# Use Apricot Seed Peels as Adsorbents to Removal of Mn2+ and Zn2+ Ions from Aqueous Solutions

Mohammed Challab, Firas Alhameedawi and Salam Al-Alaq



December 25, 2020

# Use apricot seed peels as adsorbents to removal of $Mn^{2+}$ and $Zn^{2+}$ ions from aqueous solutions

Mohammed Khlaif Challab., Firas Ali Hussein Alhameedawi., Salam Hussein Al-Alaq


## Abstract

This research included the use of apricot seeds peels after converted into activated carbon and carbon nano as low cost adsorbents for removal of $Zn^{2+}$ and $Mn^{2+}$ from aqueous solutions. It was a perfect time (25min), initial concentration (5mg.L$^{-1}$), weight adsorbent (0.5g), temperature (30°C) and the optimum of pH was (3-4) for adsorption $Mn^{2+}$ and $Zn^{2+}$ respectively by adsorbents. Technique FTIR were used to determine the capability of this sample to the removal of heavy metal and technique TEM on sample from carbon nano. The ability of the adsorbents $Mn^{2+}$ to adsorb high than $Zn^{2+}$ and the removal by carbon nano was higher than that of activated carbon.


**Keyword:** Activated carbon, Apricot seed peels, Carbon nano, Sewage water.

## 1-Introduction

The application of the rules of environmental monitoring in the area of freshwater management plays an important role in preserving the purity of this water and avoiding the population and the economic organisms the risk of infection or infection of many diseases resulting from the  of organic pollution and spread of microorganisms and parasites of these important sources in the life human communities that rely directly on these waters in most of their social, agricultural and life activities **Ram *et al.* (2011).** Become it has more complicated when different industries and technologies have grown and the resulting of chemical residues, toxins and environmentally hazardous waste, as well as the huge expansion in the use of pesticides, disinfectants, sewage and industrial wastewater and the random spread of service workshops. All these activities contaminate water resources, especially rivers, streams, canals and inland lakes for various types of pollutants, including toxic metals **Abdul Razzak and Sulayman (2009)**. The sources of water available for drinking and household purposes must be of high purity and free from chemical pollution and microorganisms. The pollution of the aquatic environment with heavy elements become an important problem around the world because most of them have toxic effects on living organisms. Some of them are harmful even in their low concentrations. Because are not fully degradable and remain partially stuck or dissolved in the water column and enter the body through food, air or contaminated water and accumulate over time causing various damage to the organism **Borul and Banmero (2012).** Some researchers have conducted many experiments to estimate and remove heavy metals from different water sources. Studied **Demirbas *et al*. (2009)**. Removal of Cu(II) by hazelnut shell as activated carbon from aqueous solutions. A compare of the kinetic models on the overall adsorption rate display that the adsorption system was best pseudo second-order for equation. Studied **Nair *et al*. (2010).** on the pollution of the Meenachil River in India with heavy elements, the water of this river is not suitable for drinking purposes due to the high concentration of iron, lead and cadmium. This has been attributed to the discharge of domestic waste water, cities waste and agricultural activities, how to remove them.Search **HALBOOS (2012).** Green tea waste was used to remove the Ni(II) of its water solutions. Adsorption experiments were conducted under different conditions where the batch method was used to estimate the best adsorption rate. The results showed that the best concentration was 10mg, where the adsorption rate was 92%. **Bernard *et al*. (2013)**. Activated carbon Prepared by coconut shell was used to adsorption Cu(II), Fe(II), Zn(II) and Pb(II) from industrial wastewater. The activated carbon produced was chemically activated by $ZnCl_2$. Explained **Jarullah *et al*. (2014).** The removal Ni(II) from water solution using prepared charcoal from the Bitter Orange and commercial activated charcoal the as adsorbent surfaces. Adsorption was at pH(5). The latter was analyzed according to Langmuir and Freundlich models.

**Zahir (2016)** Included the study of extracting a natural substance (tank acid) from pomegranate husks, which is used as a basic material in the treatment of water pollution in heavy elements using high performance liquid chromatography technique. Studied **Basu *et al*. (2017).** Cucumber peel were used remove Pb(II) from sewage water, was conducted under the influence of the initial concentration of metal and the contact time, acidity and the efficiency of adsorption reaches 96.6% at the contact time 60s pH(5) Studied **Sajid *et al*. (2018).** Adsorption of organic pollutants and heavy metals from waste water using dendritic some polymers based adsorbents**.** The discovery of carbon nanotubes (CNTs) as a modern type of adsorbent because their unique properties, which leads to water treatment. Removal of heavy metals from industrial wastewater leads to the biggest challenge nowadays. To reduce environmental problems, the CNTs new type for the removal of heavy metals suggested by **Mubarak *et al*. (2014)**. Included the study **Zhu *et al*. (2016).** Multi-walled carbon nanotubes (MCNTs) were sparse in graphene oxide (GO) colloids to be further functionalized with (DETA), resulting in GO–MCNTs–DETA nanocomposites, the GO–MCNTs–DETA was successfully used to separation Pb(II), Mn(II), Cr(III) and Fe(III) ions in sewage samples**.** Explained **Ghasemi *et al*. (2017).** A New nano sorbent were synthesized, EDTA functionalized $Fe_3O_4$ nanoparticles was and used for the adsorption and removal of Zn(II), Pb(II), Hg(II), Ag(I), Cd(II) and Mn(II). The results detect that the nano adsorbent could be used as a high functional, fast functional, reusable and cost-effective material for the removal of polluted ions, from contaminated water and soil samples.

## i- Experimental

## 1- Instrumentals

The important devices were used in the adsorption experiments was following Flame atomic absorption spector photometer (AAS), Muffle furnace, FTIR spectroscopy, Transmission electron microscopy (TEM) and Ball mill.

## 2- Materials and solution

### 2-1- Chemical materials

High purity chemicals were used as $MnSO_4$ and $ZnCl_2.2H_2O$, $C_2H_5OH$ and KBr) distilled water was used in diluted solutions for washing tools and samples. Deionized water was also used to wash samples.

### 2-2- Manganese and Zinc standard solution

An adsorbate standard solution of 100 $mg.L^{-1}$ of $Zn^{2+}$ and $Mn^{2+}$ as salts, $MnSO_4$ and $ZnCl_2.2H_2O$ in 1000 mL of distilled water used in this experiment.

## ii- procedures

### 1- Activated carbon

The apricot seed peels was washed, after that it was dried to production the dry phase sample then grind peels into smallest size sieving the sample and the thermal activation method by converting the material into a fixed carbon mass by heating without the air after that use muffle furnace to activate the sample at (850 °C ) with an oxidizing substance (water vapor).

### 2- Carbon nano

Dried by oven at 70 °C for 30 min then grind for 20 hours by a ball mill instrumental.

### 3- Characteristic and analysis of carbon nano

## 3-1- FT-IR

The fourier transform infrared spectroscopy (FT-IR) test was performed on the carbon nano for the apricot seed peels after mixing a small amount of sample with an appropriate amount of (KBr).

## 3-2- TEM

Dissolved a quantity was of carbon nano for the apricot seed peels in 2.0mL of methanol and a quantity of solution was withdrawn and after that was analyzed by transmission electron microscope (TEM).

## 4- Removal of heavy metals by activated carbon

The procedures of adsorption by activated carbon and carbon nano

1-The adsorption of heavy metals from its solutions were by method (batch adsorption experiment) (25 mL) of a known concentration.

2-Added the adsorbent 0.5g (activated carbon) and 0.05g (carbon nano) separately to flasks at a temperature (30$^{o}$C) contact time (25min) and pH=(3-4) to $Mn^{2+}$ and $Zn^{2+}$ respectively, were shaken in a controlled shaker incubator at a constant speed (10 rpm) for the required equilibrium time.

3-The mixtures were then separated by centrifugation instrumental at (1500 rpm) for (10 min) for activated carbon samples and (6000 rpm) for (10 min) for carbon nano samples .

4-The equilibrium concentrations were measured by AAS.

## 5- Factors affecting adsorption of heavy metals by adsorbents:

Experiments were conducted under different conditions that may influence metal sorption that can be described as follows:

1- **Effect of pH:** The experiment was carried to adsorption the heavy metals from solutions out at pH (3, 4, 5, 6, 7 and 9).
2- **Effect of temperature**: The adsorption of heavy metals ions were studied at ( 20, 30, 40 and 50°C )with fixation of the others factors.
3- **Effect of weight adsorbent**: The percentage of adsorption for different weights which (0.2, 0.3, 0.4, 0.5, 0.6 and 0.7g)was determined with keeping all other factors constant.
4- **Effect of contact time** : The effect of period of contact time which are (10 , 15 , 20 , 25 , 30 and 35min) between the adsorbent and adsorbate on the removal of the heavy metal ions.
5- **Effect of initial concentration:** This experiment was conducted with several concentrations which were: (3, 5, 7 and 9mg.$L^{-1}$) with fixing other factors.

The removal percentage was calculated by applying the relation :

$$\textbf{(Removal\% =} \frac{C_0 - C_e}{C_0} \textbf{ x 100)}$$

**$C_e$**= Equilibrium concentration (mg.$L^{-1}$).

**$C_o$**= Initial concentration (mg.$L^{-1}$).

## iii- Application

After applying the factors affecting the removal of heavy metals ions $Mn^{2+}$ and $Zn^{2+}$ from aqueous solutions, the optimum conditions were applied to remove these minerals from the water (Al-Hussainiyah River in Karbala).

## iiii- Result and discussion

## 1- Characteristic and analysis of activated carbon and carbon nano

### 1-1- The (FT-IR) of activated carbon

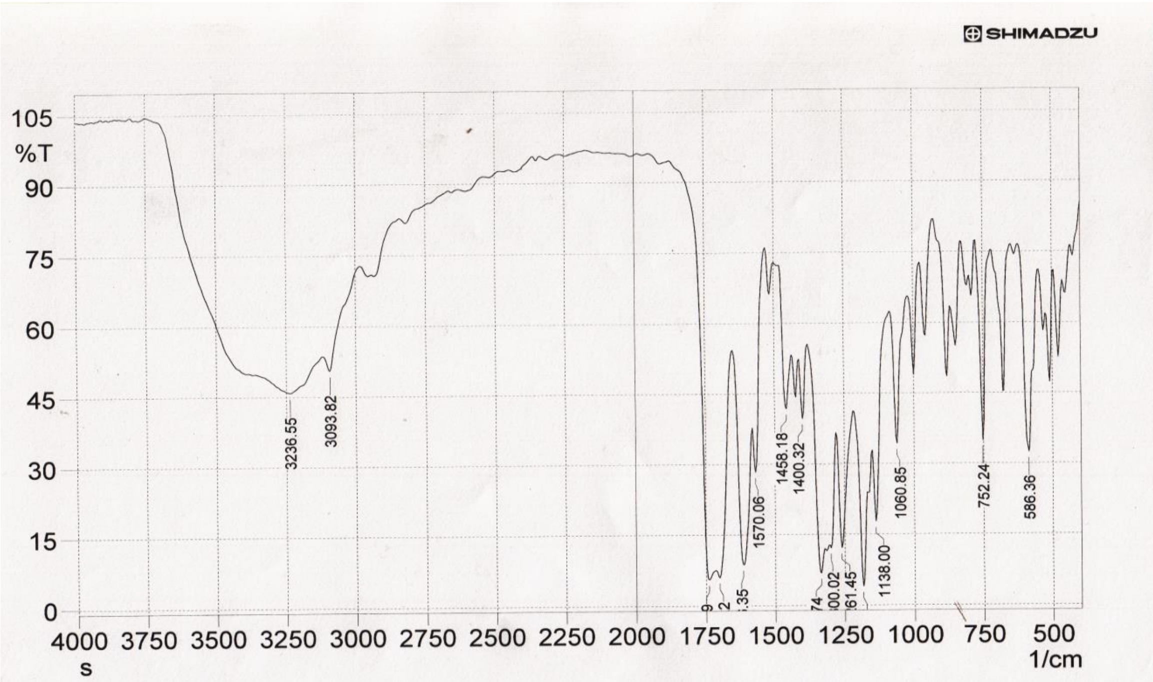


**Fig. (1): Spectrum FT-IR for activated carbon of apricot seed peels**

### 1-2- The (TEM) of carbon nano

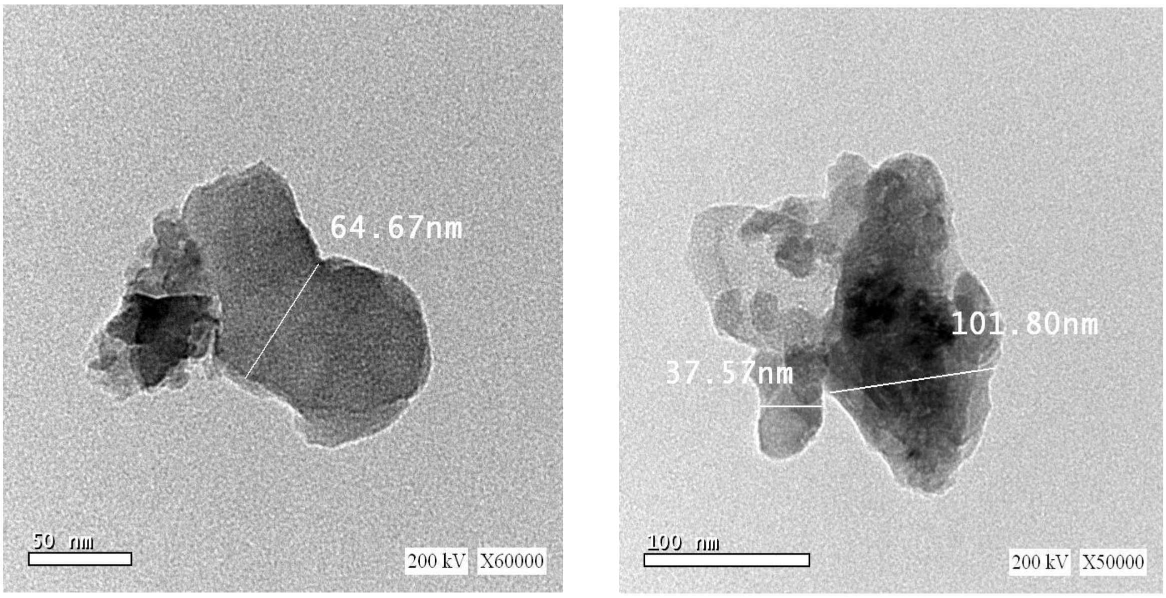


**Fig.(2): Analysis TEM for nano carbon carbon of apricot seed peels**

## 2- Factors affecting adsorption of heavy metals

## 2-1- Effect of pH

The pH is one an important factor that effect on the removal process for heavy metals, in addition plays an important role in determining the velocity of surface reactions, and the difference in the adsorption capacity at a certain range of pH. This is due to the significant influence of pH on surface adsorption properties and the effect on the adsorption process of the metal ions on the activated carbon surface Fig.(3-4) showed the highest adsorption with pH value (3) at adsorption of $Mn^{+2}$, and with pH value (4) at adsorption of $Zn^{2+}$, these values were chosen for all subsequent adsorption experiments, **Pagnanelli *et al*. (2003)**.

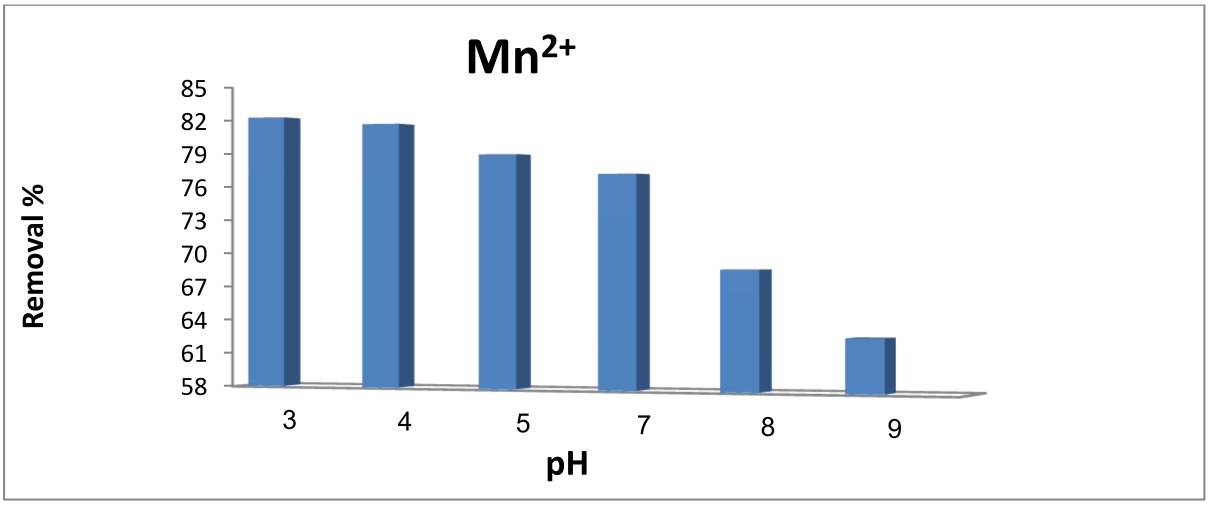


**Fig. (3): The effect of pH on the adsorption of $Mn^{2+}$**

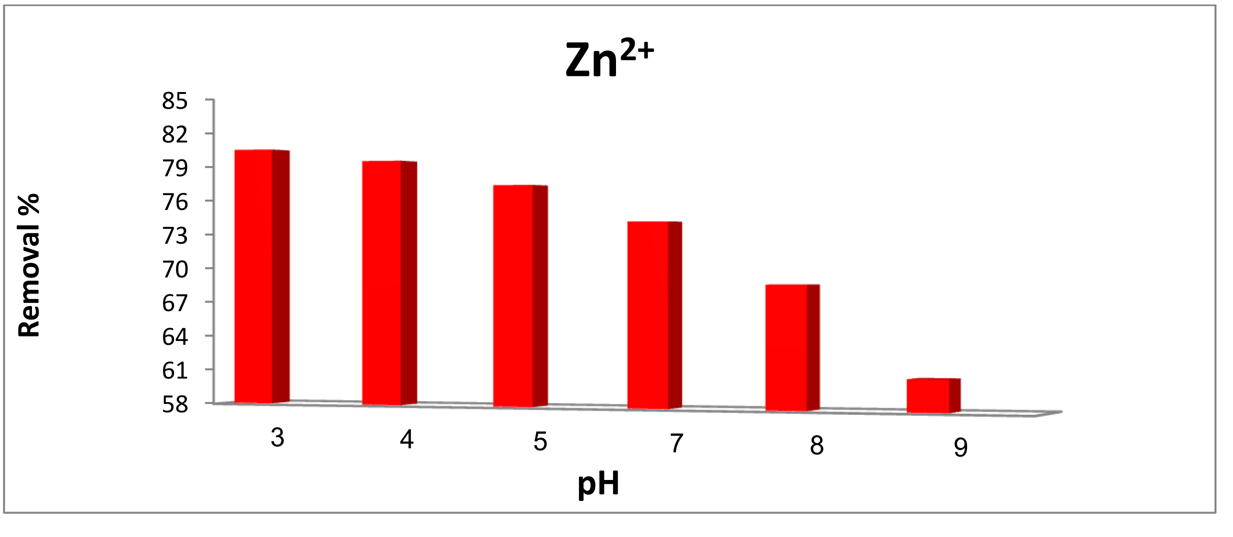


**Fig. (4): The effect of pH on the adsorption of $Zn^{2+}$**

## 2-2- Effect of temperature

A temperature is important factor that effected on the adsorption the Fig. (5 and 6) showed the adsorption percentage of $Mn^{2+}$ between (78.3-75.1) and adsorption percentage of $Zn^{2+}$ ranging between (77.5-74.8) as temperature increase, where the increase in temperature leads to an increase in the kinetic energy of the particles, which helps to separate them from the surface and return to the inside of the solution and in addition to the adsorption process, the absorption process may be a contributing factor in the removal process, **Martins *et al*. (2004)**.

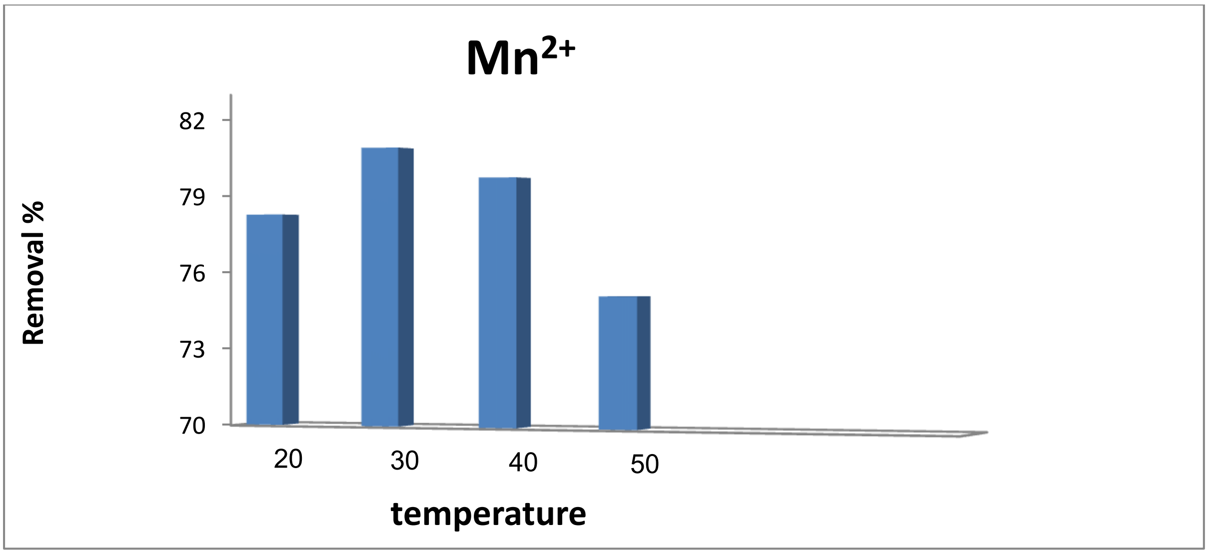


**Fig. (5): The effect of temperature on the adsorption of $Mn^{2+}$**

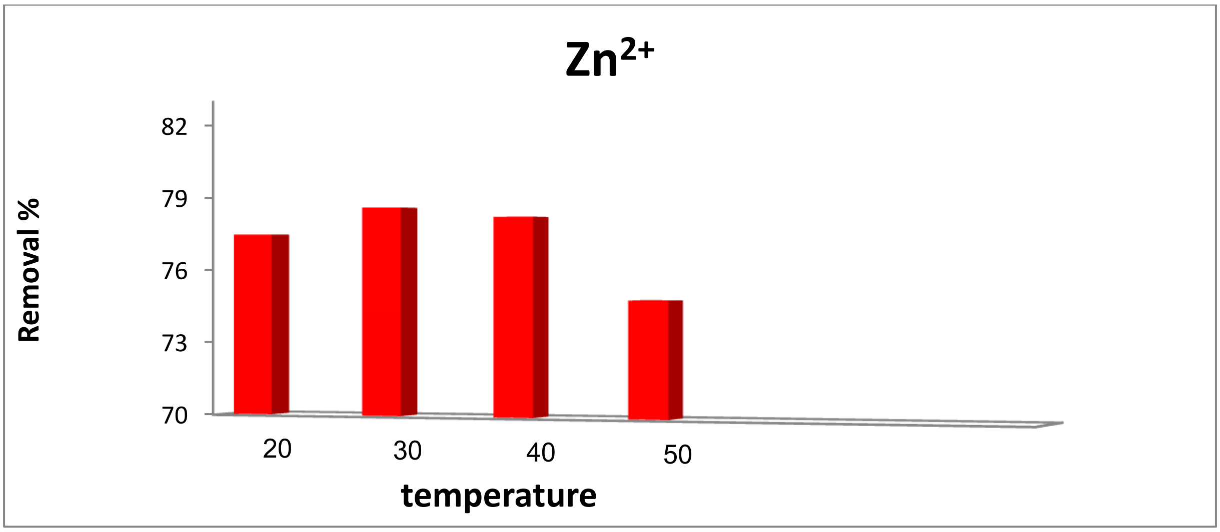


**Fig. (6): The effect of temperature on the adsorption of $Zn^{2+}$**

## 2-3- Effect of adsorbent weight

The percentage of removal of ions increases with increases the weight of the adsorbent material. The weight of 0.5g was very perfect and appropriate to obtain at best adsorption for the $Mn^{2+}$ and $Zn^{2+}$ ions studied. This is when increasing the weight of the adsorbent substance, which means increasing the number of active sites prepared for adsorption of ions on the surface, and then the amount of adsorbed ions from the solution increases, so the percentage of removal increases **Singanan, M. (2011),** as showed in Fig.(7-8).

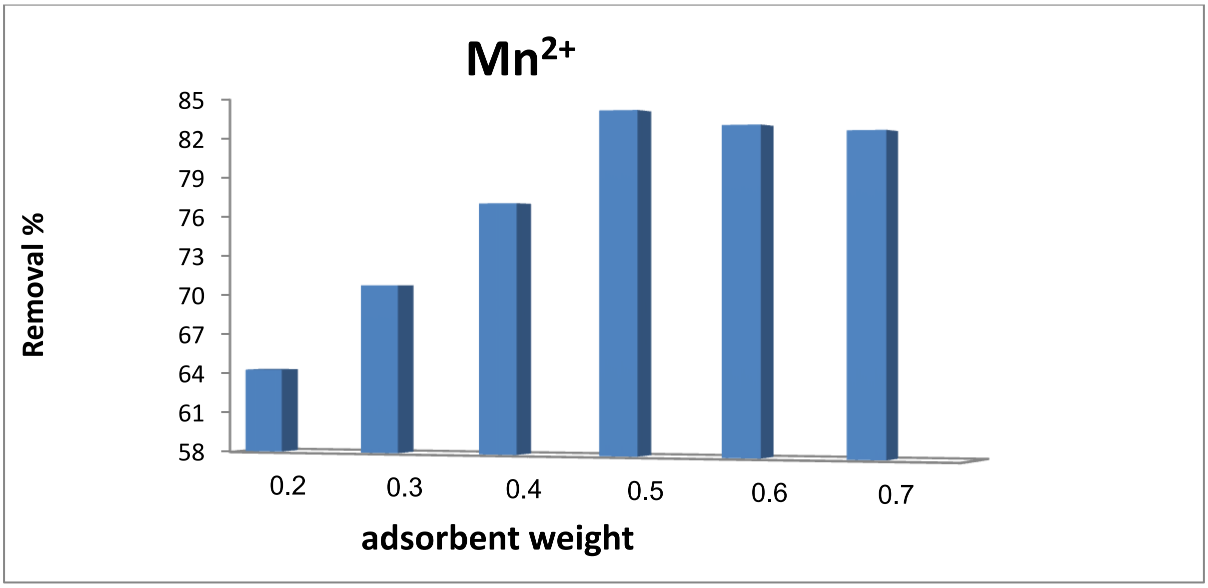


**Fig. (7): The effect of adsorbent weight on the adsorption of $Mn^{2+}$**

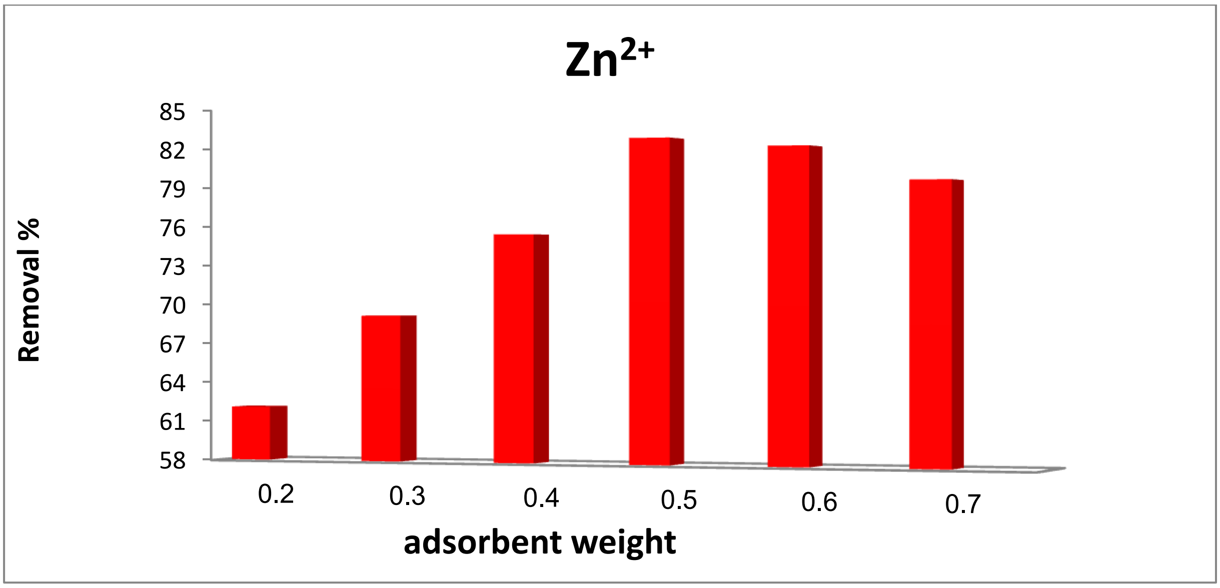


**Fig. (8): The effect of adsorbent weight on the adsorption of $Zn^{2+}$**

## 2-4- Effect of contact time

Adsorption was studied at different regular contact times ranging from (10 to 35) minutes. The results indicated that the removal process increased with increasing contact time until all active sites were satiated, as the highest absorption of $Mn^{2+}$ and $Zn^{2+}$ ions was at 25 min, **Chen *et al.* (2011),** as showed in Fig.(9-10).

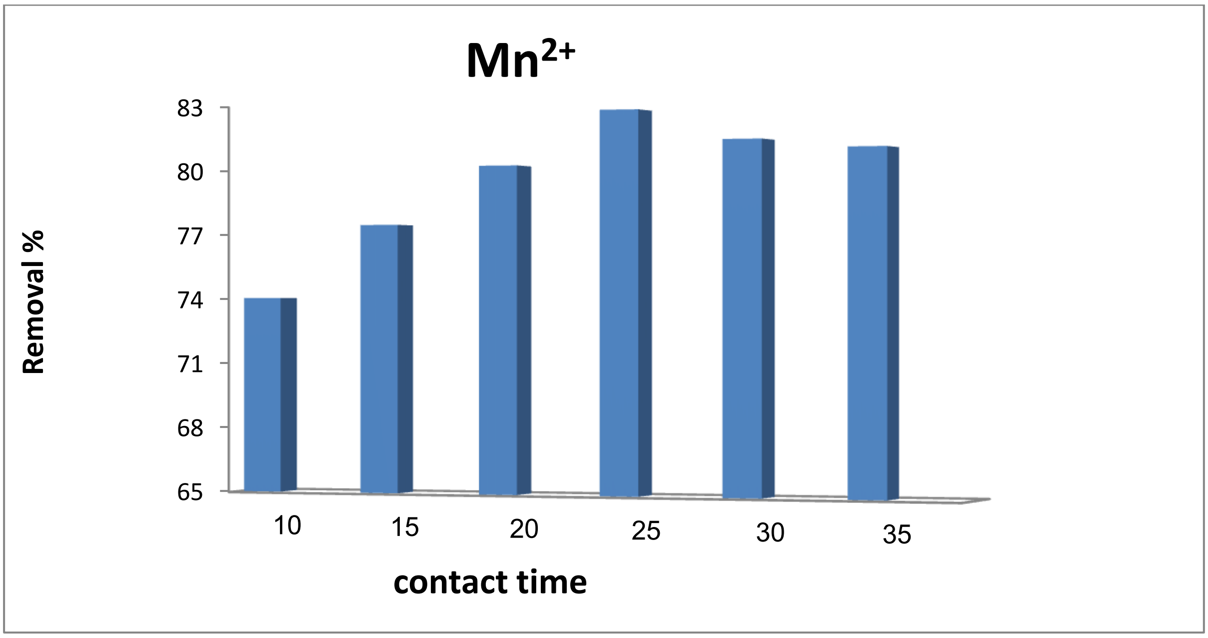


**Fig. (9): The effect of contact time on the adsorption of $Mn^{2+}$**

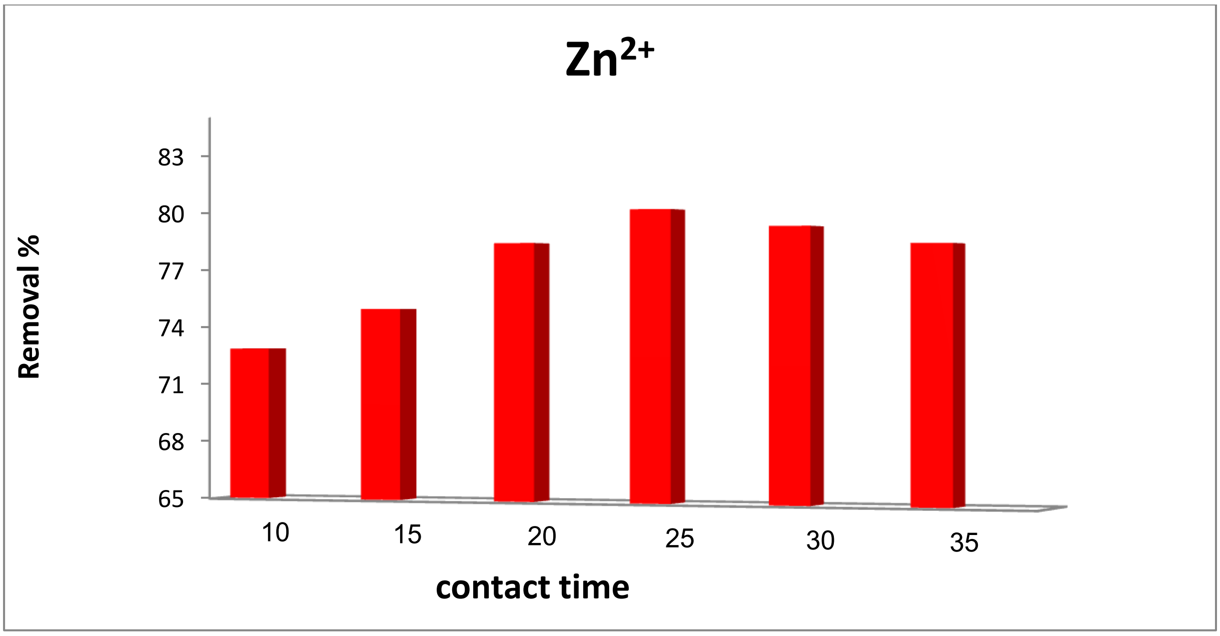


**Fig. (10): The effect of contact time on the adsorption of $Zn^{2+}$**

## 2-5- Effect of initial concentration for heavy metal

The percentage of adsorption decreases with the increase in the initial concentration of heavy metals, and this is due to the increase in concentration with the effective sites available for adsorption remaining constant. This makes the amount of the remaining substance greater, thus decreasing the percentage of adsorption of these ions, **Padmavathy *et al*. (2016)**. as showed in Fig.(11-12).

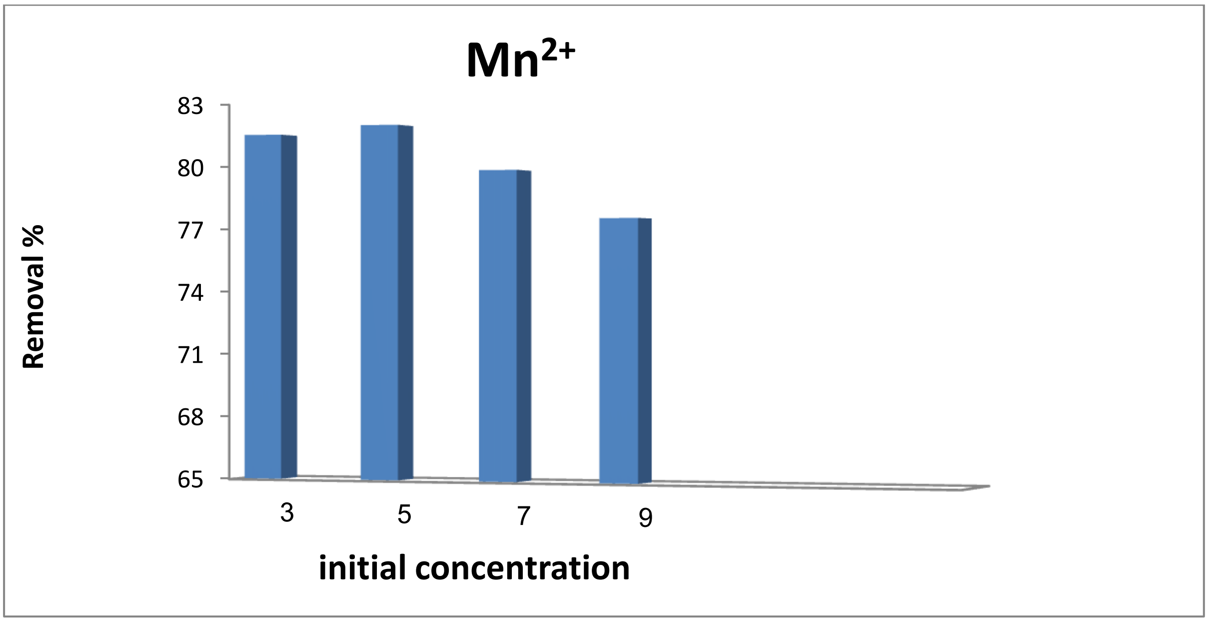


**Fig. (11): The effect of initial concentration on the adsorption of $Mn^{2+}$**

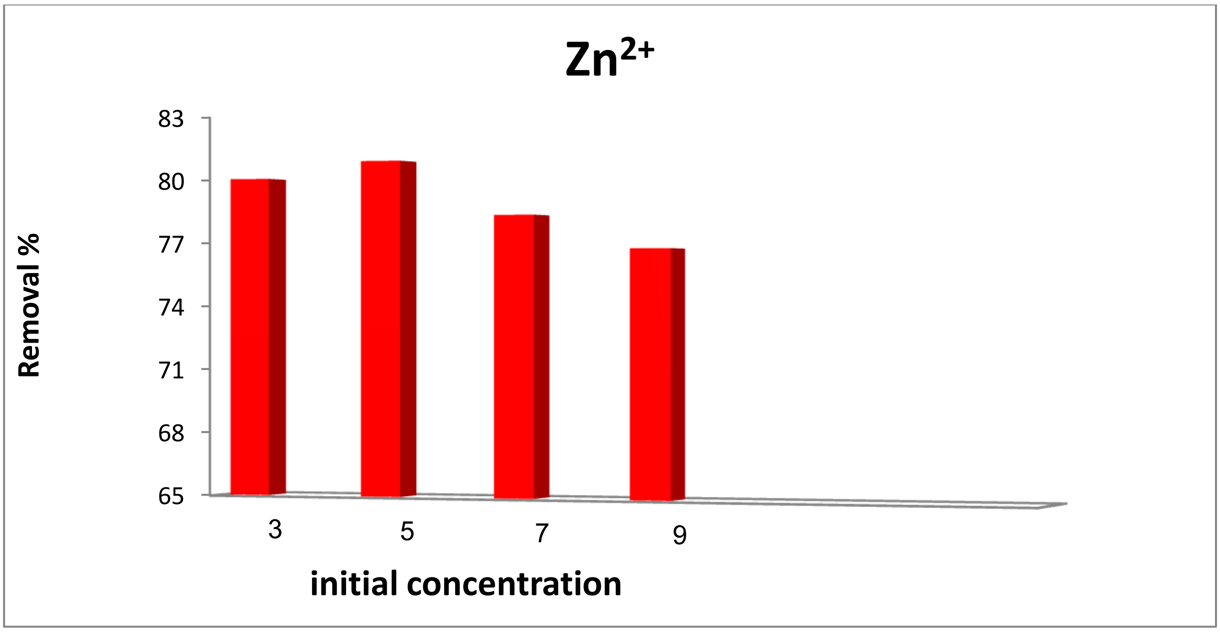


**Fig. (12): The effect of initial concentration on the adsorption of $Zn^{2+}$**

## 4- Applications of removal

### Removal of heavy metal from Al-Hussainiyah River in Karbala by carbon nano

The aim of this research was to remove heavy metals ($Zn^{2+}$ and $Mn^{2+}$) from river water using activated carbon, and to determine the optimum conditions (pH, temperature, contact time and weight). There was a decrease in the removal rate due to competition between studied ions and other ions in the water.

The effect of the size of the adsorbent particles (specific surface area) under optimal conditions using carbon nano has been applied in the adsorption process for heavy metal ions ($Zn^{2+}$ and $Mn^{2+}$). The results shown in Fig.(13) show that the percentage of adsorption increases with a decrease in the size of the adsorbent particles (increase in the surface area). The increase in the specific surface area (decrease in the volume of minutes) compared to activated carbon means an increase in the number of effective sites exposed to the adsorbent material, and the more the greater the number of active sites on the surface, the greater the percentage of adsorption **Khongkasem *et al.* (2010).**

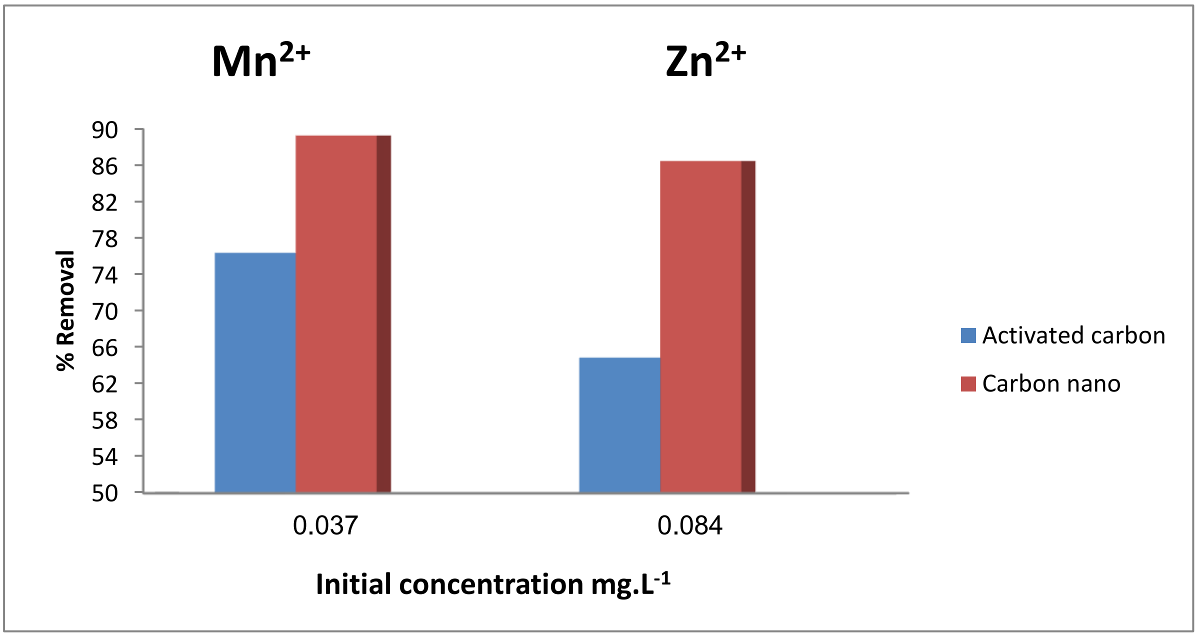


**Fig. (13): The removal of $Mn^{2+}$ and $Zn^{2+}$ ions from river water**

## 5-Conclusion

The present study shows the possibility of using agricultural wastes (apricot seed peels) in the form of activated carbon or carbon nano as a low-cost sorbent in the removal of river water contamination with heavy metals ($Zn^{2+}$ and $Mn^{2+}$) under ideal conditions that were identified during the experiment. The results indicate the adsorbent's ability to absorb these minerals in the following order: $Mn^{2+} > Zn^{2+}$. The removal by carbon nano is higher than the activated carbon.

## References:


- **Abdul Razzak, I. A. and Sulayman, A. H. (2009).** Effects of Discharging Sewage of Baghdad To Tigris River on The Water Quality, *International Journal of Engineering & Technology*, 27(16).
- **Borul, S. B., & Banmeru, P. K. (2012).** Physiochemical analysis of ground water for drinking from selected sample points around the Manmeru Science College, Lonar Buldana district of Maharashtra. *Journal of chemical and pharmaceutical research, 4(5), 2603-2606.*
- **Ram, S. L.; Pravin U. S. and Deepali, S. (2011)**. Pollution in Water of Kasardi River Flowing along Taloja Industrial Area of Mumbai, India. *World Environ. 1(1): 6-13.*
- **Nair, I. V., Kailash, S., Arumugam, M., Gangadhar, K., & Clarson, D. (2010).** Trace metal quality of Meenachil river at Kottayam, Kerala (India) by principal component analysis. *World Applied Sciences Journal, 9(10), 1100-1107*.
- **HALBOOS, M. H. N. (2012).** Adsorption of Nickel Ions From Aqueous Solutions by Green Tea Waste. *journal of al-qadisiyah for pure science (quarterly), 17(4), 59-70.*

- **Demirbas, E., Dizge, N., Sulak, M. T., & Kobya, M. (2009)**. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Chemical Engineering Journal, 148(2-3), 480-487.*

- **Bernard, E., Jimoh, A., & Odigure, J. O. (2013**). Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell. *Research Journal of Chemical Sciences ISSN, 2231, 606X.*

- **Zahir,S.A. (2016)** Study of tannic acid extraction from Pomegranate husks and applications in ion removal Chromium(III) of industrial water, *22 (94), 137-154.*

- **Jarullah, A. A., Alias, M. F., & Hassan, K. H. (2014).** Purification of Aqueous Solution from Ni (II) Ions Using Commercial and Bitter Orange Leaves Activated Charcoal. *Al-Nahrain Journal of Science, 17(1), 32-40.*

- **Basu, M., Guha, A. K., & Ray, L. (2017).** Adsorption of lead on cucumber peel. *Journal of Cleaner Production, 151, 603-615.*
- **Sajid, M., Nazal, M. K., Baig, N., & Osman, A. M. (2018).** Removal of heavy metals and organic pollutants from water using dendritic polymers based adsorbents: a critical review. *Separation and Purification Technology, 191, 400-423*.
- **Mubarak, N. M., Sahu, J. N., Abdullah, E. C., & Jayakumar, N. S. (2014).** Removal of heavy metals from wastewater using carbon nanotubes. *Separation & Purification Reviews, 43(4), 311-338.*
- **Zhu, X., Cui, Y., Chang, X., & Wang, H. (2016).** Selective solid-phase extraction and analysis of trace-level Cr (III), Fe (III), Pb (II), and Mn (II) Ions in wastewater using diethylenetriamine-functionalized carbon nanotubes dispersed in graphene oxide colloids. *Talanta, 146, 358-363.*
- **Ghasemi, E., Heydari, A., & Sillanpää, M. (2017).** Superparamagnetic Fe3O4@ EDTA nanoparticles as an efficient adsorbent for simultaneous

removal of Ag(I), Hg(II), Mn(II), Zn(II), Pb(II) and Cd(II) from water and soil environmental samples. *Microchemical Journal, 131, 51-56.*

- **Pagnanelli, F., Esposito, A., Toro, L., & Veglio, F. (2003).** Metal speciation and pH effect on Pb, Cu, Zn and Cd biosorption onto Sphaerotilus natans: Langmuir-type empirical model. *Water research, 37(3), 627-633.*
- **Chen, Y. G., Ye, W. M., Yang, X. M., Deng, F. Y., & He, Y. (2011)**. Effect of contact time, pH, and ionic strength on Cd (II) adsorption from aqueous solution onto bentonite from Gaomiaozi, *China. Environmental Earth Sciences, 64(2), 329-336.*
- **Padmavathy, K. S., Madhu, G., & Haseena, P. V. (2016).** A study on effects of pH, adsorbent dosage, time, initial concentration and adsorption isotherm study for the removal of hexavalent chromium (Cr(VI)) from wastewater by magnetite nanoparticles. *Procedia Technology, 24, 585-594.*
- **Martins, R. J., Pardo, R., & Boaventura, R. A. (2004).** Cadmium (II) and zinc (II) adsorption by the aquatic moss Fontinalis antipyretica: effect of temperature, pH and water hardness. *Water Research, 38(3), 693-699.*
- **Singanan, M. (2011).** Removal of lead (II) and cadmium (II) ions from wastewater using activated biocarbon. *Science Asia, 37(2), 115-119.*
- **Khongkasem, E., Khlongkarnpanich, N., Weangkaew, W., & Wantala, K. (2010).** Effect on adsorption of Cd(II) ions by modified coir pith as agricultural waste. *Journal of Metals, Materials and Minerals, 20(3), 73-76.*