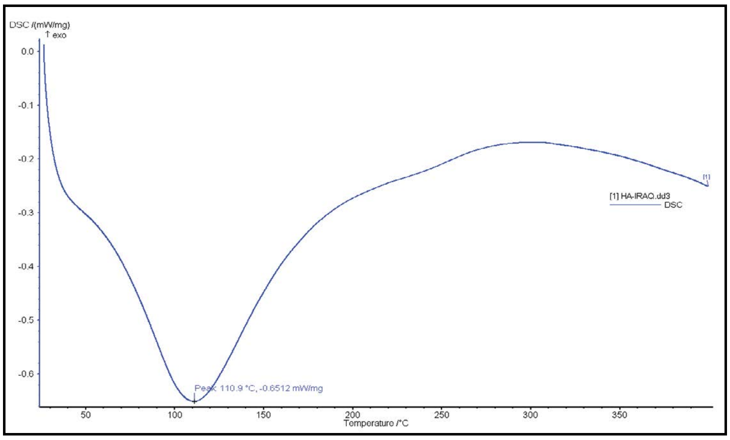

Fig. 4. Analysis of INaHA using DSC.

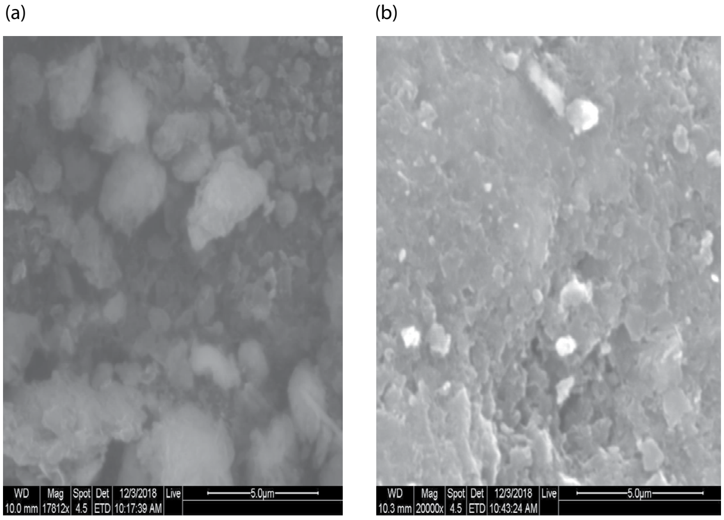

Fig. 5. SEM of (a) INaHA and (b) Pb(II)-INaHA, magnification power 17,800× and 20,000, respectively.

35.0°C and 45.0°C. Fig. 6a showed the uptake was rapid after 20 min for all temperature values that means many vacant sites were available. It was noticed that no change in the uptake after 1 h, due to the saturation of the monolayer, the full coverage was attained. The highest coverage was at 35.0°C.

### 4.2. *Effect of pH*

pH is an important factor to investigate the adsorption process because it determines the charge of the surface of the adsorbent and the degree of ionization of adsorbate in the aqueous solution. The removal of Pb(II) ions by INaHA was studied under different pH values (3.00°C, 4.00°C and 5.00°C) at 25.0°C as shown in Fig. 6b. The maximum adsorption value was noticed at pH 4.00 which about (55.15%). At pH = 5.0 the removal was (49.28%), the decreasing of removal of lead ions may be due to increasing of the negative charge for both adsorbent and adsorbate, the repulsion increases, while at pH 3 the number of hydrogen ions increased this will caused competition between positively charged ions $H^+$ and Pb(II) towards the surface of solid-phase INaHA and the removal is about (23.92%). The optimum pH was found to be 4.0 [8,19].

Table 1
Elemental analysis of INaHA

| Elements | % Found |
|---|---|
| N | 1.64 |
| C | 6.35 |
| H | 1.49 |

### 4.3. *Effect of temperature*

The effect of temperature of the removal of lead ions was studied at 25.0°C, 35.0°C and 45°C. The results indicate that the uptake increased by increasing the temperature. The % removals obtained were 43.91%, 57.89% and 45.72% respectively, the highest % removal increasing from 25.0°C

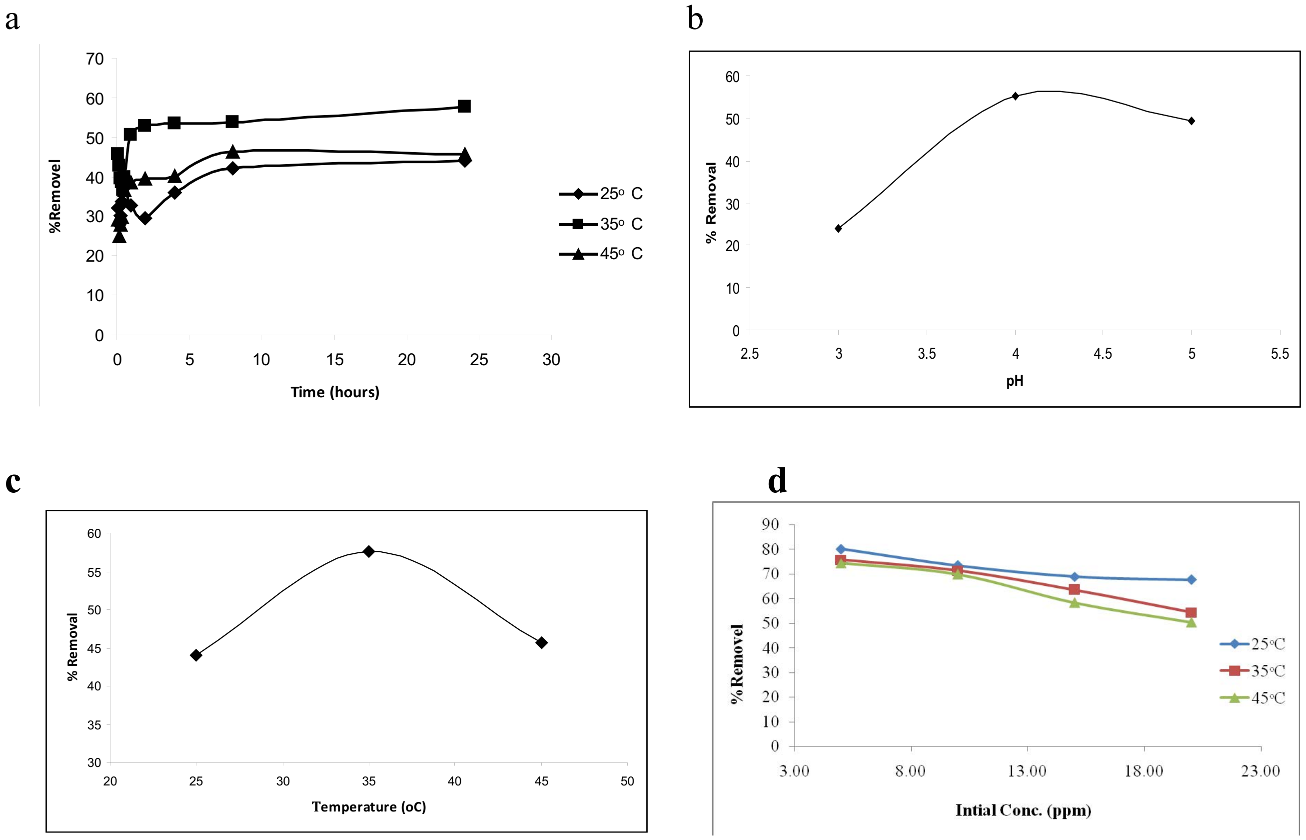

Fig. 6. Effect of different variables on % removal of Pb(II) by 20.0 mg INaHA at pH = 4.0. (a) Effect of contact time, (b) effect of pH, (c) effect of temperature, and (d) effect of initial concentration at different temperatures.

to 35.0°C; at these temperatures, the removal was an endothermic reaction but at higher temperature 45.0°C the removal decreases 45.72%. The decrease in adsorption percentage with rising temperatures may be due to desorption caused by the existing thermal energy. The temperature has a different effect on physisorption and chemisorptions. In physisorption the process is exothermic, but the reverse process "desorption" is endothermic. Increasing temperature may be caused by escaping of the species of energetic adsorbates from the surface of the solid adsorbent as shown in Fig. 6c [20].

### 4.4. *Effect of initial concentration*

The removal of lead ions was investigated at different initial concentrations in the range of 5–20 mg/L as shown in Fig. 6d the temperature values were in the range of 25°C–45°C. The figure showed that as the concentration increases the adsorption decreases, which means no more sites at the surface of the solid material for the Pb ions are available [8].

## 5. Adsorption kinetic

The adsorption kinetic of Pb(II) ions by INaHA was studied under different time (0.08, 0.17, 0.25, 0.33, 0.42, 0.5, 1.00, 2.00, 4.00, 8.00 to 24.00 h) at different temperatures (25.0°C, 35.0°C and 45.0°C) and at pH 4.00 with initial Pb(II) concentration 20 mg/L. The evaluation of this kinetic adsorption was done using two kinetic models which are pseudo-first-order and pseudo-second-order. Depending on the experimental data it is observed that this removal does not follow pseudo-first-order at different temperatures (25.0°C, 35.0°C and 45.0°C) with respect to the correlation coefficients $R^2$ which are 0.243, 0.376 and 0.336 respectively. The removal followed pseudo-second-order depending on the correlation coefficients $R^2$ which are shown in Table 2. From Table 2 we can see that the calculated experimental $q_e$, and adsorption rate constant $k_2$ of pseudo-second-order for removal of Pb(II) by INaHA somewhat increased by increasing the temperature which means that the adsorption is endothermic. From the values of %SSE [21] which are shown in Table 2, it is found that there is a good agreement between the equilibrium experimental capacity and the calculated one at all temperature values.

### 5.1. *Activation energy*

The activation energy ($E_a$) was determined from the slope of $\ln k_2$ vs. $1/T$, where $k_2$ is the rate constant of pseudo-second-order according to the following equation:

$$\text{Ln}\left(k_2\right) = \text{Ln } A - \frac{E_a}{RT} \tag{12}$$

Table 2
Pseudo-second-order model for the removal of Pb(II), 20.0 mg INaHA, pH = 4.0 and at different temperatures

| Temperature | $q_{e,\text{exp.}}$ | $k_2$ | $R^2$ | $q_{e,\text{cal.}}$ | SSE% |
|---|---|---|---|---|---|
| 25°C | 10.98 | 0.30 | 1.00 | 11.04 | 0.170 |
| 35°C | 14.39 | 0.37 | 1.00 | 14.43 | 0.088 |
| 45°C | 11.43 | 0.50 | 1.00 | 11.52 | 0.249 |

The experimental activation energy ($E_a$) of adsorption Pb(II) by INaHA is calculated using the linear regression equation from Fig. 7, it was 20.26 kJ mol$^{-1}$, The experimental activation energy value lies within the normal range of (8–22 kJ/mol), this range indicates that the mechanism of adsorption process is physisorption [22]. Also, it was reported that if the ($E_a$) lies in the range of 20–40 kJ/mol, then the rate-limiting process is the pore diffusion, our experimental ($E_a$) is within this range, then the rate-limiting process is the pore diffusion [15].

## 6. Adsorption isotherm

Different initial Pb(II) concentrations were used such as (5, 10, 15 and 20 mg/L) at different temperatures (25.0°C, 35.0°C and 45.0°C). These experiments were carried out to investigate the adsorption isotherm behavior of INaHA to remove the Pb(II) ions from aqueous solution. The results for the isotherm experiments are presented in Figs. 8a–c indicated that the adsorption behavior of INaHA belongs to *L*-type isotherm, the high affinity of the adsorbate for the adsorbent. This kind of isotherms occurs when adsorbate-solution interaction is weaker than adsorbate-adsorbent interaction [3,8]. The linearized equilibrium constants for Langmuir(III), Freundlich, and Dubinin–Radushkevich at pH = 4.0, are illustrated in Table 3.

The adsorption isotherms for Pb(II) by INaHA by Langmuir, Freundlich, and Dubinin–Radushkevich models, based on the values of correlation value $R^2 \geq 0.89$ (Table 3).

Langmuir isotherm parameters $q_m$ and $K_L$ will be used to estimate the adsorption capacity. The Langmuir model postulates that the adsorption of adsorbates on some sites with uniform binding energies and a monolayer is formed on the surface of the adsorbent. There is no interaction “physical attraction” between the adsorbed ions.

Freundlich isotherm parameters ($n$ and $K_F$) indicated that the adsorption sites were non-uniform and nonspecific in nature. The adsorption of adsorbate on sorbent is complex and it involves more than one mechanism or can describe the adsorption undergo on a heterogeneous surface. The values of $n$ represent the degree of favorability of adsorption if the value of $n \geq 1.00$ which means the adsorption of Pb(II) by INaHA was favorable as shown in Table 3. $K_F$ values slightly decrease with temperature increase for adsorption Pb(II) ions [3,8].

The Dubinin–Radushkevich isotherm model is more general than Langmuir isotherm; it rejects the homogenous surface or constant adsorption potential. Table 3 shows that the $R^2$ value is low at low temperature which means this model is not fitting the equilibrium experimental data, but $R^2$ at higher temperature values 35°C and 45°C is high so

Table 3
Langmuir, Freundlich, and Dubinin–Radushkevich isotherm parameters for remove Pb(II) by 20.0 mg INaHA adsorbent, at pH = 4.0

| *T* (°C) | Langmuir model | | | Freundlich model | | | Dubinin–Radushkevich model | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_F$ | $n$ | $R^2$ | $q_{\text{DR}}$ (mg/g) | β (mol²/kJ²) | E (kJ/mol) |
| 25.0 | 0.93 | 29.68 | 0.18 | 1.00 | 4.98 | 1.56 | 0.89 | 14.44 | 0.37 | 1.16 |
| 35.0 | 1.00 | 18.83 | 0.30 | 0.96 | 4.62 | 4.62 | 0.97 | 12.88 | 0.46 | 1.04 |
| 45.0 | 1.00 | 16.45 | 0.33 | 0.95 | 4.49 | 2.09 | 0.98 | 11.95 | 0.47 | 1.03 |

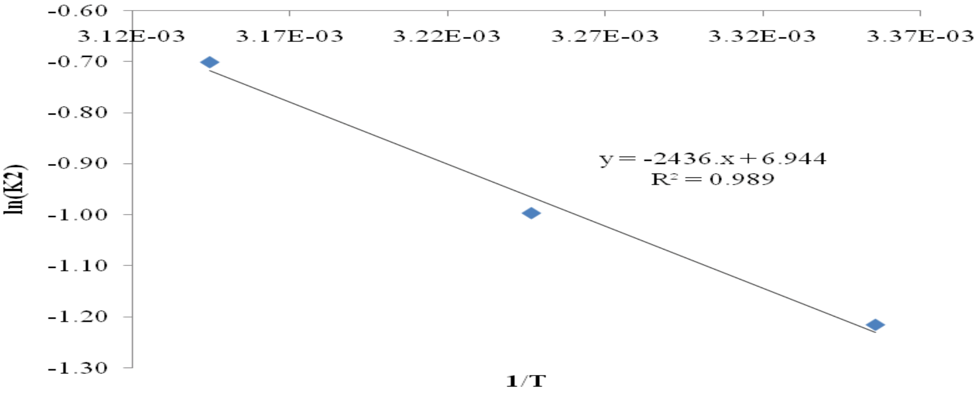

Fig. 7. Plot of ln$k_2$ against temperature for Pb(II) onto 20.0 mg INaHA at pH = 4.0.

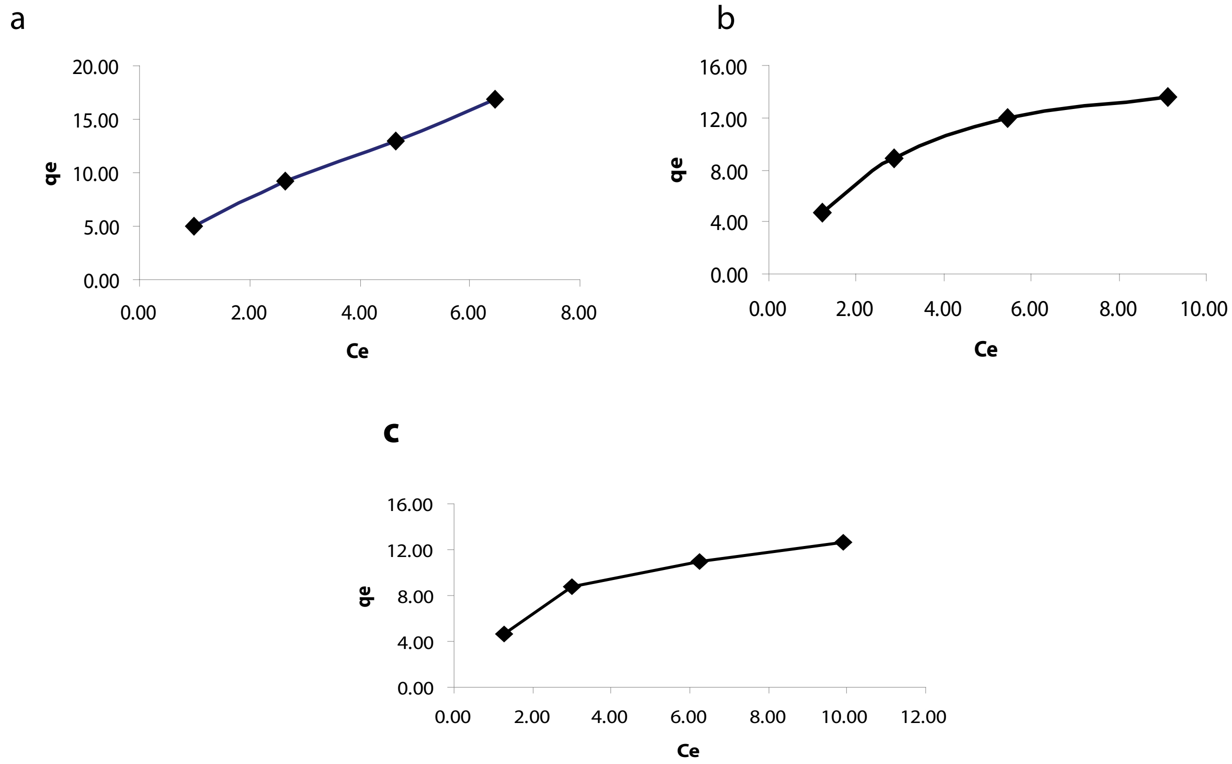

Fig. 8. *L*-adsorption isotherm of Pb(II) at pH = 4.0, by 20.0 mg INaHA at different temperatures. (a) at 25.0°C, (b) at 35.0°C, and (c) at 45.0°C.

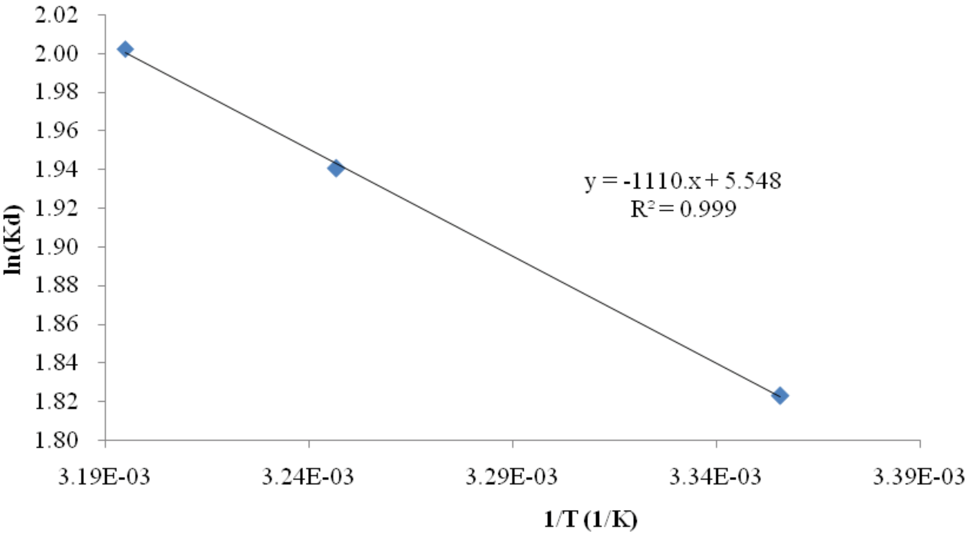

Fig. 9. Temperature dependence of ln$K_d$ for Pb(II) adsorbed by 20.0 mg INaHA at pH = 4.0.

the fitting is achieved. The calculated amount of ($E$) using the linearized equation of Dubinin–Radushkevich isotherm gives an idea about the overall mechanism of the adsorption, from Table 3 at all temperature values the experimental magnitude of the $E$ is less than 8.00 kJ/mol which indicates that physisorption process is taking place. The experimental maximum capacity values of $q_{\mathrm{DR}}$ of the Pb(II) by INaHA decreased by increasing the temperature. It was noticed that there are significant differences between values of $q_m$ which are derived from the Langmuir model and $q_{\mathrm{DR}}$ values derived from the Dubinin–Radushkevich model at all temperature values as shown in Table 3. The differences may be attributed to the definitions of $q$ in the two models, in the Langmuir model; $q_m$ represents the maximum adsorption of Pb(II) at monolayer coverage, whereas in Dubinin–Radushkevich model; $q_{DR}$ represents the maximum adsorption of Pb(II) at the total specific site of the sorbent [13].

### *6.1. Thermodynamic parameters*

Using Van't Hoff equation a plot of ln$K_d$ vs. 1/$T$ for the adsorption processes of Pb(II) ions by INaHA was illustrated in Fig. 9, from this plot thermodynamic parameters $\Delta H°$, $\Delta S°$ were calculated from the slope and the intercept respectively, and $\Delta G°$ at $T$ = 25°C at were obtained at pH = 4.0 as shown from the plot. According to Van't Hoff plot, all are classified endothermic physical case at pH = 4.0. The value of $\Delta G°$ is –4.50 kJ/mol, because $\Delta G° < 0$ the process is the favorable one, the obtained $\Delta H°$ is 9.23 kJ/mol, the positive value of $\Delta H°$ means that the nature of the removal of lead ions is endothermic, and the positive value of $\Delta S°$ 46.13 J/mol K reflects the affinity of this solid surface to the Pb ions and may be structural changes for the solid surface during its interaction with the metal ions and the whole system is less order [13].

## 7. Loading of Pb(II) on INaHA using column

The adsorption of Pb(II) by INaHA using continuous column experiments was investigated using 1,000 mg/L initial Pb(II) concentration at pH = 4.0°C, 25.0°C and flow rate of 0.56 mL/min. The %uptake of lead ions was found to be 93.91.

### *7.1. Desorption of Pb(II) on INaHA studies*

The %cumulative recoveries were calculated for loaded lead ions by the column that is described in section 9.1 using 1 M $HNO_3$ and 1.0 M HCl as eluting agents with a flow rate of elution 0.56 mL/min and found to be 24.06 and 5.09 respectively. This is may be due to the chemical differences between $Cl^-$ and $NO_3^-$ as ligands, the lead ions can make a stable complex with $NO_3^-$ anion than $Cl^-$ anions [23].

## 8. Conclusions

This study found that INaHA which is a low-cost adsorbent has high efficiency in the removal of lead ions from aqueous solutions. The mechanism of adsorption was studied by applying kinetic and isotherm equilibrium models. The interaction between lead ions and the INaHA was done under different conditions like contact time, temperature, initial concentration of lead ions and pH. The batch experiments showed that the optimum equilibrium uptake time was at 1 h, at 35°C and the optimum pH value was 4. The pseudo-second-order kinetic model fitted well for this adsorption, the activation energy $E_a$) was estimated (20.26 kJ/mol) using $k_2$, which means the physisorption process was obtained and the rate-limiting process is the pore diffusion. Langmuir isotherm model found to be the best model that fits this adsorption because it has the highest ($R^2$) among the other isotherms. The calculated $E$ from the Dubinin–Radushkevich isotherm was less than 8 kJ/mol, the physisorption process was attained. The adsorption process is highly favorable because of the negative values of $\Delta G°$, with endothermic nature because of the positive value of $\Delta H°$, the entropy-driven force ($\Delta S°$) has a positive value. The %uptake of lead using the adsorption column experiment was found to be 93.91%. The recovery of desorbed Pb(II) using 1 M $HNO_3$ is higher than using 1 M HCl.

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