REMOVAL OF MANGANESE FROM DRINKING WATER USING NANOHYDROXYAPATITE

Sameh M. Fouad[(1)]; Noha S. Donia[(2)]; Taha A. Mohamed[(2)] and Mohamed A. Reda[(3)]

1) Post Grad, Institute of Environmental Studies and Research, Ain Shams University 2) Institute of Environmental Studies and Research, Ain Shams University3) Teacher at The Canadian International University

ABSTRACT

In this work ,nanohydroxyapatite was synthesized by two methods, the first method is the natural method which is synthesized from tilapia fish bone, The second method is the chemical method via wet method as model adsorbent for the removal of manganese which often occurs as geogenic contaminants in untreated surface water, ground water and drinking water. The prepared samples were characterized by Energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Fourier Transformation infrared (FTIR) spectroscopy, (BET) Brunauer Emmett Teller surface area device, scanning electron microscope(SEM), The Bruker Senterra spectrometer (Raman) and The Inductively coupled plasma mass (ICP–MASS7700). The characterization study demonstrated a substantial improvement in several adsorptive parameters of natural (nHAPn) and chemical nanohydroxyapatite (nHAPE) like surface area and surface morphology, where the surface area of nHAPE and nHAPn were observed (78.019 m^2/g) and (26.028 m^2/g), respectively.The particles size of nHAPE and nHAPn were (169.9-251.5) nm, (471.5-514.6), nm 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=7, optimum dose of nHAPE and nHAPn at 0.3 g, initial concentration 25 ppm and contact time at 60 min. The maximum removals efficiency of nHAPE and nHAPn were (99.59 %) and (83.73%) for manganese. The maximum adsorption capacity of nHAPE and nHAPn were (4.22mg/g) and (3.2mg/g) for manganese.

Key words: Adsorption; Heavy metals; Natural nanohydroxyapatite and Chemical nanohydroxyapatite.

INTRODUCTION

Chemical wastewater largely possess organic and inorganic materials such as dyes, phenol compounds, aromatic compounds and heavy metals(Caron *et al.*, 2016). 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).In 2019 according to the world health organization (WHO) pollution killed 7 million people all over the world annually(Mannucci and Franchini, 2017).According to the pollution of toxic air, water, soils and workplaces, which is triple the number of deaths caused by AIDS. tuberculosis and malaria combined and 15 times higher than deaths caused by wars and other forms of human violence (Mannucci and Franchini, 2017).These consequences are reduced by limiting the variety and concentration of heavy metals that present in the chemical 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).

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

$nHAP_E$ and $nHAP_n$ can remove some heavy metal ions like Cd, Mn, Zn, Co, Fe and Pb ions, High exposure to manganese has been associated with toxicity to the nervous system producing a syndrome that resembles Parkinsonism, manganese is unlikely to produce other types of toxicity such as cancer or reproductive damage, it effects occur mainly in the respiratory tract and in the brains, symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage (Tobiason *et al.*, 2016) ,natural nanohydroxyapatite is easier to produce than synthetic nanohydroxyapatite, The manufacturing process price of the $nHAP_n$ costs nothing because it was manufactured from fish bones waste and it is very friendly for environment and didn't cause any pollution, There is no a big difference in the removal efficiency and adsorption capacity between $nHAP_n$ and $nHAP_E$ according to the price,a number of physical and chemical methods have been investigated to modify the natural and chemical nanohydroxyapatite(Elnsar *et al.*, 2017).

The $nHAP_n$ and $nHAP_E$ need for research and development in the field of modification to enhance their adsorptive properties (Wang *et al.*, 2018).Among the available adsorbents, the natural and the chemical nanohydroxyapatite are classified as the promising material for heavy metals removal from aqueous systems(Yang *et al.*, 2019).

MATERIALS AND METHODS

Materials:Natural and chemical nanohydroxyapatite (NHA) used in this study were obtained from tilapia fish bones from river Nile and calcium carbonate $CaCO_3$,calcium phosphate dihydrate $CaHPO_4.2H_2O$, these materials were converted to nanohydroxyapatite(Ibrahim *et al.*, 2020).

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 1000 mg/L of (manganese standards for ICP) were dissolved appropriate in 1 liter ultra-pure water, sodium hydroxide (NaOH) 98 %, nitric acid (HNO_3) 99 %, the stock solution was used to prepare dilute solutions of different concentrations (5 ppm - 10 ppm -25 ppm -50 ppm-100 ppm), the pH adjusted at 7 by using 0.1M (HNO_3) and 0.1M (NaOH).

Preparation of natural nanohydroxyapatite: Nanohydroxyapatite was prepared from fish bone using tilapia fish bones, 5 kg of tilapia fish was brought from local market, The meat was removed from both sides of the fish, then bones were boiled in the water for 2 hours.

Bones were cleaned from meat several times, then dried for 24 hours at room temperature, this process was repeated for three days.

Bones were calcined in a furnace at 700 °C for 1 hour by using Forced air drying oven ZRD -7080 made in USA, bones were grounded in a mortar to a powder and submitted to physico chemical analysis(Hammood *et al.*, 2019).

Synthesis of chemical nanohydroxyapatite via wet chemical method:Nanohydroxyapatite was prepared via wet chemical precipitation method using calcium carbonate $CaCO_3$, calcium phosphate dihydrate $CaHPO_4.2H_2O$ and ammonium acetate buffer (pH = 10) for pH adjustment from HACH company made in USA, 14 grams of calcium carbonate $CaCO_3$ were mixed with 6 grams of calcium phosphate dihydrate $CaHPO_4.2H_2O$ in 250 ml of high grade ultra pure water ,the mixture was vigorously stirred at constant temperature 25 °C by using Hot plate stirrer HSD-330 made in Korea, ammonium acetate buffer (pH = 10) was added for pH adjustment which was kept at 10 ,the mixture was allowed to remain stirred for 24 hours, a white precipitate was formed, the precipitate HA was removed from the solution by the centrifuge method at a rotation speed of 700 rpm, the resulting solution was dried at 200 °C to remove the water by using Forced air drying oven ZRD -7080 made in USA then, the precipitate was calcined at oven with 800 c for 1 hour by using Sturat scientific furance device made in UK(Yelten-Yilmaz and Yilmaz, 2018).

Characterization of nanohydroxyapatite: The natural and chemical nanohydroxyapatite were analyzed using Brannuer-Emmet-Teller (BET) device, fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD)device, Bruker Senterra Raman spectrometer and Inductively coupled plasma mass (ICP – MASS)7700 (Phan, Nguyen *et al.* 2017).

Batch adsorption experiments: It was conducted using 0.1, 0.2, 0.3, 0.5 g of nanohydroxyapatite in 50 ml of solutions containing manganese ions in 50 ml glasses, adsorption of manganese on ($nHAP_n$) and ($nHAP_E$) were carried out in a batch system, the effect of various operational parameters such as contact time, temperature, initial concentration, pH have been adjusted in room temperature and the concentration in the supernatant was determined by the Agilent ICP-MS 7700.

Effect of pH: The effect of pH on the adsorption was studied by agitated 50 ml of manganese standard solution (10 mg/L) with (0.1) g of ($nHAP_n$) and ($nHAP_E$) at different pH values (4 -7-10) with shaking for (60 min) at a constant speed of (150) rpm at room temperature.

Effect of the dose: The effect of mass of nanohydroxyapatite (NHA) on the adsorption was studied by using 50 ml of manganese standard solution (10 mg/L at pH 7) onto (0.1 - 0.2 - 0.3 - 0.5) g of ($nHAP_n$) and ($nHAP_E$) with shaking for (60 min) at a constant speed of (150) rpm at room temperature.

Effect of the contact time: The effect of contact time of ($nHAP_n$) and ($nHAP_E$) on the adsorption was studied by using (0.3) g onto 50 ml of standard solution (10 mg/L at pH 7) with shaking for (5 - 10 - 15 - 20 - 30 - 45 - 60 -70 min) at a constant speed of (150) rpm at room temperature.

Effect of the initial concentration: The effect of initial concentration of ($nHAP_n$) and ($nHAP_E$) on the adsorption was studied by using (0.3) g onto 50 ml of manganese standard solution at different concentration (5 mg/L – 10 mg/L – 25 mg/L – 50 mg/L – 100 mg/L) at pH 7 with shaking for (60 min) at a constant speed of (150) rpm at room temperature.

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Adsorption capacity of natural and chemical nanohydroxyapatite: 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 natural and chemical nanohydroxyapatite (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).

$$Re = \frac{(C_0 - C_t))}{C_0} X100$$

Adsorption isotherms: The Langmuir and Freundlich equations were commonly used for describing adsorption equilibrium of adsorbate onto the adsorbent, the Langmuir isotherm is applicable to monolayer chemisorptions, while the Freundlich isotherm is used to describe adsorption on surfaces having heterogeneous energy distribution.

The linear equation for Freundlich is given by: $\log q_e = 1/n \log c_e + \log k_f$

where k_f (L/mg),1/n Freundlich empirical constant related to the total adsorption capacity of the solid.

The Langmuir equation is given by: $c_e / q_e = 1/k_L q_{max} + c_e/q_{max}$

where q_e (mg/g) is the amount adsorbed on natural and chemical nanohydroxyapatite at equilibrium .

q_{max} (mg/g) is the maximum adsorption monolayer capacity, k_L is the Langmuir constant related to the affinity between the adsorbate and the adsorbent, and is related to the free energy of adsorption.

C_e (mg/L) is the concentration of iron or manganese in liquid phase at equilibrium (Narwade and Khairnar 2017).

RESULTS AND DISCUSSION

Surface area analysis of nanohydoxyapatite: The effects of natural and chemical nanohydroxyapatite on the surface area were evaluated by the BET specific surface area device.

the surface area for the samples are reported in Table (1), the results refer to that the surface area of the $nHAP_E$ is larger than $nHAP_n$ about three times, (Oberbek, Bolek *et al.* 2018, Thanh, Novák *et al.* 2018, Coelho, Grenho *et al.* 2019, Nam, Van Hoa *et al.* 2019).

Table(1): The surface area of Chemical and Natural nanohydroxyapatite

NO.	Chemical name	Temperature	Surface area	Surface area according to the latest methods and results
1	nHAPE Experimental anohydroxyapatite (chemical)	200Cº (device default)	78.019 m²/g	66.3 m²/g (Oberbek, Bolek et al. 2018)
				101.2 m²/g (Thanh, Novák et al. 2018)
2	nHAPn Natural anohydroxyapatite	200Cº (device default)	26.028 m²/g	32.83 m²/g (Nam, Van Hoa et al. 2019)
				13.2 m²/g (Peng, Yu et al. 2017)

Morphological analysis: In figure (1) the SEM images of chemical and natural nanohydroxyapatite showed that enamel surface is generally smooth with a regular pattern, it observed porous crystalline structure with particle aggregation of various sizes as a heterogeneous surface morphology, the occurrence of pores in the hydroxyapatite is very vital as this would affect greatly the uptake of the heavy metals ions and the reactant molecules from the solution.

The average size of $nHAP_E$ and $nHAP_n$ were observed at (169.9 – 251.5) nm and (471.5 – 514.6) nm respectively.

The average size of chemical and natural nanohydroxyapatite according to latest methods and results were observed at (209.9) nm and (200) nm respectively (Peng, Yu *et al.* 2017, Rafie and Nordin 2017).

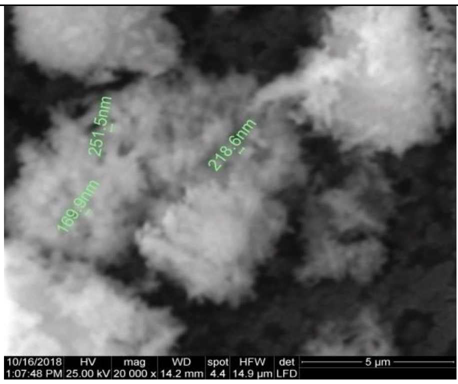
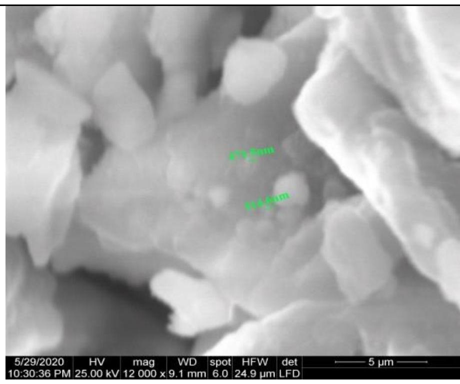
	
Chemical nanohydroxyapatite	Natural nanohydroxyapatite

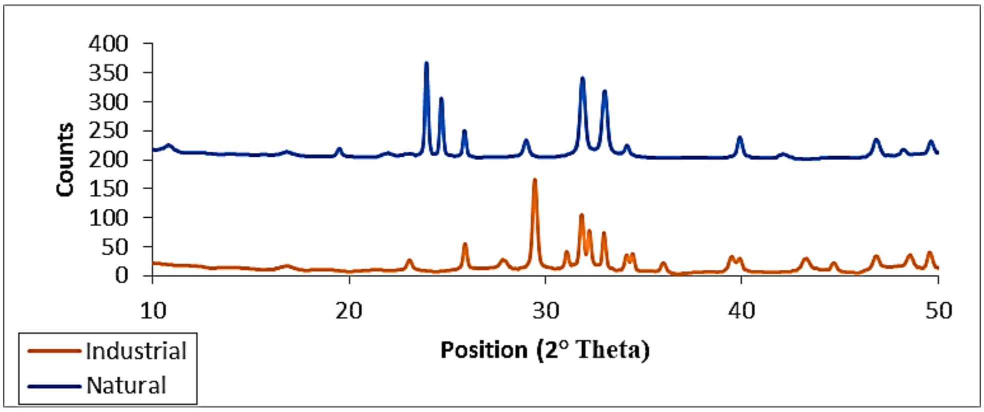
Fig.(1): Images SEM nanohydroxyapatite particles using (EDX) device

Table(2): The EDX analysis of ($nHAP_n$) and ($nHAP_E$)

NO.	Element (Wt %)	Ca	O	P
1	Chemical nanohydroxyapatite	55.24	31.38	13.38
2	Natural nanohydroxyapatite	49.92	29.96	20.12

X-ray diffraction analysis: The XRD patterns of the natural and chemical nanohydroxyapatite shows sharper peaks which indicate better crystallinity ,the appearance of $nHAP_E$ and $nHAP_n$ were identified from the peaks angle at 2 theta (θ) =(26°,29°,32°,32.5°,33°,34°,40°,47°,48° and 49°) with high intensities at (002, 210, 211, 300, 202, 310, 212, 312 and 213).

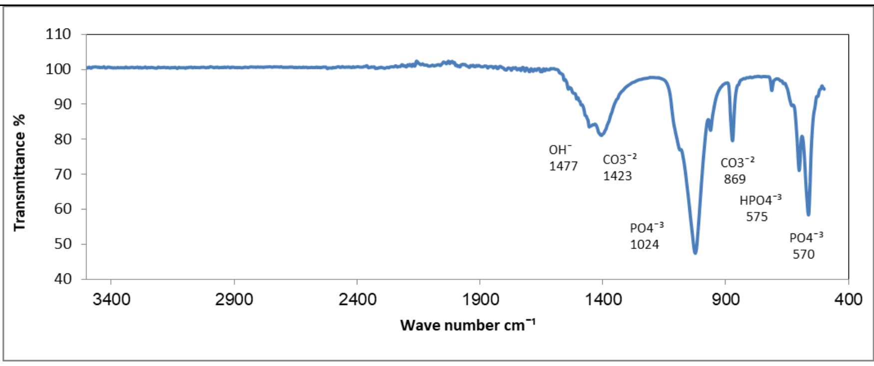
The presence of peaks angle at 2 theta with its high intensity is evidence of successful manufacturing of natural and chemical nanohydroxyapatite as shown in Figure (2) (Elnsar, Soliman *et al.* 2017, Rafie and Nordin 2017, Elkady, Shokry *et al.* 2018).



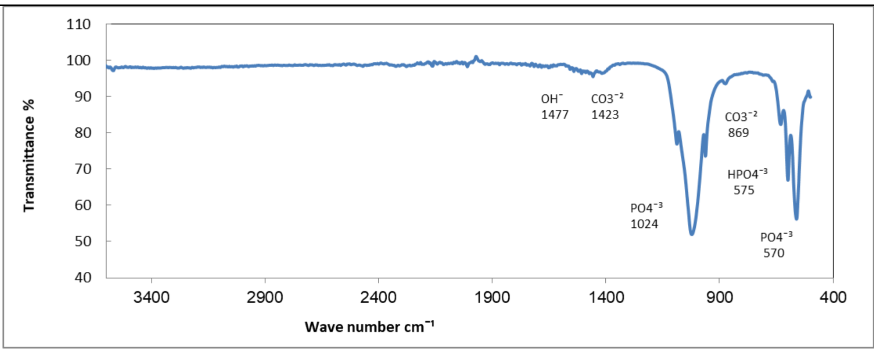
Fig(2): XRD Spectra of nanohydroxyapatite

FTIR spectral analysis: The FTIR spectra of chemical and natural nanohydroxyapatite were carried out in the range from 400-3600 cm^{-1}, the spectrum reveals the hydroxyapatite characteristic peaks, namely phosphate groups at 570 cm^{-1} and 1024 cm^{-1}, apatite group observed at 575 cm^{-1} ,the band at 1477 cm^{-1} is related to OH^{-} vibrational and stretching modes, the existence of peaks at 869 cm^{-1} and 1423 cm^{-1} are due to the presence of carbonate group, the broad band at 3200 - 3600 cm^{-1} indicate the presence of adsorbed water on the material.

The success formation of $nHAP_E$ and $nHAP_n$ can be indicated by the appearance of transmittance peaks at wave numbers (570, 575, 869, 1024, 1423 and 1477cm^{-1}) which related to phosphate, apatite, carbonate and hydoxyl groups shown in figure (3) (Rafie and Nordin 2017, Oberbek, Bolek *et al.* 2018, Coelho, Grenho *et al.* 2019).



Chemical nanohydroxyapatite



Natural nanohydroxyapatite

Fig(3): FTIR spectra of (nHAP$_n$) and (nHAP$_E$)

Raman spectrometer for analysis of the prepared sample: In figure (4) spectra of chemical and natural nanohydroxyapatite particles using (RAMAN) spectroscopy shows a series of bands in the mid infrared region.

The spectrum reveals the hydroxyapatite characteristic peaks, phosphate groups observed at (431, 590, 963, 1047 and 1077 cm^{-1}), the main and the strongest band at 963 cm^{-1} for nHAP$_E$ and nHAP$_n$.

The success formation of $nHAP_E$ and $nHAP_n$ can be indicated by the appearance of transmittance peaks at wave numbers (431, 590, 963, 1047 and 1077 cm^{-1}) which related to phosphate (Stammeier, Purgstaller *et al.* 2018, Timchenko, Timchenko *et al.* 2018).

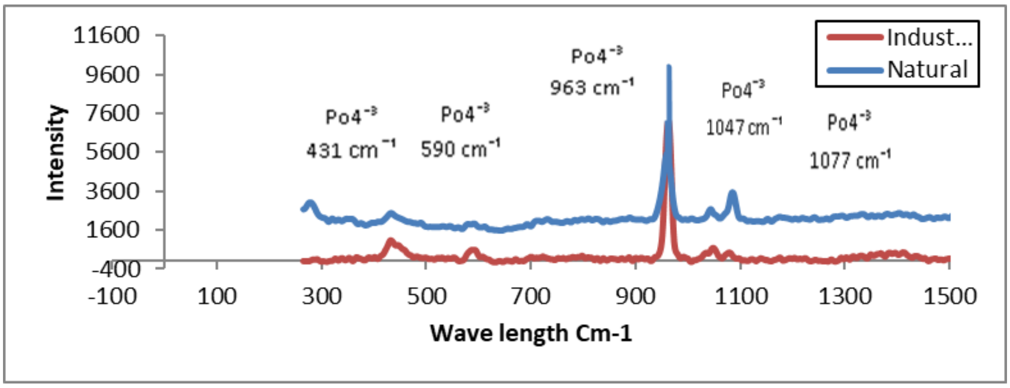


Fig.(4): Spectra of $nHAP_E$ and $nHAP_n$ using (RAMAN) spectroscopy Factors on adsorption process:

Effect ofoptimumpH: The pH is an important factor in the adsorption process of ($nHAP_n$) and ($nHAP_E$).

At pH 7, the maximum removal efficiency for Mn were (63.89%) and (84.46%) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (5), From pH 4 until 7, as pH increased the removal efficiency increased, above pH 7 the removal efficiency decreased (Elnsar, Soliman *et al.* 2017, Elkady, Shokry *et al.* 2018), The optimum pH according to the latest methods and results were 6 (Adekola) and 8 (Shokry and Hamad 2016, Elnsar, Soliman *et al.* 2017) respectively for $nHAP_n$ and $nHAP_E$.

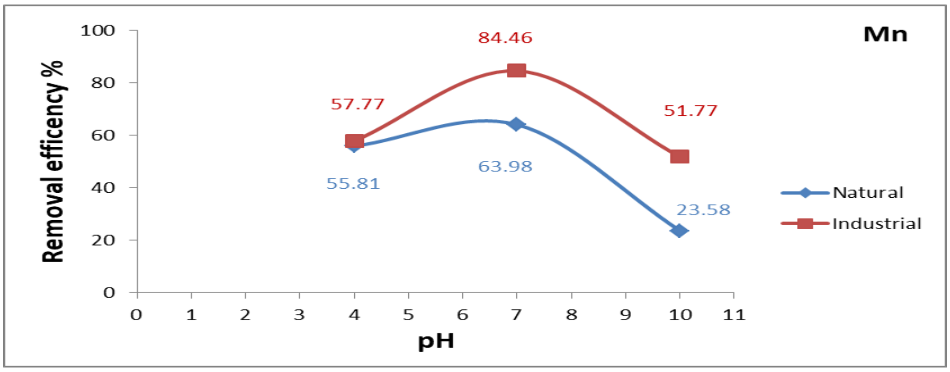


Fig.(5): Effect of pH on removal efficiency

At pH 7, the maximum adsorption capacity for Mn were (3.2 mg/g) and (4.22 mg/g) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (6).

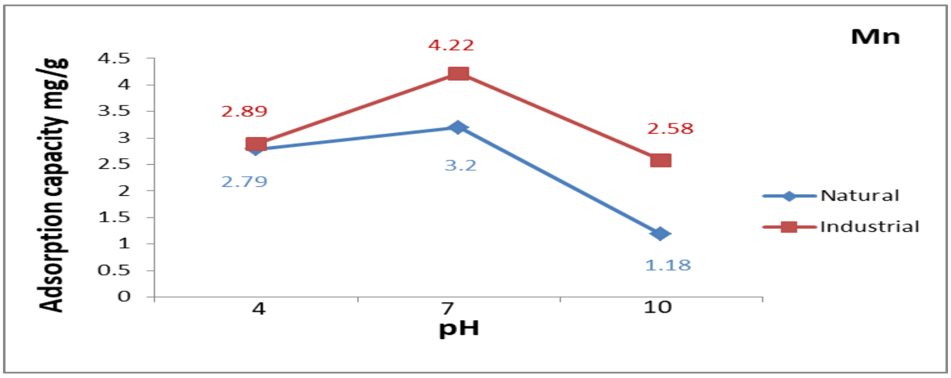


Fig.(6): Effect of pH on adsorption capacity

Effect of the optimum dose: When the material dosage of $nHAP_n$ and $nHAP_E$ at 25 °C solution temperature and pH = 7, the removal efficiency of Mn increases, this may be regarded to the increment of more surface area and new binding sites available for metal binding.

The optimum dose of $nHAP_n$ and $nHAP_E$ were recorded as 0.3 g, as the adsorbent dosage (0.5) g increased above the optimum dosages, no significant enhancement in the removal efficiency was recorded for either Mn.

At adsorbent dose equal 0.3 gram, the maximum removal efficiency for Mn were (80.59%) and (96.73%) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (7) (Shokry and Hamad 2016).

The optimum adsorbent dose according to the latest methods and results were 0.05 gram (Adekola) and 2 gram (Shokry and Hamad 2016, Elnsar, Soliman *et al*. 2017) respectively for natural NHA and chemical NHA.

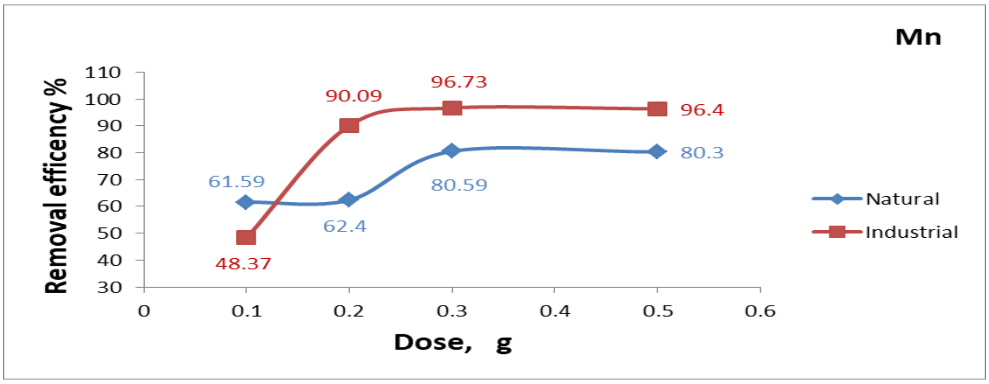


Fig.(7): Effect of adsorbent dose on removal efficiency at pH 7

At adsorbent dose equal 0.1 gram, the maximum adsorption capacity for Mn were (3.07 mg/g) and (2.43 mg/g), respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (8).

The sorption efficiencies of Mn were found to increase exponentially with the increase of adsorbent dose up to 0.3 g, this may be due to the increase in availability of surface active sites resulting from the increased dose of adsorbent, at higher dosages, 0.3 g and 0.5 g, sorption was almost the same and at maximum.

The adsorption site was used up when the adsorption dose reached a certain rate, hence it leads to reduced tendency of the particles to adsorb more ions to its surface (Adekola).

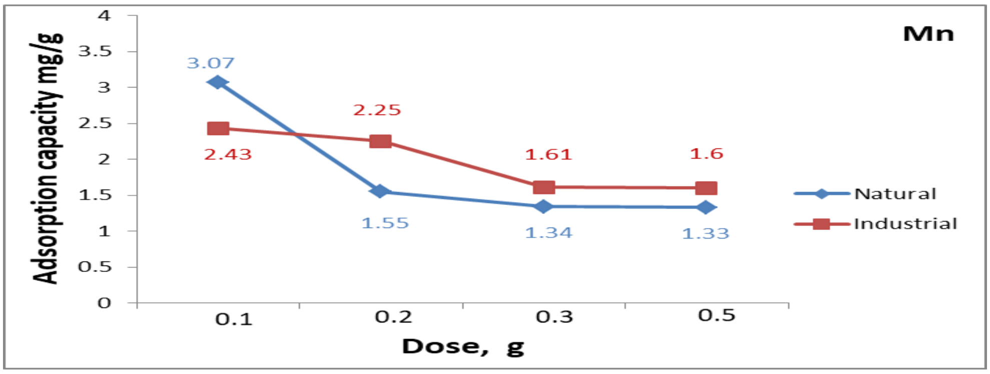


Fig.(8): Effect of adsorbent dose on adsorption capacity at pH 7

Effect of the optimum contact time: The results showed that the removal process proceeds within (5-70) minute and reach to maximum removal efficiency at 60 min.

The adsorption rate was increased in contact time from 5 to 60 minute but further increase in contact time up to 70 min led to a slight decrease in the percentage of removal as shown in Figure (9).

The rapid percentage removal obtained initially for metal ions are due to the presence of abundant active sites on the surface of natural and chemical nanohydroxyapatite which were later occupied as time progress, thereby resulting in the inability of nanohydroxyapatite to remove the metal ions after 60 min.

At 60 minute, the maximum removal efficiency for Mn were (83.73%) and (99.59%) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (9) (Shokry and Hamad 2016, Elnsar, Soliman *et al.* 2017).

The optimum contact time according to the latest methods and results were 70 minute (Adekola) and 90 minute (Shokry and Hamad 2016, Elnsar, Soliman *et al*. 2017), respectively for natural NHA and chemical NHA.

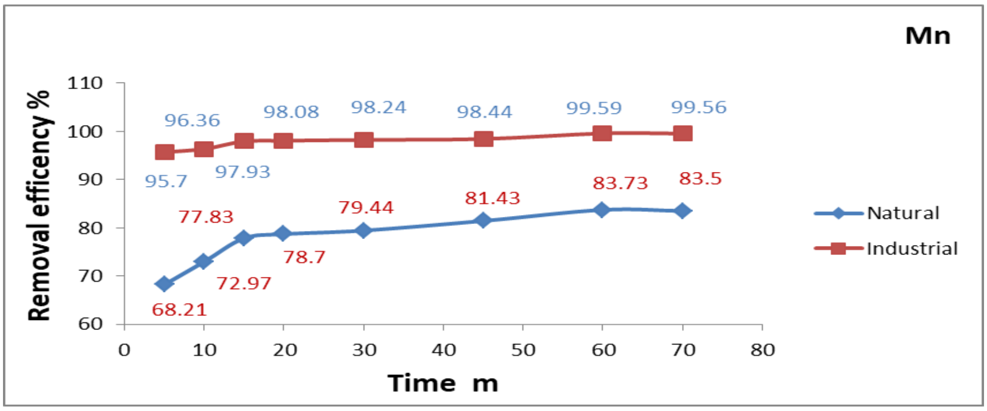


Fig.(9): Effect of time on removal efficiency at pH 7

The effect of contact time on the adsorption capacity of Mn ions were studied at different time intervals ranging from (5-70) minute, The rapid increase in initial uptake of Mn ions onto the prepared materials takes place in the beginning contact time period after this period, the rate of sorption process increases gradually with increasing contact time.

This phenomenon might be explained in two different steps; the first involved a rapid large removal of amounts of metal ions then the process reached equilibrium gradually, the rapid reaction rate supported the ion exchange mechanism of Fe and Mn adsorption onto the surface of $nHAP_n$ and $nHAP_E$, this rapidity is might be due to vacancy of all active sites on the $nHAP_n$ and $nHAP_E$ surfaces that give high chance of metal ions to bind with the functional groups resulting in initial fast adsorption step, As contact time increased after this period, the materials sites were gradually occupied that decline the rate of metal adsorption with time.

The maximum adsorption capacity for Mn were (1.4 mg/g) and (1.66 mg/g) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (10) (Shokry and Hamad 2016).

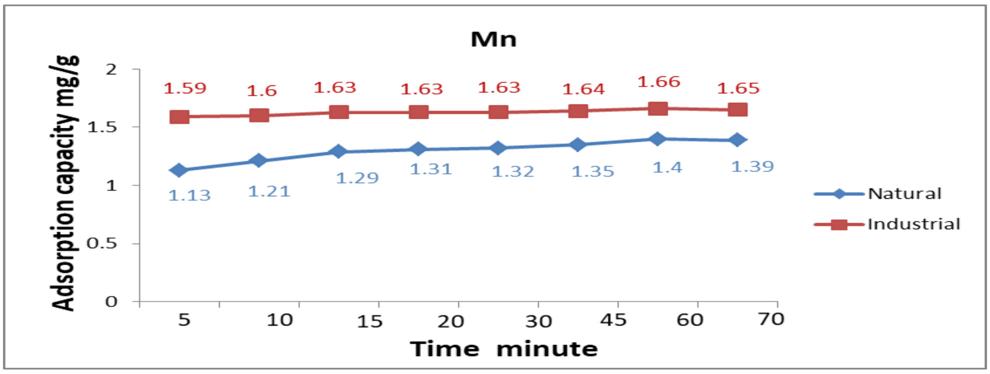


Fig.(10): Effect of time on adsorption capacity at pH 7

Effect of the optimum initial concentration : Figure (11) shows the percentage removal efficiency of Mn at different initial concentration from (5 mg/L to 100 mg/L), The new $nHAP_n$ and $nHAP_E$ have a specific number of active adsorption sites which can adsorb more metal ions at different concentrations of solution, at high concentrations the active sites becomes saturated leading to a medium reduction in the percentage of removal efficiency, but at low concentrations the active sites in nanohydroxyapatite had absorb more metals leading to increasing of the percentage of removal efficiency, at initial concentrations equal 25 ppm ,the maximum removal efficiency for Mn were (37.64%) and (83.58%) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (11) (Elnsar, Soliman *et al*. 2017).

The optimum concentration according to the latest methods and results were 80 ppm (Adekola) and 2 ppm (Shokry and Hamad 2016, Elnsar, Soliman *et al*. 2017) respectively for natural NHA and chemical NHA.

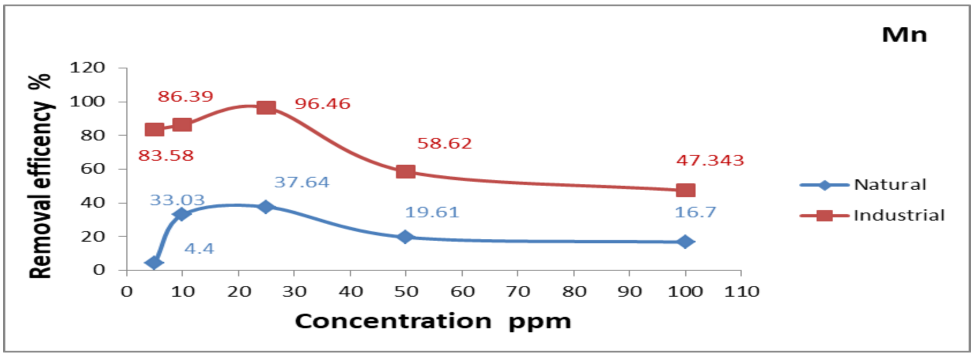


Fig.(11): Effect of concentration on removal efficiency at pH 7.

At initial concentrations equal 25 ppm, the maximum adsorption capacity for Mn were (2.78 mg/g) and (7.89 mg/g) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (12).

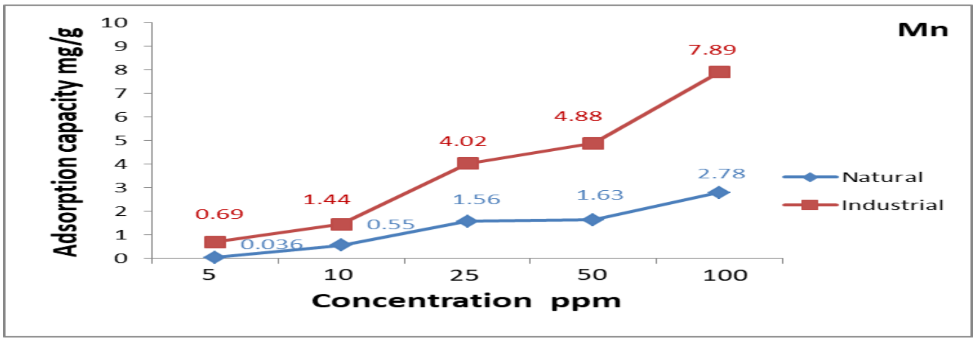


Fig.(12): Effect of concentration on adsorption capacity at pH7

Adsorption isotherms using The Freundlich and Langmuir equations: The Freundlich and Langmuir equations are commonly used for describing adsorption equilibrium of adsorbate onto the adsorbent, the Freundlich isotherm is used to describe adsorption on surfaces having heterogeneous energy distribution, while the Langmuir isotherm is applicable to monolayer chemisorptions, the linear equation for Freundlich is given by: ($\log q_e = 1/n \log c_e + \log k_f$) where k_f (l/mg) ,1/n Freundlich empirical constant related to the total adsorption capacity of the solid and slope (m) = 1/n, the slope, the intercept and the correlation factors were gotten from the plots ,Freundlich adsorption constant k_f was calculated from the equations and relations. The Freundlich adsorption constant k_f for Mn were (0.48) and(3.14) respectively for $nHAP_n$ and $nHAP_E$ while the correlation factor R^2 was (0.747) and (0.74) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (13).

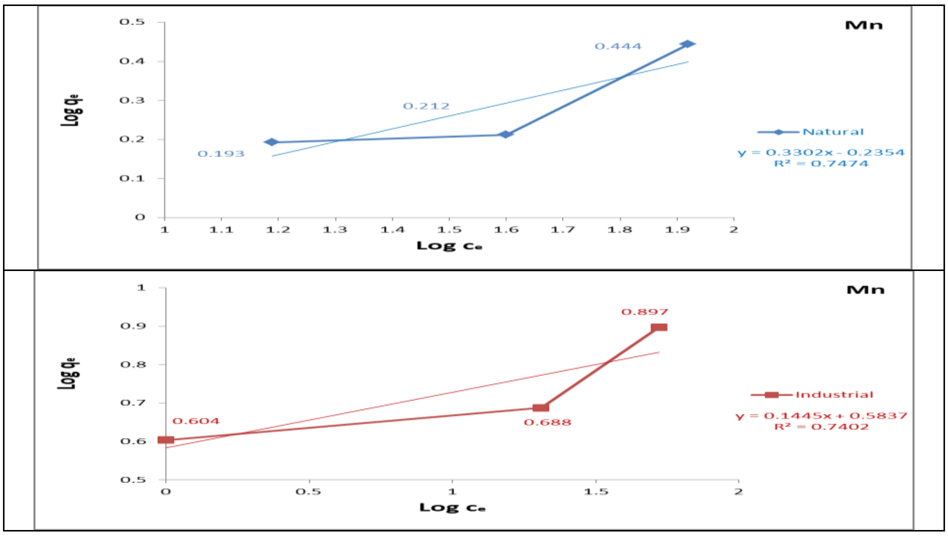
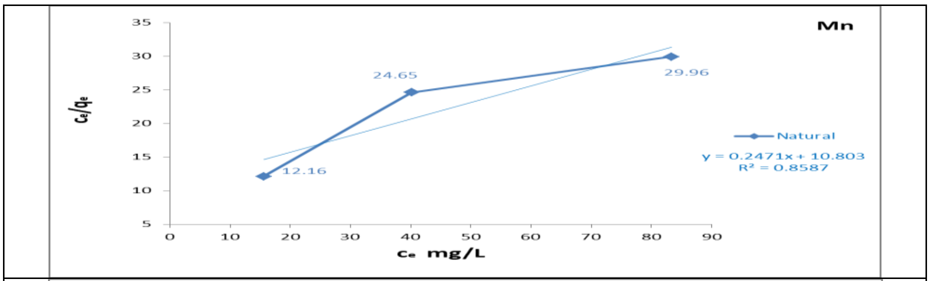
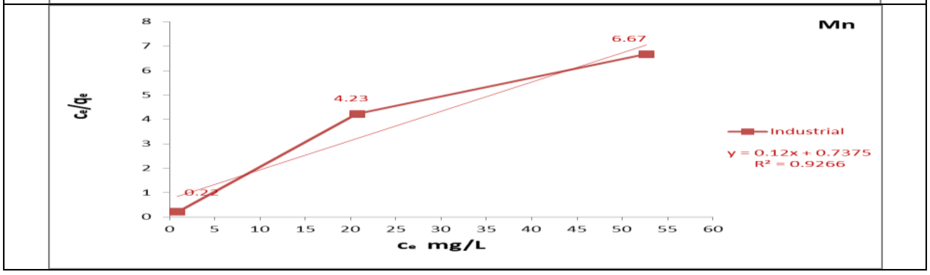


Fig.(13): The Freundlich isotherm plot for Mn

The Langmuir equation is given by : (c_e / q_e = 1/k_L q_{max} + c_e / q_{max}) where q_e(mg/g) is the amount adsorbed on natural and chemical nanohydroxyapatite at equilibrium,the maximum adsorption monolayer capacity is q_{max} (mg/g) where k_L is the Langmuir constant related to the affinity between the adsorbate and the adsorbent, and is related to the free energy of adsorption ,the concentration of iron or manganese in liquid phase at equilibrium is C_e (mg/l), y = mx + b where (m) is the slope and b is the intercept which (b) = 1/ q_{max} k_L,the slope, the intercept and the correlation factors were gotten from the plots, Langmuir adsorption constant k_L was calculated from the equations and relations,the Langmuir adsorption constant k_L for Mn were (0.035) and (0.078) respectively for $nHAP_n$ and $nHAP_E$ while the correlation factor R^2 was (0.858) and (0.926) respectively for $nHAP_n$ and $nHAP_E$ as shown in Figure (14) (Shokry and Hamad 2016, Elnsar, Soliman *et al*. 2017).





Fig(14): The Langmuir isotherm plot for Mn

According to the model results, the Langmuir isotherm model is better than Freundlich isotherm model in case of (Mn) (Shokry and Hamad 2016, Elnsar, Soliman *et al*. 2017).

Using $nHAP_n$ and $nHAP_E$ to remove manganese from drinking water: Two samples of drinking water were collected from water tanks in cairo-suez road ,by using ICP/MS 7700 device the concentration of Mn were (2.18 ppm) and (2.32 ppm) in water tank number (1) and water tank number (2) respectively.

At pH 7, adsorbent dose equal 0.3 gram and temperature 25 c^o, the maximum removal efficiency of Mn were (44.03%) and (94.03%) respectively for $nHAP_n$ and $nHAP_E$ for water tank number (1) while the maximum removal efficiency of Mn were (52.58%) and (98.96%) respectively for nHAPn and $nHAP_E$ for water tank number (2).

The maximum adsorption capacity of Mn were (0.12mg/g) and (0.27mg/g) respectively for $nHAP_n$ and $nHAP_E$ for water tank number (1) while the maximum adsorption capacity of Mn were (0.16mg/g) and (0.3mg/g) respectively for nHAPn and $nHAP_E$ for water tank number (2).

CONCLUSION

The results showed that the manfacturing processes of the two methods were succeeded.

The best results were identified at specific conditons (pH equal 7), (adsorbent dose 0.3 gram), (initial concentration 25 ppm) and (contact time 60 minute).

The surface area of $nHAP_E$ and $nHAP_n$ were (78.019 m^2/g) and (26.028 m^2/g) respectively, the surface area of $nHAP_E$ equal three times the surface area of $nHAP_n$.

The particles size of $nHAP_E$ and $nHAP_n$were(169.9-251.5) nm and(471.5-514.6) nm respectively, the particles size of $nHAP_E$ equal almost three times the particles size of $nHAP_n$.

The manufacturing process price of the $nHAP_E$ for (1) kilo costs about (250) Egyptian pound while the manufacturing procees price of the $nHAP_n$ for (1) kilo costs nothing because it was manufactured from fish bones waste.

According to the results of the correlation coefficient R^2, the Langmuir isotherm model is better than Freundlich isotherm model in case of manganese (Mn) .

So by using all these results ,items and conditions, it is better to use the natural nanohydroxyapatite than chemical nanohydroxyapatite to remove manganese from drinking water acoording to :

- The manufacturing process price of the $nHAP_n$ for (1) kilo costs nothing because it was manufactured from fish bones waste.
- The manufacturing process of the $nHAP_n$ is very friendly for environment and didn’t cause any pollution.

There is no a big difference in the removal efficiency and adsorption capacity between natural and chemical nanohydroxyapatite according to the price.

RECOMMENDATIONS

So it is better to use the natural nanohydroxyapatite than chemical nanohydroxyapatite to remove manganese from drinking water especially there is a small difference in the removal efficiency and adsorption capacity between natural and chemical nanohydroxyapatite according to the price, the manufacturing process price of the $nHAP_n$ costs nothing because it was manufactured from fish bones waste and it is very friendly for environment and didn’t cause any pollution, also nanohydroxyapatite can be used to remove heavy metals to replace the high cost adsorbents such as activated carbon.

RECOMMENDED FUTURE STUDIES

It is suggested to study the effect of chemical and natural nanohydroxyapatite to remove organic pollutants from waste water.

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إزالة المنجنيز من مياه الشرب بإستخدام الهيدروكسى أباتيت النانونى

سامح محمد فؤاد[١]**– نهى سمير دنيا** [٢]**– طه عبدالعظيم محمد**[٢]**– محمد أحمد رضا**[٣]

١) طالبة دراسات عليا بمعهد الدراسات والبحوث البيئية، جامعة عين شمس ٢) معهد الدراسات والبحوث البيئية، جامعة عين شمس ٣) مدرس بالجامعة الكندية الدولية

المستخلص

فى هذا البحث، تم تخليق الهيدروكسى أباتيت النانونى الطبيعى من خلال طحن عظام السمك البلطى وتحويلها إلى الهيدروكسى أباتيت ثم تنشيطه بإستخدام درجة حرارة تصل إلى ٧٠٠ درجة مئوية ليتحول لمادة نانونية وأيضا تم تخليق الهيدروكسى أباتيت النانونى الصناعى عن طريق تفاعل كربونات الكالسيوم وفوسفات الكالسيوم المائية وتحويلها إلى الهيدروكسى أباتيت ثم تنشيطه بإستخدام درجة حرارة تصل إلى ٨٠٠ درجة مئوية ليتحول لمادة نانونية . تم توصيف العينات التى تم تحضيرها بإستخدام التحليل الطيفي للأشعة السينية المشتتة من الطاقة (EDX)، حيودالأشعة السينية (XRD) ،التحليل الطيفي للأشعة تحت الحمراء (FTIR)، مساحة السطح (BET)، الميكروسكوب الإلكتروني الماسح الضوئي (SEM) ,التحليل الطيفى للأشعة تحت الحمراء (RAMAN) .أظهرت دراسة التوصيف تحسناً كبيراً في العديد من الخواص الإمتزازية للهيدروكسى أباتيت المخلق (الصناعى) والطبيعى، مثل مساحة السطح، الشكل السطحي حيث تم تسجيل زيادة في مساحة سطح الهيدروكسى أباتيت على أنها ٧٨,٠١٩ م٢ / جم و ٢٦,٠٢٨ م٢ / جم لكل من الهيدروكسى أباتيت الصناعى والطبيعى على التوالي . تمت دراسة تأثير الأس الهيدروجينى والتركيز وكمية الهيدروكسى أباتيت وأفضل وقت على قدرة الإدمصاص. أظهرت النتائج أن أفضل أس هيدروجينى كان عند درجة التعادل (٧)، والجرعة المثلى عند ٠,٣ جرام، وأفضل وقت (٦٠) دقيقة. تم الحصول على أقصى إزالة للفلزات الثقيلة (المنجنيز) بواسطة الهيدروكسى أباتيت النانونى الصناعى بنسبة (٩٩,٥٩ ٪) للمنجنيز، بواسطة الهيدروكسى أباتيت النانونى الطبيعى بنسبة (٨٣,٧٣ ٪) للمنجنيز. من النتائج الواردة يفضل إستخدام الهيدروكسى أباتيت الطبيعى عن الصناعى لإزالة المنجنيز من مياه الشرب حيث أنه صديق للبيئة ويتم إنتاجه من مخلفات الأسماك وعديم التكلفة .

الكلمات الدالة : الإمتزاز، المعادن الثقيلة، الهيدروكسى أباتيت الصناعى والطبيعى.