



## **Conversion of Natural Bentonite into Effective Adsorbents for Removing of Pb<sup>2+</sup> Ions from Wastewater**

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### **Abstract**

Adsorption is an effective techniques using for removing heavy metal contamination from wastewater. In order to study the capacities of both natural and modified bentonite (synthetic analcime zeolite (ANA)) samples to remove lead ions, batch adsorption experiments of Pb<sup>2+</sup> were conducted under various conditions. Most essential parameters such as initial solution pH, adsorbent mass and contact time were studied. Bentonite clay was activated and went through various thermal and chemical processes. The result from this route shows that zeolite ANA crystals with regular icositetrahedron have been successfully synthesised. The efficiency of both natural bentonite and zeolite ANA converted from natural bentonite and their ability for the reducing of Pb<sup>2+</sup> ions from industrial wastewaters have investigated and the results show that heavy metal removal was enhanced with increased initial solution pH, greater mass of absorbent and fast in the in the first hour. The uptake of Pb<sup>2+</sup> ions from solution by synthetic zeolite type ANA was improved compared to natural bentonite.

### **Introduction**

Aquatic system and water quality have disturbed due to increasing in population growth, industrialization mankind, urbanization and economic development. Discharges of extraordinary quantity of waste including toxic heavy metal into aquatic bodies has become major problems and causes damage to the environment. Heavy metal contamination has impact on the human health, animal health and ecology due to their toxicity, bioaccumulation and biosorption [1- 4]. Pb<sup>2+</sup> is a heavy material with a high density occurs naturally in the earth's crust and known as a toxic metal at low concentration that is affecting human, animal, and environmental ecosystem [5] and [6]. Pb<sup>2+</sup> can enter aquatic system from natural sources include the forest fires, volcanoes and weathering of soil [5] [7] and [8]. However, human activities are another sources of Pb<sup>2+</sup> such as discharge of ammunition, industrial processes, smelters, military activities, transportation, waste management, various processes in metal production, manufacturing, household uses, lead paint, batteries, cosmetics and sewage treatment plant [5-7] and [9-10]. Bentonite is aluminium phyllosilicate clay created from the alteration of volcanic ash which is mainly composed of clay minerals such as montmorillonite, hectorite, beidelite, saponite and nontronite. Bentonite consists of two tetrahedral sheets and an octahedral sheet [11] and [12]. The smectite group have interlayer space characterise which is easily accessible to water [13]. Bentonite can be used as adsorbents in sanitisation processes especially removal of heavy metals ions due to its high adsorption capacity [11- 17]. Bentonite also have excellent cation exchange capacity which contains hydrated cations such as K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in their interlayer surfaces [11] and [12]. Cations can be easily exchanged by heavy metals ions because the charge is so weak [12] and [18]. Bentonite have

some other important uses include foundry, cat litter, pelletizing, construction, oil and water well drilling, animal feed supplement, paints and catalyst [19]. Synthetic zeolites ANA have excellent adsorption capacities to purify wastewater therefore, in the present study, the synthetic zeolite type ANA was produced after activation of bentonite clay and treated with various thermal and chemical applications via hydrothermal synthesis technique. The clay mineral used in the present investigation collected from Injana Formation (20 cm to 100 cm thickness) near Goma-zard village at Garmain site in the north east of Iraq (Figure: 1). For the purpose of the wastewater purification and removal of toxic  $Pb^{2+}$  metals from wastewaters, adsorption is one of the most effective and efficient technique. The success of the purification process mainly depends on the physicochemical properties and quality of an effective adsorbent in both natural and modified form [20- 24]. In this research, both natural bentonite and zeolite ANA (converted from bentonite clay minerals) have used as low cost and effective adsorbent for the removal of  $Pb^{2+}$  metals from synthetic industrial wastewater.



Figure-1: Location site and sampling areas where bentonite clay (red circle) were sampled.

## Materials and methods

### A. Adsorbents Preparation

The synthesis of zeolite ANA materials by hydrothermal transformation of bentonite using a conventional hydrothermal method was investigated conforming with European Standards. The bentonite samples were passing through 60  $\mu m$  sieve. Bentonite is characterized according to EN 197-1 [25]. This standard specifies that the reactive  $SiO_2$  content shall be not less than 25% by weight. The raw material samples were used as received without any modification from their natural state. Samples were washed with deionised water to remove unwanted dust from their surfaces before use and then dried at room temperature for about 8 hours as described by Nones *et al.* (2015) [26]. The clay used as a sources of silicon and aluminum was used to the synthesis zeolite ANA with formula of  $(Na_{16} (Al_{16}Si_{32}O_{96}) 16H_2O)$ . Bentonite clay powder ( $< 100 \mu m$ ) was calcined at temperature of 600°C for 3 hours to transform bentonite to metabentonite with fix increment 150°C. The produced metabentonite mixed up with three mole of sodium hydroxide solution (3M NaOH) using stainless steel autoclaves with a Teflon liner heated to 200 °C in an oven for 4 hours in order to insert the sodium ion into the metabentonite structure. The acid treated bentonite clay was washed with deionised water

three times to remove the excess unreacted NaOH. It was then filtered and dried in an oven at 100 °C overnight as shown in (Figure: 2) [27].

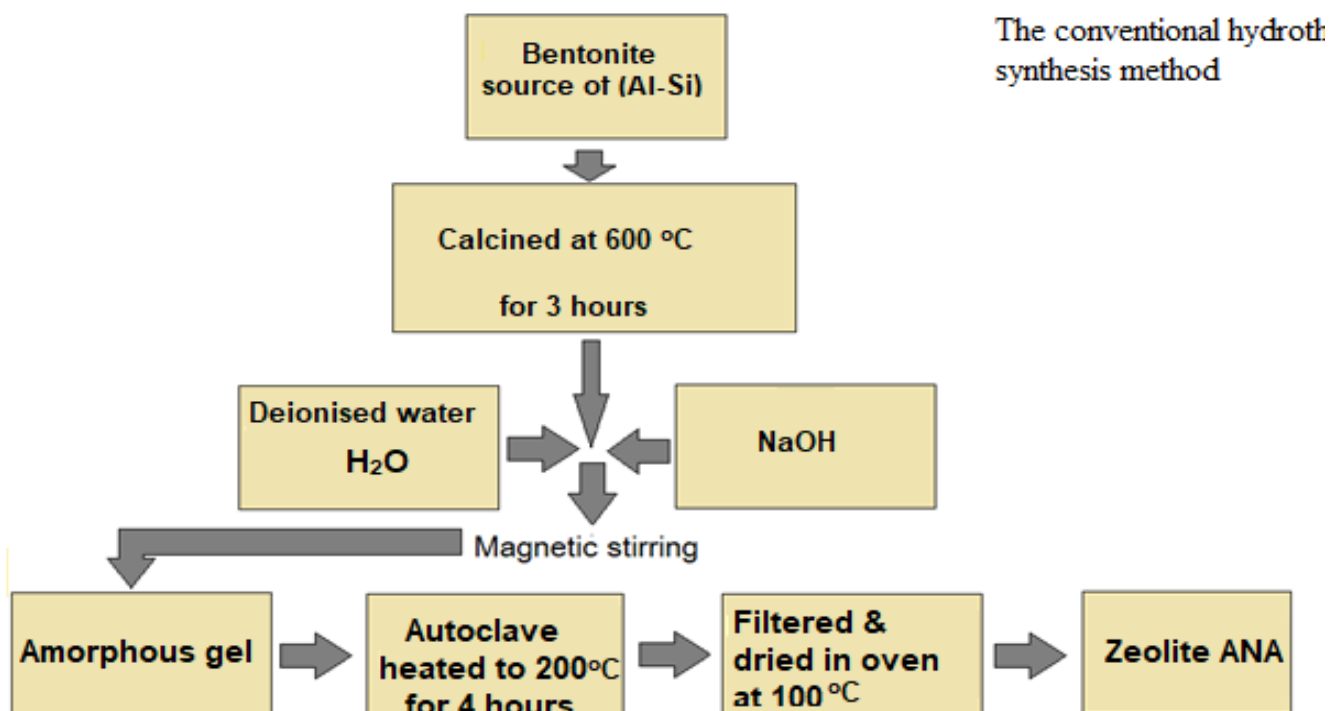


Figure-2: Flow chart showing the transform of the bentonite raw materials into zeolite ANA using conventional hydrothermal synthesis method [27].

### ***B. Adsorbent Characterization***

In this study different analytical techniques were used to study starting materials and synthesis product samples. This used analytical techniques including: Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X – Ray Diffraction (XRD), X – Ray Fluorescence (XRF) and Fourier Transform Infrared (FT-IR) and Inductively Coupled Plasma-Optical Emission Spectrometers (ICP-OES). Scanning Electron Microscope (SEM) type ZEISS EVO50 (Wolverhampton, UK) was used to diagnose surface morphology, topography of bentonite samples before and after modification under the following analytical conditions: EHT = 20.00 kV and 20.00 kV, Signal A = VPSE, WD = 8.5mm at different magnifications. Elemental analysis and chemical composition of four samples was obtained using both PANalytical X – Ray Fluorescence (XRF) spectrometer (Wolverhampton, UK) and Energy Dispersive Spectroscopy (EDS) (Wolverhampton, UK). Phase identification of natural bentonite and zeolite ANA materials were carried out using Empyrean, PANalytical X-ray diffractometer EMPYREAN system (Wolverhampton, UK), Cu-K $\alpha$  radiation generated at 40 kV and 40 mA, Divergence Slit Size 0.2500° with Specimen Length 10mm . The procedure was carried out and data were collected in the range from 5° to 79.9° 2 $\theta$  with a measuring time of 8.67 sec per step at measurement at temperature 25°C.

### C. Adsorbate Preparation

Synthetic solutions of  $Pb^{2+}$  prepared by dissolving 0.33 g of acetate trihydrate ( $C_4H_{12}O_7Pb$ ) in 150 mL glass vessel containing 100 ml of deionised water. The  $Pb^{2+}$  ion concentrations in the solution were determined using Agilent 5100 ICP-OES at University of Wolverhampton from United Kingdom. The standard solutions for metal analysis using the ICP-OES were prepared from standard metal solutions to determine the amount of  $Pb^{2+}$  ion concentrations which present in the solutions before and after the exchange. To examine the reproducibility of the results, the procedure duplicated three times. The mean value was selected for all obtained data. Samples were filtered before being analysed to remove any contained solids using Whatman filter papers. 2% nitric acid was used to dilute all samples, standards and prepare a blank solution. Samples were diluted to a concentration of acid into the specified range of less than 5%. The sample volume was 10ml in a 15ml centrifuge vial then analysed. The pH was adjusted to 2, 4, and  $6 \pm 0.1$  by adding hydrochloric acid (HCl) or bases sodium hydroxide (NaOH) using a pH meter (Microprocessor pH Meter – pH 211-HANNA instruments).

### D. Batch Adsorption Studies

Batch adsorption technique for removal of  $Pb^{2+}$  from synthetic metal solutions was used under various conditions. The data obtained from the batch adsorption tests were used to determine the removal capacity,  $q_e$  (mg/g) of the different adsorbents using the following equation:

$$q_e = (C_o - C_e) \times V / m \quad (1)$$

The percentage removal of  $Pb^{2+}$  ions from solution was also determined using the equation below:

$$\text{Percentage Adsorbed (\% removal)} \quad q_e = \{(C_o - C_e) \times 100\} / C_o \quad (2)$$

Where,

$q_e$  amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)

$C_o$  and  $C_e$  are the initial and final metal ion concentrations in solution (mg/l) respectively,  $V$  is the solution volume (l) and  $m$  is the weight of the zeolite used (g) [28].

## Results and discussion

### A. Sample characterisation

Photomicrograph were obtained from SEM analysis shows natural bentonite crystal structure is not well defined and they casually oriented crystallites (**Figure: 3**). As represented in (**Figure: 4**), after thermal and chemical treatment applied on natural bentonite well-formed typical trapezohedron shaped crystals have appeared, which is moral indicate of zeolite ANA formation.

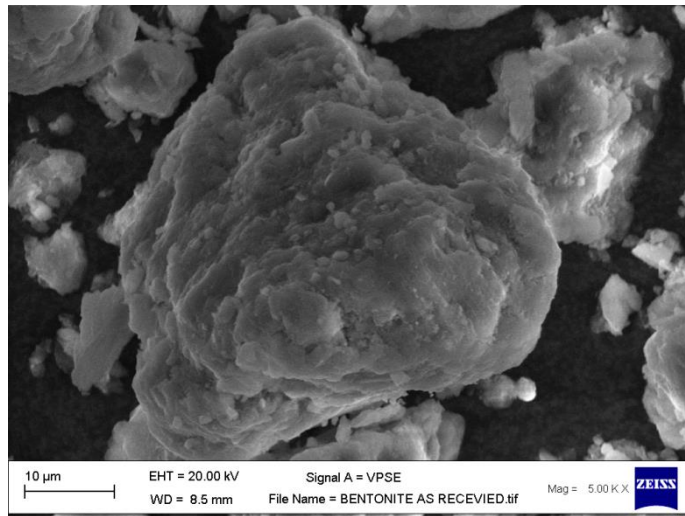


Figure-3: SEM photomicrograph shows the crystalline nature of bentonite.

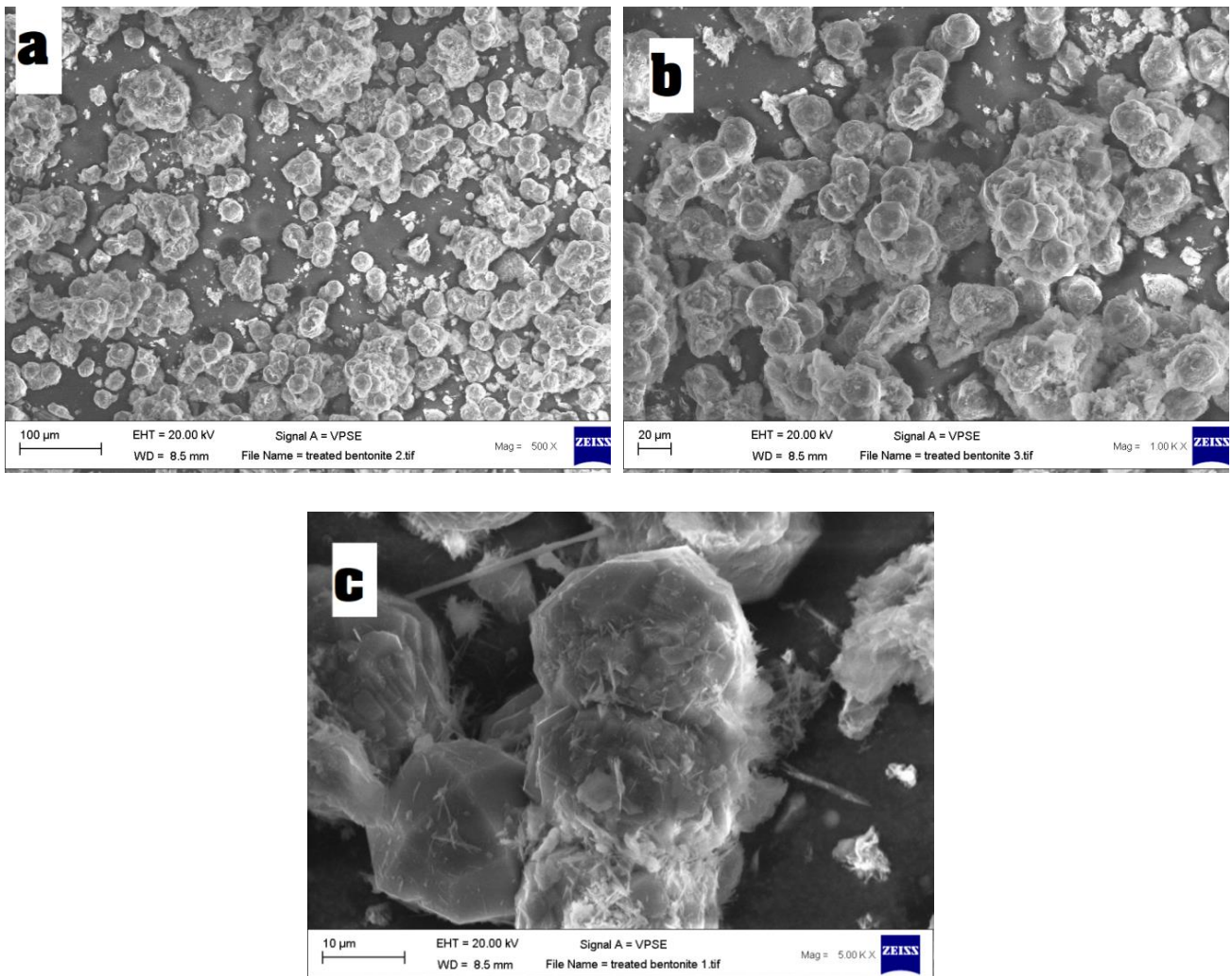


Figure-4: SEM microstructure showing the oriented crystallites of zeolite ANA at a magnification of (a) 500x, (b) 1000x (c) 5000x.

The result from both PANalytical X – Ray Fluorescence (XRF) spectrometer and Energy Dispersive Spectroscopy (EDS) were showing that the main chemical composition of bentonite and the existence of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the raw bentonite as an aluminosilicate source used in this study are presented in ( **Table:1**).

Table-1: The chemical composition (wt. %) of the bentonite using XRF and EDS analytical techniques.

<i>Element</i>	<i>SiO<sub>2</sub>%</i>	<i>Al<sub>2</sub>O<sub>3</sub>%</i>	<i>Fe<sub>2</sub>O<sub>3</sub>%</i>	<i>CaO%</i>	<i>Na<sub>2</sub>O%</i>	<i>MgO%</i>	<i>K<sub>2</sub>O%</i>	<i>TiO<sub>2</sub>%</i>
<i>XRF</i>	40.08	14.938	15.30	24.418	2.043	2.5	1.276	0.364
<i>EDS</i>	42.45	13.40	15.22	24.96	1.04	1.29	1.65	1.22

The result from Empyrean, PANalytical X-ray diffractometer EMPYREAN system (Wolverhampton, UK) have indicated that the raw material contained calcite, quartz and montmorillonite (**Figure: 5**).

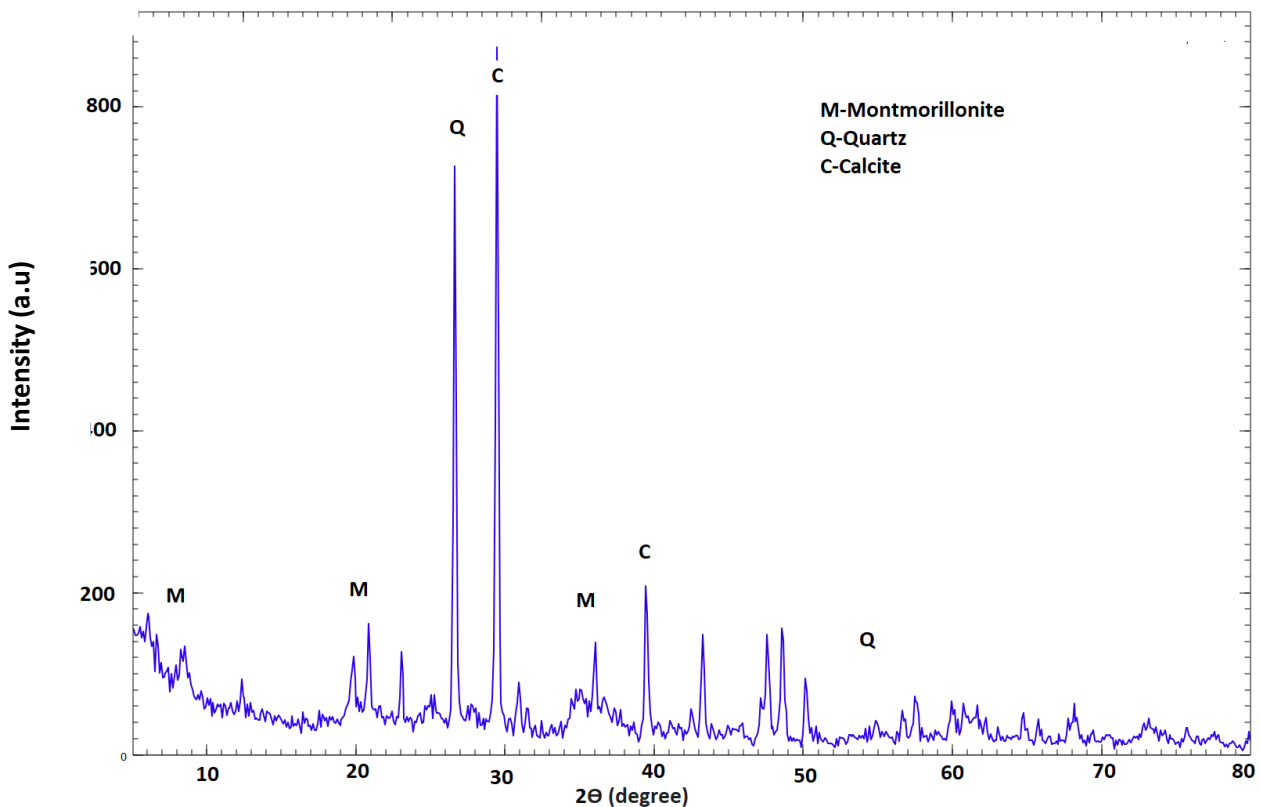


Figure-5: Graphic analysis shows XRD pattern of the natural bentonite.

The X-ray diffraction (XRD) patterns of zeolite type ANA are represented in (**Figure: 6**). Zeolite ANA materials contained quartz, analcime, cancrisilite as a majority. These patterns for ANA zeolite show a novel

crystalline phase with reflections in the  $2\theta = 16, 26, 30, 32$  and  $33$  the characteristic of analcime zeolite [29-31].

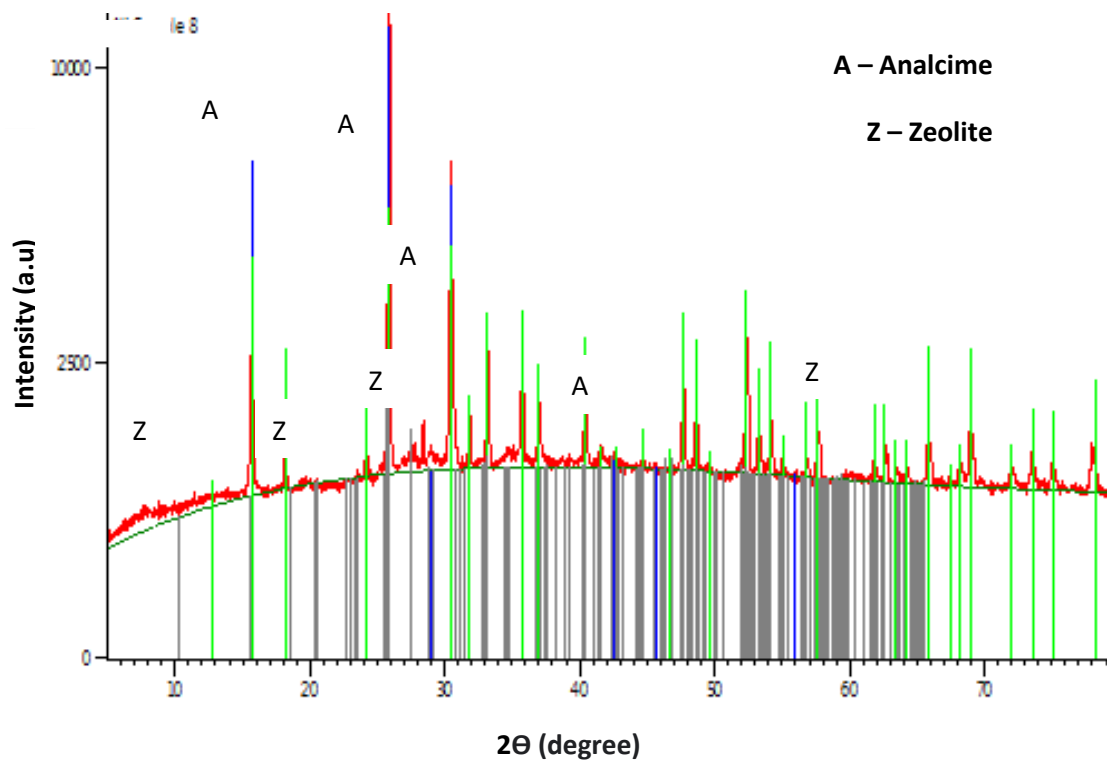


Figure-6: Graphic analysis shows XRD pattern of zeolite ANA.

## B. Adsorption Studies

### Effects of contact time

Both natural bentonite and synthetic zeolite have displayed similar reaction for heavy metal removal under all applied conditions. The result shows that generally the removal of  $Pb^{2+}$  ions mostly fast and occurred in the in the first hour this is an agreement with Statillan-Medrano and Jurinak, 1975 [32] (Figures: 7, 8, 9 and 10); While there was slow improvement for  $Pb^{2+}$  metal removal in the later stages. The metal removal efficiency of synthetic zeolite ANA in the first hour with all solutions pH2, pH4 and pH6 values were ( 75.5%, 90.5% and 80.5%) achieved ( 72.5 %, 90.5 % and 94.5 %) in the first hour when 2 g , 4 g and 6 g of synthetic zeolite ANA was used with solution (Figure: 7) and (Figure: 9). The metal removal efficiency of untreated natural bentonite in the first hour with all solutions pH2, pH4 and pH6 values were ( 71.5%, 85.5% and 78.5%) and achieved (70.5 %, 85.5 % and 87.5 %) in the first hour when 2 g , 4 g and 6 g of natural bentonite was used with solution Fig.8 and Fig 10. This indicates that more sites were available at the first stage and strong competition among the heavy metals ions happening in the early phase. Adsorption sites were saturating with increasing contacting time until equilibrium was totally reached [33; 34]. The results indicate that  $Fe_2O_3$  are a main components of bentonite are present in the structure. Therefore, the  $Fe_2O_3$  are efficient adsorbents for the removal of  $Pb^{2+}$  ions, mainly because of a synergetic effect provided by the metal oxides and high surface area which improve the efficiency of metal removal [35].

### Effect of initial solution pH

Different values of pH 2, 4 and  $6 \pm 0.1$  were analysed by adding 4g of adsorbent to 150 mL glass vessel containing 100 mL of the solution. The mixture was agitated for 360 minutes while every 60 minutes 15 mL of the filtered solution were taken for metal ion concentration analyses. The particle size of the zeolite samples used was 250  $\mu\text{m}$ . The agitation speed was 150 rpm at room temperature. This experiment was initially done using fixed metal concentrations of  $\text{Pb}^{2+}$ . The results show that initial solution pH on heavy metal removal from industrial wastewater is critical parameter. Any increase in initial solution pH value led to increase in ion exchange process. The highest  $\text{Pb}^{2+}$  removal from solution were obtained at pH with values of 4 followed by 6 respectively. This result confirmed the previous conclusions which have discusses that the optimum value for ion exchange process can be achieved between pH4 and pH6. Initial solution pH values below pH 4 ( $< 4$ ) and above pH7 ( $> 7$ ) can cause damage the adsorbent structure and reduces removal rate of heavy metal [36- 41]. It was observed that both natural and modified bentonite shows different metal removal rate under the applied condition. The metal removal efficiency of synthetic zeolite ANA are generally higher with all solutions pH2, pH4 and pH6 values (81.4%, 96.4% and 87.4%) compared to the untreated natural bentonite which have recorded lower metal removal efficiency from solution ( 80.4%, 91.4% and 84.4%) (**Figure: 7**) and (**Figure: 8**). This may refer to the improvement made in the zeolite ANA structure chambers and canals, reaction to applied thermal and chemical treatment. Moreover, the well-formed unique typical trapezohedron shaped crystals of zeolite ANA was formed.

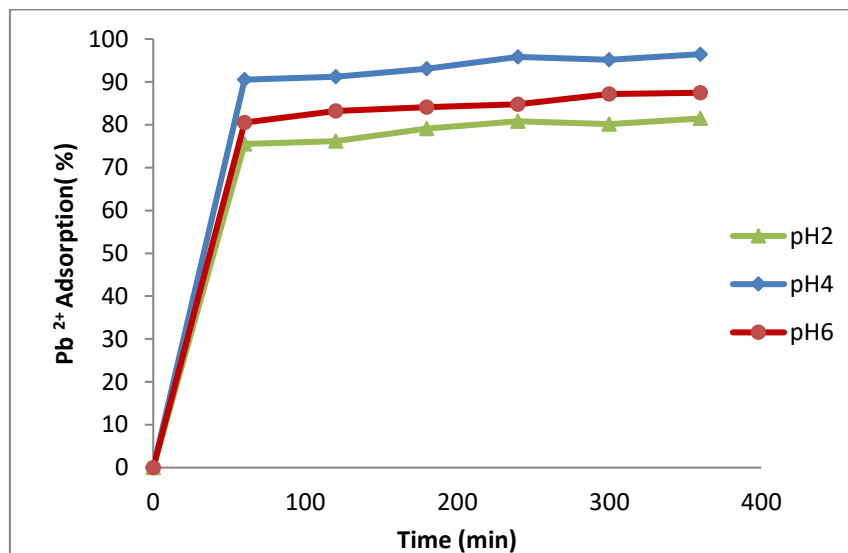


Figure-7: Effect of initial solution pH on lead removal process using synthetic zeolite ANA.

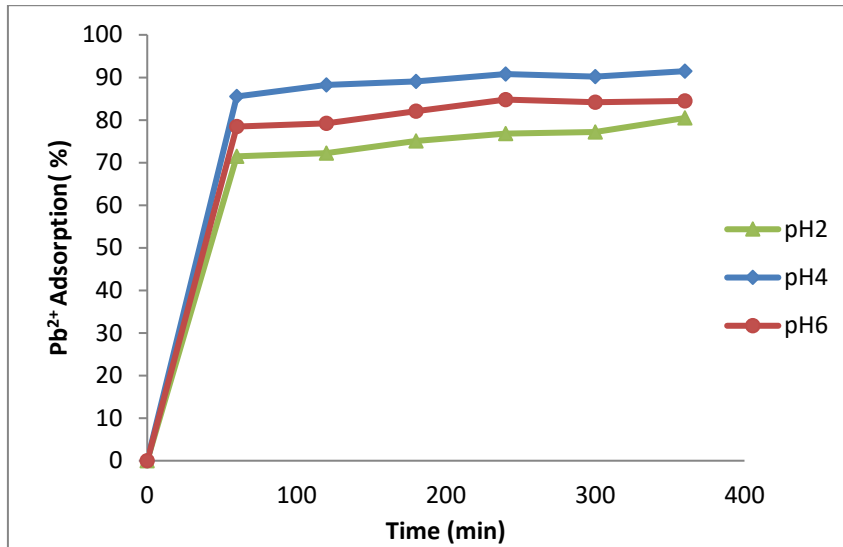


Figure-8: Effect of initial solution pH on lead removal process using natural bentonite.

### ***Effect of adsorbent mass***

The effect of the dose of adsorbent mass on the adsorption of  $Pb^{2+}$  from industrial wastewater was investigated using various masses of the adsorbent (2 g, 4 g and 6 g). Adsorbent masses of 2 g, 4 g and 6 g of adsorbent were added to 150 mL glass vessel containing 100 mL of the solution. The mixture was agitated for 360 minutes while every 60 minutes 15 mL of the filtered solution were taken for metal ion concentration analyses. The particle size of the zeolite samples used was 250  $\mu m$ . The agitation speed was 150 rpm at room temperature with fixed pH  $4 \pm 0.1$ . This experiment was initially done using fixed metal concentrations of  $Pb^{2+}$ . The results in Figs.9 and 10, show that the removal rate of  $Pb^{2+}$  metal ions increases with increasing adsorbent mass [42]. The increased adsorbent dose resulted in an increased number of active sorption sites and surface area available for the  $Pb^{2+}$  adsorption [43] and [44].

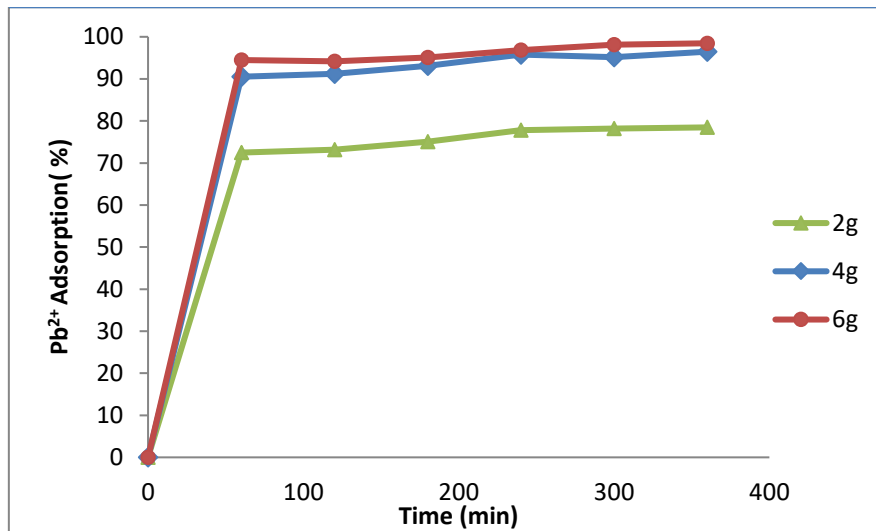


Figure-9: Effect of adsorbent mass on lead removal process using synthetic zeolite ANA.

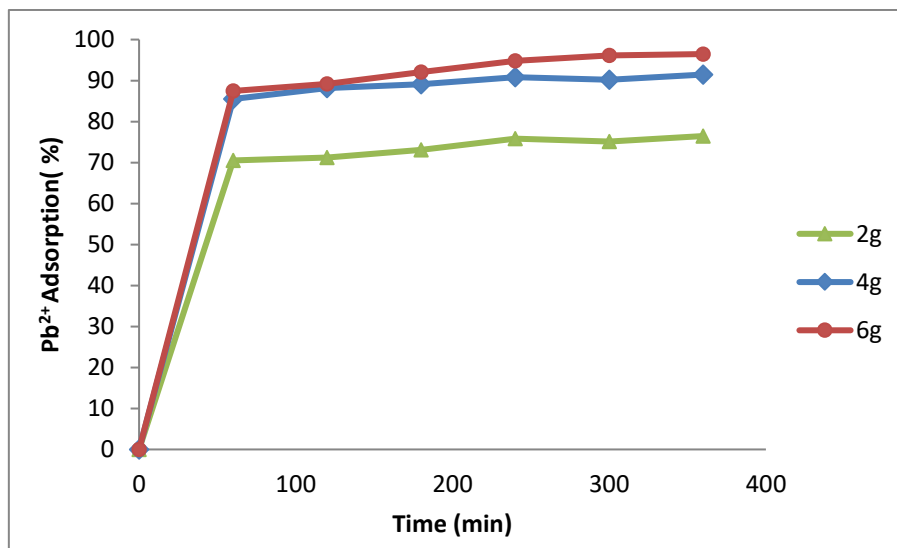


Figure-10: Effect of adsorbent mass on lead removal process using natural bentonite.

It was notice that the highest removal ratio of  $Pb^{2+}$  ions was achieved 98.4 %, 96.5 % and 78.4 % when 6 g , 4 g and 2 g of synthetic zeolite ANA was used with solution pH4 (**Figure: 9**). While the percentage  $Pb^{2+}$  metal removal using natural bentonite reached lower rate of 96.5 %, 91.4 % and 76.4 % with 6 g, 4 g and 2 g adsorbent mass with solution pH4 (**Figure: 10**).

## Conclusions

The following conclusions could be made based on the experimental results:

- This study demonstrated the applicability of Iraqi clay minerals as a sustainable adsorbent for the removal of  $Pb^{2+}$  from wastewater.

- The synthetic zeolite type ANA was successfully achieved and can be used as a sustainable, low cost, effective and environmentally friendly adsorbent for purifying industrial wastewaters.
- Both natural and synthesized zeolite ANA has good adsorption removal capacities for heavy metals from wastewater, while synthesized zeolite ANA shows little improvement this may be due to application of pre-treatment.
- The results of the batch experiments indicated that the adsorption process was affected by contact time, adsorbent dose and adsorbent initial solution pH. Thus the contact time, adsorbent initial solution pH and adsorbent mass in the case of batch experiments are usually the most influential parameters.

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