

## **SYNTHESIS AND CHARACTERIZATION OF ACTIVATED BENTONITE / Fe<sub>3</sub>O<sub>4</sub> COMPOSITE FOR DECONTAMINATING HEAVY METALS FROM WASTEWATER**

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### **ABSTRACT**

In this work, modification of calcium bentonite was carried out by three chemical methods converted calcium bentonite to sodium bentonite then acid activation by sulfuric acid (3M) and finally combined activated bentonite to Fe<sub>3</sub>O<sub>4</sub> nano composite was prepared by chemical co-precipitation method. The prepared samples were characterized by Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Fourier Transformation Infrared (FTIR) spectroscopy, (BET) surface area, scanning electron microscope (SEM) and High resolution transmission electron microscope (TEM). The characterization study demonstrated a substantial improvement in several adsorptive parameters of modified bentonite, like surface area, surface morphology, and active sites where increase in surface area of the modified bentonite was recorded as 25.259 m<sup>2</sup>/g, 31.86 m<sup>2</sup>/g, 62.194 m<sup>2</sup>/g and 107.998 m<sup>2</sup>/g by Ca- bentonite, Na-bentonite, acid activated bentonite and nano composite bentonite, respectively. Effects of pH, initial concentration, mass of the adsorbent and the contact time on the adsorption capacity were studied. The results showed that the best pH for adsorption was at pH=6, optimum dose of modified bentonite at 0.5 g and contact time at 15 min. The maximum removal for heavy metals were obtained by bentonite nano

composite as (98.4 %) for chromium, (98.8 %) for arsenic, (91.3 %) for selenium, (90.8 %) for molybdenum, (79.1 %) for antimony, (75.3 %) for barium .

**Key words:** Adsorption, Heavy metals, Activated bentonite / Fe<sub>3</sub>O<sub>4</sub> nano composite.

## INTRODUCTION

Industrial wastewater largely possess organic and inorganic materials such as dyes, phenol compounds, aromatic compounds and heavy metals (Fu *et al.*, 2014). Heavy metals constitute one of the most dangerous groups because of their persistent nature, toxicity and tendency to accumulate in organisms and are non biodegradable (Walker *et al.*, 2016). These consequences are reduced by limiting the variety and concentration of heavy metals that present in the industrial and discharged wastewater (Hieu *et al.*, 2016). Various waste water remediation technologies such as membrane filtration, flocculation, adsorption, precipitation, electrolytic removal, ion exchange, reduction and reverse osmosis have been reported, However these technologies have various limitations i.e., costly equipment, high operational cost, high maintenance cost (Adeleye *et al.*, 2016).

Bentonite clays are acquiring its prominence as low-cost adsorbents over the last decades due to their local and abundant availability and the capability to undergo modification to enhance the surface area, adsorption capacity and range of applicability (Cai *et al.*, 2018). Bentonite is an absorbent aluminium phyllosilicate clay consisting mostly of montmorillonite (Okoye, 2016).

The adsorption capacity of natural bentonite is low due to its small surface area. This led to the need for research and development in the field of modification of clay surfaces to enhance their adsorptive properties (Uddin, 2017a). A number of physical and chemical methods have been investigated to modify the bentonite, including heat treatment, acid activation, treating the cationic surfactants and polymer modification (Kausar *et al.*, 2018).

Acid activation is a common chemical modification of clays, usually bentonite, with a hot solution of a mineral acid (typically HCl or H<sub>2</sub>SO<sub>4</sub>), and it is used for both scientific and industrial purposes. The aim is to obtain partly dissolved material of increased specific surface area, porosity and surface acidity (Uddin, 2017a).

Nanotechnology has been mentioned as one of the most advanced method for wastewater treatment. It can be classified depend on the nano-materials nature into three main categories: nano-adsorbents, nano-catalysts and nano-membranes (Machado *et al.*, 2019).

Among the available adsorbents, nanosized metal oxides, including nano sized ferric oxides, manganese oxides, aluminium oxides, titanium oxides, magnesium oxides and cerium oxides, are classified as the promising ones for heavy metals removal from aqueous systems (Nejad *et al.*, 2018).

Iron and its oxides are widely used in the environmental treatment applications. Iron is a ferromagnetic material; at room temperature it has a high magnetic capability. It can be easily magnetized in presence of a weak magnetic field. Moreover, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> show super paramagnetic

behaviour. Iron-based magnetic materials are very cheap and can be easily synthesized (Cardoso *et al.*, 2018).

## MATERIAL AND METHODS

**Material:** The Egyptian clay mineral, calcium bentonite, used in the study was obtained from Red Sea for Phosphate Company. This calcium bentonite was converted chemically to sodium bentonite (Uddin, 2017b).

**Chemicals:** All the reagents used in this study were of analytical grade obtained from sigma aldrich and were used without further purification, a stock solution containing 500 mg/L of (arsenic (III) standard for ICP as (III) in hydrochloric acid - selenium standard for ICP Se in nitric acid - chromium standard for ICP (Cr) in nitric acid prepared with Cr (NO<sub>3</sub>)<sub>3</sub>. 9H<sub>2</sub>O - barium standard for ICP (Ba) in nitric acid - antimony standard for ICP (Sb) in nitric acid - molybdenum standard for ICP (Mo) in hydrochloric acid) was dissolved appropriate in 1 liter distilled water. Sodium chloride (NaCl) 99.5%, nitric acid silver salt (AgNO<sub>3</sub>) 99 %, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 95-97 %, iron(III) chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O) 98 % and ferrous sulfate (FeSO<sub>4</sub>.7H<sub>2</sub>O) 99 %, sodium hydroxide (NaOH) 98 %, nitric acid (HNO<sub>3</sub>) 99 %. The stock solution was used to prepare dilute solutions of different concentrations (100 µg/ L - 500 µg/ L -100 mg/L - 500 mg/L), the pH adjusted at 7 by using 0.1M HNO<sub>3</sub> and 0.1M NaOH.

**Preparation of bentonite :** Calcium bentonite washed several times with distilled water then enriched with 1 M NaCl solution and left 24 hours to

make exchange then filtered and washed several times with distilled water until it is chloride free (checked by  $\text{AgNO}_3$ ) (Zhang *et al.*, 2013). Activation of Na- bentonite was conducted by adding 50 g of the bentonite to 500 ml of sulfuric acid solution (3M) and refluxing at  $130^\circ\text{C}$  under atmospheric pressure in a round bottomed flask equipped with a reflux condenser for 4 hours. The resulting bentonite suspension was then rapidly quenched by adding 500 ml ice cold water, then washed several times with de-ionized water. The washing was continued until the supernatant reached to a pH of 7 then dried in oven at  $100^\circ\text{C}$  for 6h.

Synthesis of bentonite / $\text{Fe}_3\text{O}_4$  magnetic nano composite: was prepared by dissolving 19.5 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 17.832 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 1000 ml of deionized water. The solution was heated to  $70^\circ\text{C}$  while stirring with a magnetic stirrer, the acid bentonite was mixed with the solution, and 250 mL of 5 M NaOH were added dropwise to precipitate the iron hydroxide. The bentonite / $\text{Fe}(\text{OH})_3$  was heated to  $900^\circ\text{C}$ .

**Characterization of modified bentonite:** The effect of modification on the surface properties of bentonite was analyzed using Brannuer-Emmet-Teller (BET) method, fourier transform infra red spectroscopy (FTIR), scanning electron microscopy (SEM) and high resolution transmission electron microscope (TEM).

**Batch adsorption experiments:** were conducted using 0.5 g of activated bentonite nano composite in 100 ml of solutions containing heavy metal ions in 250 ml glasses (Zhu *et al.*, 2011).

Adsorption of heavy metals on modified bentonite was carried out in a batch system. The effect of various operational parameters such as contact time, initial concentration, and pH has been adjusted in room temperature and the concentration in the supernatant was determined by the agilent 7700x ICP-MS.

**Effect of pH:** The effect of pH on the adsorption was studied by agitated 100 ml of heavy metal solution ( 100 mg/L) with (0.1) g of bentonite / Fe<sub>3</sub>O<sub>4</sub> nano composite at different PH values (3-8) with shaking for ( 90 min ) at a constant speed of (150) rpm at room temperature .

**Effect of the dose:** The effect of mass of bentonite / Fe<sub>3</sub>O<sub>4</sub> nano composite on the adsorption was studied by using 100 ml of heavy metal solution ( 100 mg/L at pH 6) onto (0.1 - 0.6) g of modified bentonite with shaking for ( 90 min ) at a constant speed of (150) rpm at room temperature .

**Effect of the contact time:** The effect of contact time of bentonite / Fe<sub>3</sub>O<sub>4</sub> nano composite on the adsorption was studied by using (0.5) g modified bentonite onto 100 ml of heavy metal solution ( 100 mg/L at pH 6) with shaking for (1- 90 min ) at a constant speed of (150) rpm at room temperature

**Effect of the initial concentration:** The effect of initial concentration of bentonite / Fe<sub>3</sub>O<sub>4</sub> nano composite on the adsorption was studied by using (0.5) g modified bentonite onto 100 ml of heavy metal solution at different concentration (100 µg/L – 500 µg/L – 100 mg/L- 500 mg/L) at pH 6 with shaking for (15 min) at a constant speed of (150) rpm at room temperature.

**Capacity of modified bentonite:** The amount of heavy metals adsorbed on the surface of adsorbent at time( t ) can be estimated from the mass balance equation (Liu *et al.*, 2014).

$$q_e = \frac{(C_0 - C_t) V}{m}$$

Where  $q_e$  is the amount of heavy metals adsorbed per unit mass of adsorbent (mg/g),  $(C_0)$  is the initial concentration of heavy metals (mg/L),  $(C_t)$  is the equilibrium concentration (mg/L),  $(V)$  is the volume of metals solution (L) and  $m$  is the mass of bentonite (g). The final concentration has been calculated in the previous section and the initial concentration is predetermined.

The removal efficiency  $Re$  % is respectively calculated using the following equation (Jerold *et al.*, 2017).

$$Re = \frac{(C_0 - C_t)}{C_0} \times 100$$

## RESULTS AND DISCUSSION

**Surface area analysis of modified bentonite:** The effect of bentonite modification on the surface area was evaluated. The BET specific surface area for the samples and the corresponding values are reported in Table 1. The results refer to the surface area of sodium bentonite is larger than the surface area of calcium bentonite due to a large interlaminar spacing that can be produced between the sodium bentonite crystal layers, while the calcium bentonite has a large electric attraction between the crystal layers (Gul *et al.*,

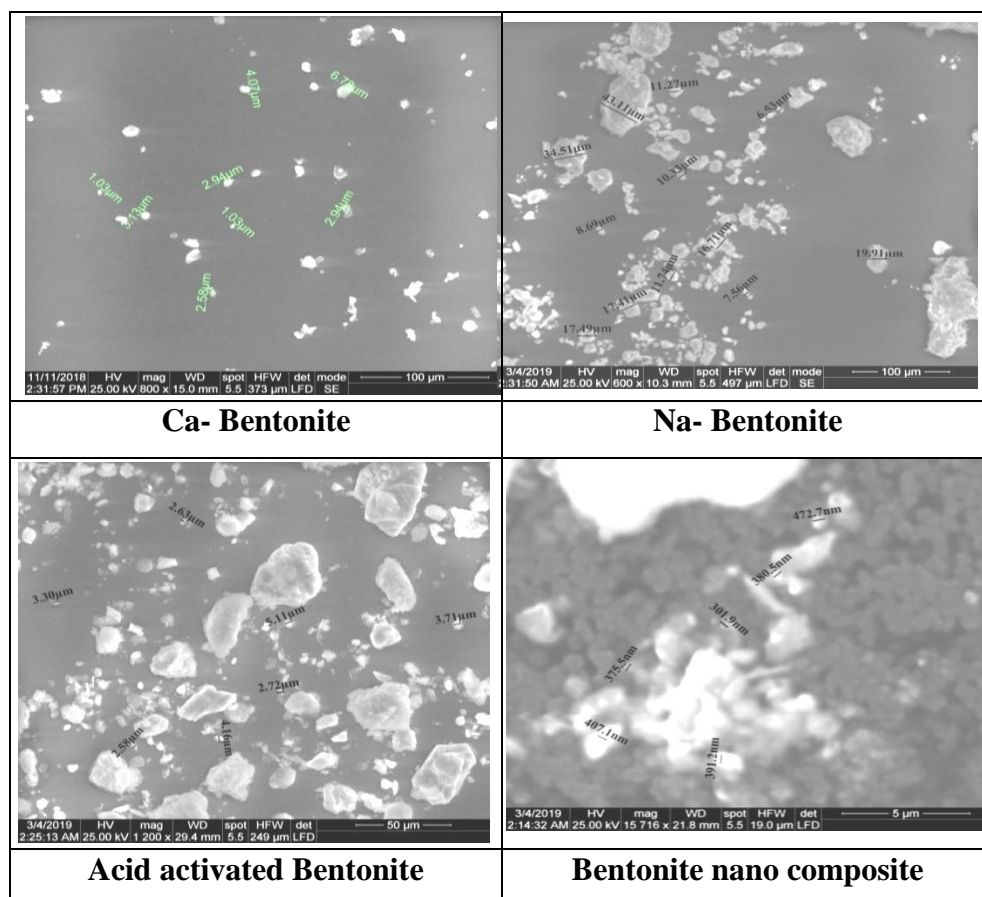
2016) while the increase in surface area of bentonite nano composite occurred due to surface area to volume ratio increases with the decrease in radius of the sphere and vice versa, so The presence of these fine particles of nano leads to increase the surface area of the modified clay (Ingole *et al.*, 2017, White, 2013) .

**Table(1):** Results of BET specific surface area of modified bentonite

Type of bentonite	Temperature (°C)	Surface Area (m <sup>2</sup> /g)
Ca- bentonite	100	25.25
Na-bentonite	100	31.86
Acid activation bentonite	100	62.194
Bentonite / Fe <sub>3</sub> O <sub>4</sub> nano composite	100	107.998

**Morphological analysis :**In figure (1), The SEM images of bentonite samples, massive plates with some phase separations are observed as a heterogeneous surface morphology, The average size of Ca -bentonite particles was observed at (1.03 – 6.78) μm, (7.56 – 43.11) μm for Na-bentonite,( 2.58 – 5.11 ) μm for acid activation bentonite and (301.9) nm for bentonite nano composite, this adsorbent has a larger active site and can act as a proper adsorbent and be useful for extracting or removing metallic ions (Shahat *et al.*, 2015). The TEM of Fe<sub>3</sub>O<sub>4</sub>/bentonite nanocomposite was shown in Figure 2.



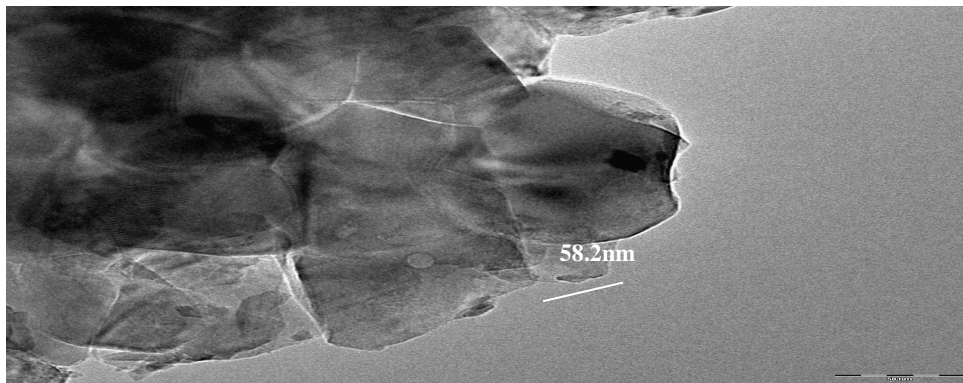


**Figure(1):** SEM of modified Bentonite

**Table(2):** The EDX analysis of modified bentonite

Element (Wt %)	O	Al	Si	Ca	Fe	Na
Ca- Bentonite	37.95	4.26	9.27	4.89	7.47	0.44
Na- Bentonite	43.64	12.03	27.6	2.4	7.47	2.7
Acid activated Bentonite	45.27	11.31	33.51	1.2	5.15	1.25
Bentonite nano composite	41.64	7.62	31.27	0.9	14.27	1.1

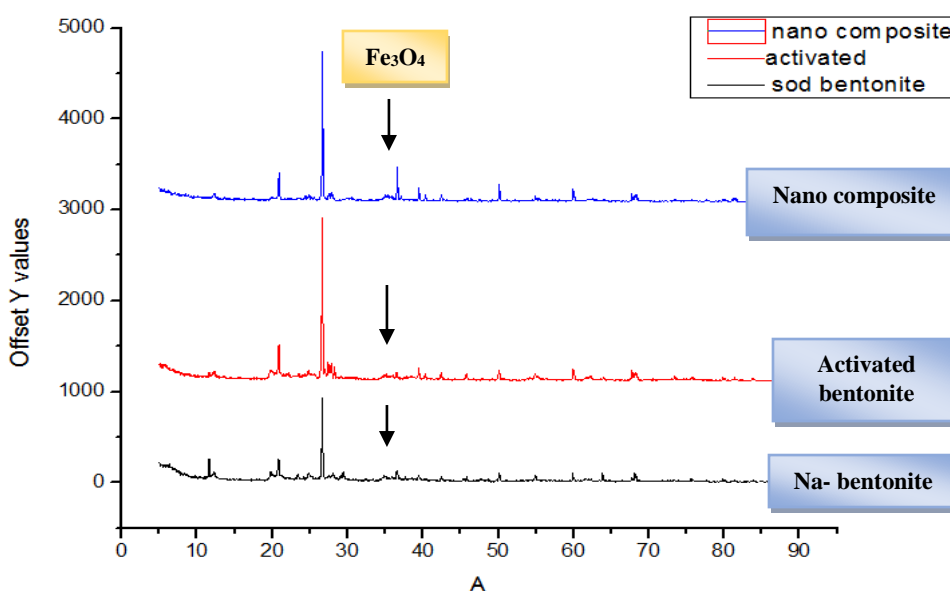
Bentonite is the one of the smectite group, composed of layers made up of two silica tetrahedral sheets with a center alumina octahedral sheet. In activation, acid and base attack the bentonite and releasing octahedral cation such as  $Al^{3+}$  and these cation dissolve in the solution, also the increase of Si and Al % in the results of EDX may be due to removal of impurities and increase of the clay mineral content (Hamadi *et al.*, 2015).



**Figure(2):** TEM micrograph of Fe<sub>3</sub>O<sub>4</sub>/bentonite nanocomposite

**X-ray diffraction analysis:** The XRD pattern of Na- Bentonite, acid activated Bentonite and Bentonite nano composite were shown in Figure 3, Fe<sub>3</sub>O<sub>4</sub>/bentonite nanocomposite can conclude that quartz is the major constituent of modified bentonite. The Appearance of metallic iron for Fe<sub>3</sub>O<sub>4</sub>/bentonite nanocomposite was identified from the peak at  $2\theta=36.56^\circ$ , the present of this peak at high intensity evidence of successful iron loading on bentonite as shown in Figure 3, The specific diffraction peak of montmorillonite in composite was observed at  $2\theta$  around  $4.20^\circ$ ,  $19.82^\circ$ ,

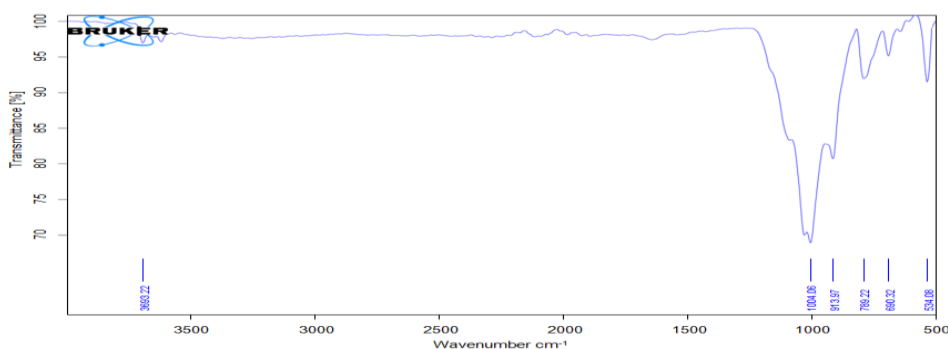
25.70°, 35.01°, and 59.94° (Arancibia-Miranda *et al.*, 2016), the presence of quartz on the bentonite was also observed, and the diffraction peaks of quartz were found at  $2\theta = 20.88^\circ$ ,  $26.45^\circ$  and  $50.01^\circ$ . The presence of calcite ( $\text{CaCO}_3$ ) was observed at  $2\theta = 29.84^\circ$ .



**Figure(3):** XRD of modified Bentonite

**FTIR analysis:** The FTIR spectra of bentonite nano composite are carried out in the range from  $500\text{-}4000\text{ cm}^{-1}$  to investigate the effect of adding  $\text{Fe}_3\text{O}_4$  nanoparticles by co precipitation on the acid activated bentonite. The changes in the functional groups provide the indication of the changes occurred during nano composite formation as shown in Figure 4, the peak bands appearing at  $911.11$  and  $789.90\text{ cm}^{-1}$  (octahedral) were the outcome of the Al–OH deformation, Al–Mg–OH deformation, and SiO stretching of the quartz and

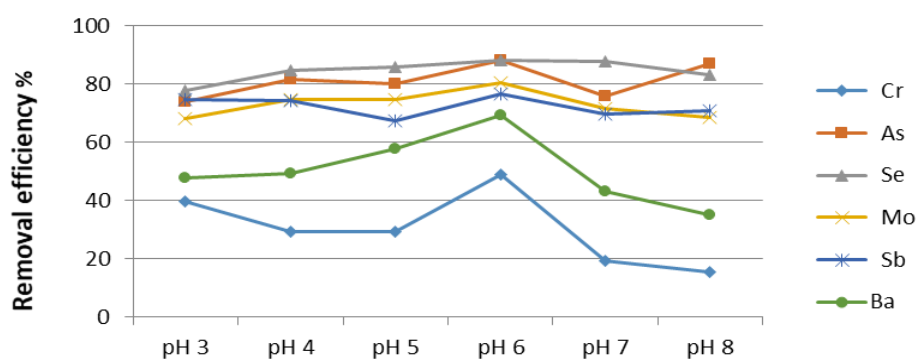
silica, respectively. In addition, the combined Al–O and Si–O bending vibration was observed at around 686.43 cm<sup>-1</sup> and the tetrahedral bending mode was observed at 531.5 cm<sup>-1</sup> which related to Al–O–Si. The bands at 534.08, 789.22, 913.97, and 1004.6 cm<sup>-1</sup> correspond to the Fe–O stretch with respect to Fe<sub>3</sub>O<sub>4</sub> (Yang *et al.*, 2016). The formation of Fe<sub>3</sub>O<sub>4</sub>/bentonite nanocomposites can be indicated by the appearance of transmittance peak at wave number 581 cm<sup>-1</sup> correspond to Fe–O stretch vibration bond of magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Lu *et al.*, 2017).



**Figure(4):** FTIR spectra of modified bentonite

**Factors on adsorption process:** Effect of optimum pH: The maximum removal efficiency was achieved at pH values were equal to 6 for ions as (49.12 %) for Cr, (88.09 %) for As , (87.99 %) for Se, (80.27 %) for Mo, (76.63 %) for Sb, (69.1 %) for Ba as shown in Figure 5 . At higher pH more than 6 the amount of adsorption decreased which may be related to the complete coverage of the modified bentonite surface by heavy metal ions due to the increase of the OH<sup>-</sup> ions in the solution which can make an

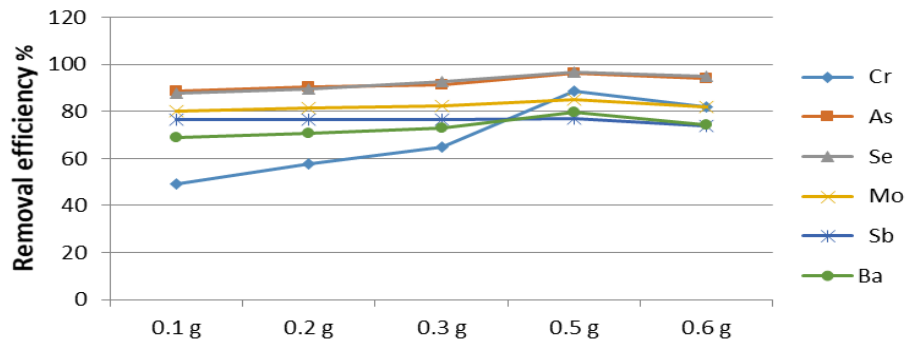
electrostatic equilibrium with the positive charge of heavy metal ions (Al-Rashdi *et al.*, 2013), while at lower pH, the removal efficiency was decreased due to competition between the high concentration of H<sup>+</sup> protons in acidic median and positive charge of heavy metal ions (Lu, 2013). This study did not use the pH above 8 to avoid any overlapping with the phenomenon of chemical precipitation of the heavy metal ions (Mohammed *et al.*, 2018).



**Figure(5):** Effect of pH on adsorption of metals using bentonite nano composite

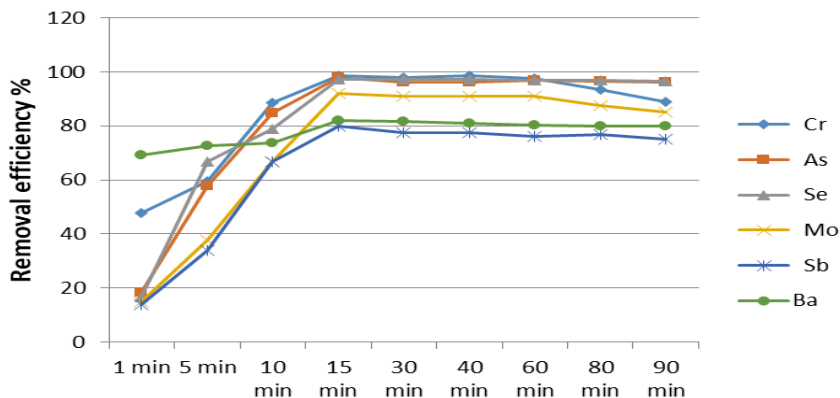
**Effect of the optimum dose:** Figure 6 shows the removal efficiency was raised as the modified bentonite dose increased and the maximum dose effect of removal efficiency for heavy metals were 0.5g as (88.79 %) for Cr, (96.25 %) for As, (96.54 %) for Se, (85.25 %) for Mo, (77.97 %) for Sb, (79.79 %) for Ba. The nanoparticles of Fe<sub>3</sub>O<sub>4</sub>/bentonite had a large number of active sites of the hydroxyl group as the amount of adsorbent increased, the metal ions were adsorbed more by active sites(Shabani *et al.*, 2019, Mohebbi *et al.*, 2018). The modified bentonite dose above 0.5 g did not significantly increase

the removal of heavy metals, which might be due to the aggregation of particles by increasing the amount of modified bentonite(Akpomie *et al.*, 2015).



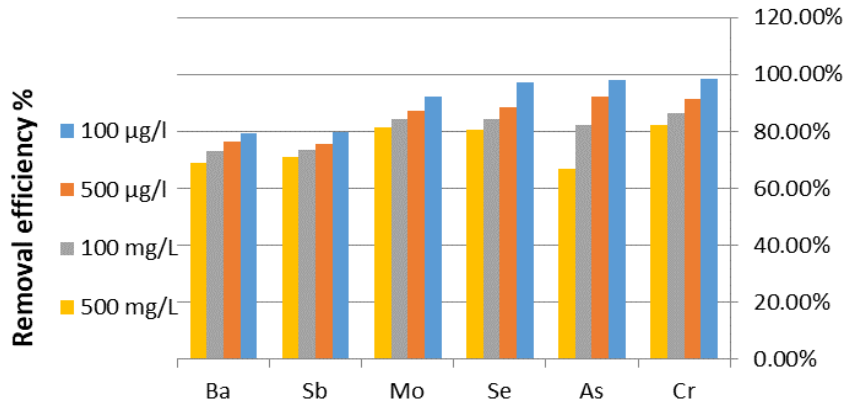
**Figure(6):** Effect of dose on bentonite nano composite

**Effect of the optimum contact time:** The result showed that the rate of removal was achieved rapid within (1- 15) min and reach to maximum removal efficiency at 15 min, the adsorption rate was constant with further increase in contact time from 15 to 80 min but further increase in contact time up to 90 min led to a slight decrease in percentage removal as shown in Figure 7. The rapid percentage removal obtained initially for metal ions are due to the presence of abundant active sites on the surface of modified bentonite which were later occupied as time progresses(Akpomie *et al.*, 2015, Tatarchuk *et al.*, 2017) thereby resulting in the inability of modified bentonite to remove the metal ions after 80 min.



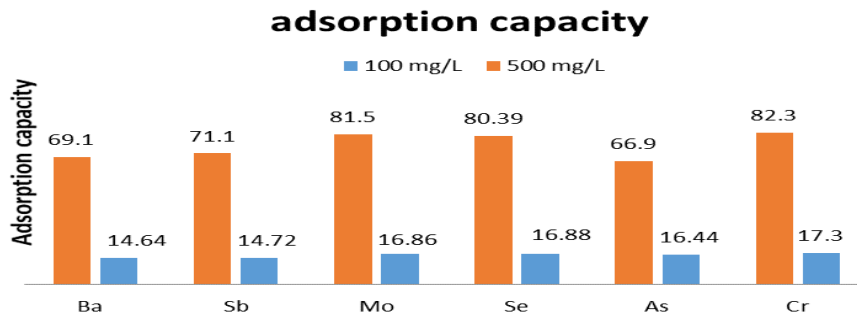
**Figure(7):** Effect of contact time on bentonite nano composite

Effect of the optimum initial concentration :Figure 8 shows the effects of the initial concentration from (100  $\mu\text{g/L}$  - 500 mg/L) on percentage removal of all metal ions ,adsorbent has a specific number of active adsorption sites, which are can adsorb more metal ions at lower concentrations of solution, but at high concentration, the active sites becomes saturated leading to a reduction in the percentage removal (Akpomie *et al.*, 2015). At lower concentrations, fewer metal ions are available in solution, therefore maximum binding of the ions on the active sites of modified bentonite was not achieved, but as the concentration increases, the presence of a high concentration gradient produce a stronger driving force which overcomes resistances to mass transfer, in the process, making maximum use of the active sites resulting in higher adsorption per unit mass of modified bentonite (Dawodu *et al.*, 2014).



**Figure(8):** Effect of initial concentration on bentonite nano composite

The maximum adsorption capacity was reported as 82.3 mg/g for (Cr), 66.9 mg/g for (As), 80.39 mg/g for (Se), and 81.5 mg/g for (Mo), 71.1 mg/g for (Sb) and 69.1 mg/g for (Br) as shown in Figure 9.



**Figure(9):** Adsorption capacity of bentonite nano composite

### CONCLUSION

The synthesis of bentonite/ Fe<sub>3</sub>O<sub>4</sub> magnetite nanoparticle was carried out to coat sodium activated bentonite by co-precipitation, after which it was used



as an adsorbent for treating water contaminated with heavy metals, the characterization study of samples done using the BET, XRD patterns, SEM images, TEM images, EDX spectra, and FTIR analysis provided evidence for several adsorptive improvements that took place in the surface morphology and surface area of the sodium activated bentonite. These properties were also significantly the modified bentonite after the adsorption, due to the contribution of the nanoparticles in the changed in removal process. The effects of amount of activated bentonite nano composite, contact time, PH, initial concentration on the adsorption of the metals were examined. The extreme adsorption effectiveness from modified bentonite was achieved, it succeeded to eliminate about (98.4 %) for Chromium, (98.8 %) for Arsenic, (91.3 %) for Selenium, (90.8 %) for Molybdenum, (79.1 %) for Antimony, (75.3 %) for Barium at pH=6, optimum dose at 0.5 g and contact time at 15 min.

The magnetic nanomaterials have large sorption capacity and are easy to recover and separate from the composite after adsorption by using strong magnets.

### **RECOMMENDATIONS**

The present study could recommend adding Fe<sub>3</sub>O<sub>4</sub> magnetite nanoparticles to activated bentonite to remove heavy metals which has the potential to replace the high cost adsorbents such as activated carbon, as bentonite is a low-cost adsorbent and is plentiful. The modification of

bentonite with acid activation is an economical method to enhance its adsorption properties.

### **RECOMMENDED FUTURE STUDIES**

It is suggested to study the effect of activated bentonite nano composite to remove radio nuclides and organic pollutants from waste water.

In this study the bentonite activated by sulfuric acid, it is suggested to study the activation of bentonite by gamma radiation at different doses.

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## تحضير وتوصيف المتراكبات النانوية للبنتونيت المنشط لإزالة الفلزات الثقيلة من المياه العادمة

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### المستخلص

في هذا البحث، تم إجراء تعديل للبنتونيت الكالسيومى بواسطة ثلاثة طرق كيميائية من خلال تحويل البنتونيت الكالسيومى إلى بنتونيت صوديومى ثم تنشيطه باستخدام حمض الكبريتيك المركز (٣) مولار ثم تحضير البنتونيت المنشط المعالج بجزيئات الحديد المغناطيسى النانوية ( $Fe_3O_4$ ) باستخدام طريقة الترسيب. تم توصيف العينات التي تم تحضيرها باستخدام التحليل الطيفي للأشعة السينية المشتتة من الطاقة (EDX)، حيود الأشعة السينية (XRD)، التحليل الطيفي للأشعة تحت الحمراء (FTIR)، مساحة السطح (BET)، الميكروسكوب الإلكتروني الماسح الضوئي (SEM) والميكروسكوب الإلكتروني النافذ (TEM). أظهرت دراسة التوصيف تحسنا كبيرا في العديد من الخواص الامتزازية للبنتونيت المعدل، مثل مساحة السطح، الشكل السطحي، والمواقع النشطة حيث تم تسجيل زيادة في مساحة سطح البنتونيت المعدلة على أنها ٢٥,٢٥٩ م<sup>٢</sup> / جم، ٣١,٨٦ م<sup>٢</sup> / جم، ٦٢,١٩٤ م<sup>٢</sup> / جم و ١٠٧,٩٩٨ م<sup>٢</sup> / جم لكل من البنتونيت الكالسيومى، والبنتونيت الصوديومى، والبنتونيت المنشط بالحمض والبنتونيت المعالج بالحديد المغناطيسى النانوى، على التوالي. تمت دراسة تأثير الأس الهيدروجيني والتركيز وكمية البنتونيت المعدل وأفضل وقت على قدرة الإدمصاص. أظهرت النتائج أن أفضل أس هيدروجيني كانت عند درجة حامضية (٦)، والجرعة المثلى عند ٠,٥ جرام، وأفضل وقت (١٥) دقيقة. تم الحصول على أقصى إزالة للفلزات الثقيلة بواسطة متراكب البنتونيت النانوى المعدل بنسبة (٩٨,٤٪) للكروم، (٩٨,٨٪) للزرنخ، (٩١,٣٪) للسيلينيوم، (٩٠,٨٪) للموليبيدينوم (٧٩,١٪) للأنتيمون، (٧٥,٣٪) للباريوم.

**الكلمات الدالة:** الامتزاز، المعادن الثقيلة، البنتونيت المنشط، مركب النانو  $Fe_3O_4$