



## Removal of Fe (II) and Zn (II) ions from Aqueous solutions by Synthesized Chitosan

Angham G. Hadi\*

Babylon University, College of Science, Chemistry Department, Hilla, 5001, Iraq.

**Abstract:** Adsorption of Fe (II) and Zn (II) ions from aqueous solution onto chitosan was investigated in a batch system. The effects of initial ions concentration, solution pH, time and temperature were studied. Results indicated that chitosan could be used as a biosorbent to remove the ions from contaminated water. Synthesis of chitosan involved three main stages, demineralization, deproteinization, and deacetylation. Chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid.

**Keywords:** Adsorption; heavy metals; Chitosan, synthesized.

### 1. Introduction

The toxic metals, existing in high concentrations (even up to  $500 \text{ mg.L}^{-1}$ ), have to be effectively removed from wastewaters<sup>1</sup>. In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely studied. Their presence in streams and lakes has been responsible for several types of health problems in animals, plants and human beings<sup>2</sup>.

There are various physical-chemical methods of such polluted water treatment e.g. neutralization, ion exchange, precipitation, sorption, membrane processes, filtration, photocatalytic degradation and adsorption<sup>3-24</sup>. The choice of the suitable methods is based not only on the concentration of heavy metals in surface water but on economical factors, too. Sorption belongs to effective and economically acceptable methods to remove heavy metals<sup>25</sup>. To see the decrease of polluted water most researches were concentrated with treatment of heavy metals from industrial wastewater. It uses normal material to removal metals from different sides because it is valid largely in agriculture processes in addition to their low price as adsorbent materials<sup>26-31</sup>. The methods of dye removal from industrial wastewaters could require many processes such as biological treatment, coagulation, electrochemical techniques, adsorption, and oxidation. Among these methods, adsorption is considered an effective and economical method to remove ions from wastewaters<sup>26-37</sup>. It has been reported that many different types of adsorbents are effective in removing ions from aqueous effluents. Natural polymeric materials are gaining more and more interest for application as adsorbents in wastewater treatment due to their biodegradable and non-toxic nature. Currently, the most common procedure involves the use of activated carbon<sup>38,39</sup>. Activated carbon is regarded as an effective but expensive adsorbent due to the high cost of manufacturing and regeneration. Because of its relatively high cost, there have been attempts to utilize low cost and naturally occurring adsorbents. There are many different studies on the use of low cost materials such as various agricultural wastes<sup>32,40-42</sup>, Chitosan (CS) offers an interesting set of characteristics, including non-toxicity, biodegradability, biocompatibility, and bioactivity. Chitosan and its derivatives have been extensively investigated as biosorbents for removal of heavy metals and dyes<sup>43,44</sup>.

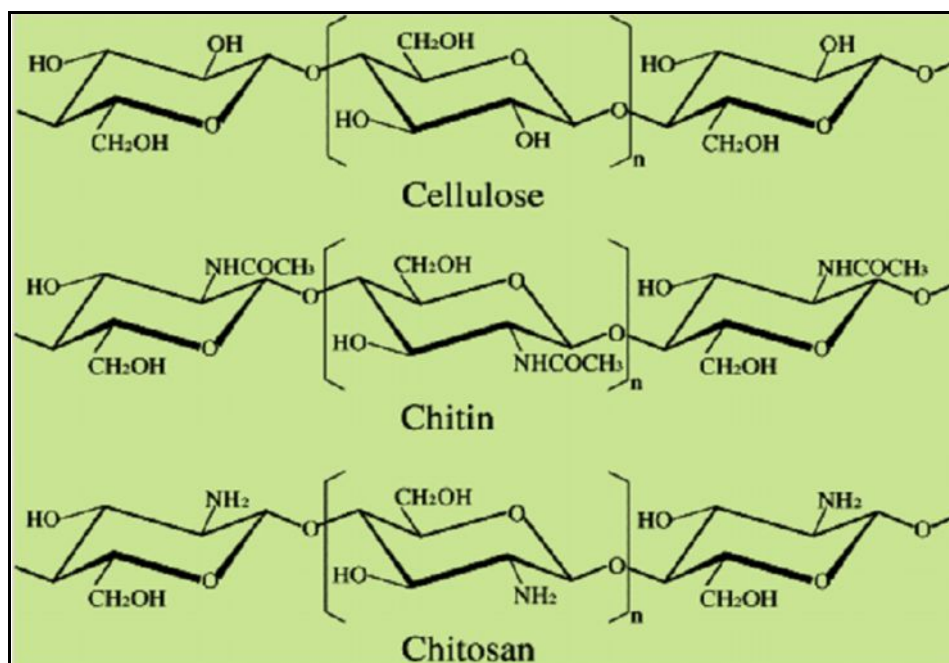


Figure1; Chemical structures of chitin, chitosan and cellulose.

The present paper is focused on utilization of the low cost sorbent chitosan to remove heavy metal ions such as  $Zn^{2+}$  and  $Fe^{2+}$  from model acidic solutions. The removal efficiency and the sorption capacity were determined. The studied parameters were heavy metal ions concentrations, contact time and changes of the pH solution during the experiment.

## 2. Materials and methods

### 2.1. Preparation of Sorbent:

Traditional isolation of chitin consists of three traditional steps as shown in (Figure 2): demineralization (DM), deproteinization (DP), and deacetylation (DA).

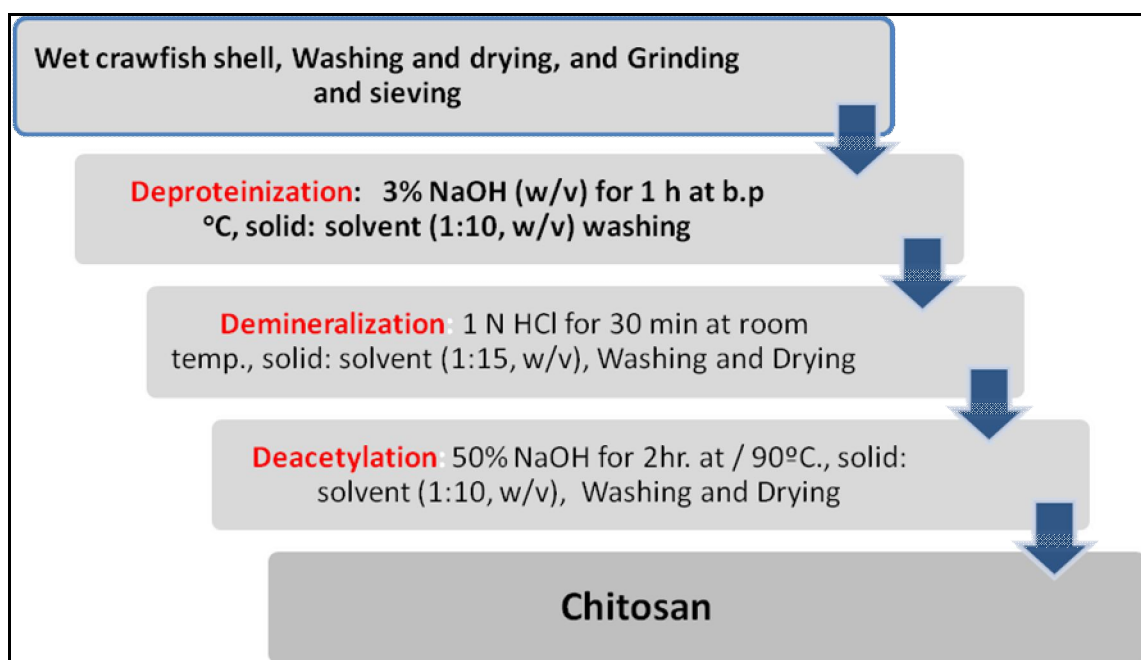


Figure 2; A simple Scheme of Chitosan Production.

## 2. 2. Batch adsorption experiments

A stock solution of heavy metals (1.0 g/L) was prepared by dissolving 1.48 and 1.13 g of  $Zn^{2+}$  and  $Fe^{2+}$  powder in 1 L of double distilled water. The desired concentrations ranging from 10 to 60 mg/L were obtained by dilution. For each adsorption experiment, 50 ml of the ions solution with a specified concentration was stirred at 100 rpm in a glass flask. The pH of solutions was adjusted to a desired value by adding dilute NaOH or HCl solution. Batch adsorption experiments were carried out using a thermo stated shaker for a certain contact time at a determined temperature at 100 rpm.

Batch adsorption experiments were carried out to examine effects of adsorbent dosage, initial dye concentration, solution pH, and time on the adsorption of ions on chitosan.

The amount of ions adsorbed on chitosan (at a predetermined time  $t$ ),  $qt$  (in mg/g), was determined using the mass balance equation:

$$qt = (C_0 - Ct) \times m / v \quad \dots\dots\dots (1)$$

The decolorization rate ( $\eta$ ) of ions was calculated by the following equation:

$$\mu = (C_0 - Ct) / C_0 \times 100\% \quad \dots\dots\dots (2)$$

Where  $C_0$  is the initial concentration of ions (in mg/L),  $Ct$  (in mg/L) is the instant concentration of ions at a predetermined time  $t$ ,  $V$  is the volume of the solution (in L), and  $m$  is the mass chitosan (in g).

## 3. Results and discussion

### 3.1. Effect of adsorbent dosage

The effect of adsorbent dosage (varied from 0.025 to 0.25 gm) on the percentage removal of 50 mg/L ions solution is shown in Fig. 3. The percentage removal of ions from the solution increased from (30% to 86%) for  $Zn^{2+}$  and (20% to 72%) for  $Fe^{2+}$  as the adsorbent dosage increased from 0.025 to 0.25 gm. This result is expected because of the increased adsorbent surface area and availability of more adsorption sites caused by increasing adsorbent dosage<sup>45</sup>.

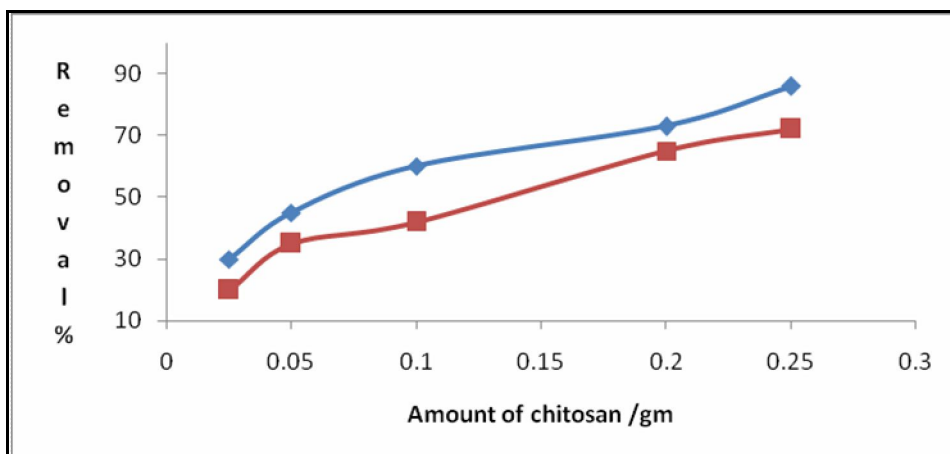
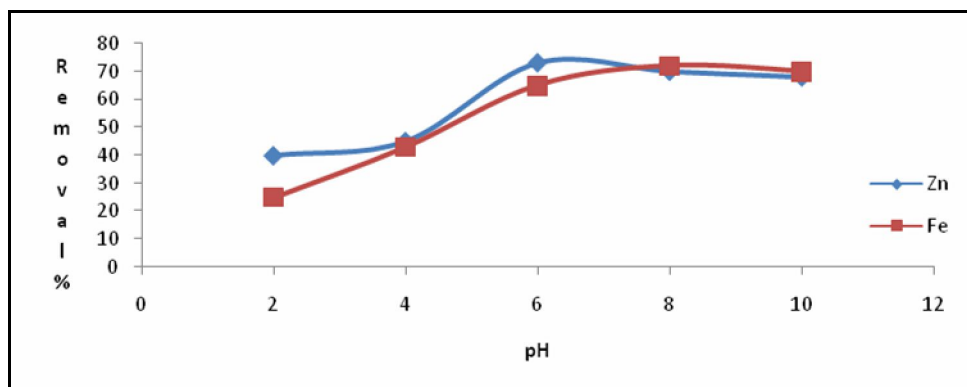


Figure3; Effect of adsorbent dosage in ions removal.

### 3.2. Effect of solution pH

The pH of the ions solution affects the surface charge of the adsorbent, the degree of ionization of the materials, and the dissociation of functional groups on the active sites of the adsorbent<sup>5,46,47</sup>. The percentage removal of ions at different pH values is plotted in Fig. 4. The percentage removal increased from 40% to 73% when pH was increased from 2 to 6 for  $Zn^{2+}$  and (25% to 72%) for  $Fe^{2+}$  when pH was increased from 2 to 8 for

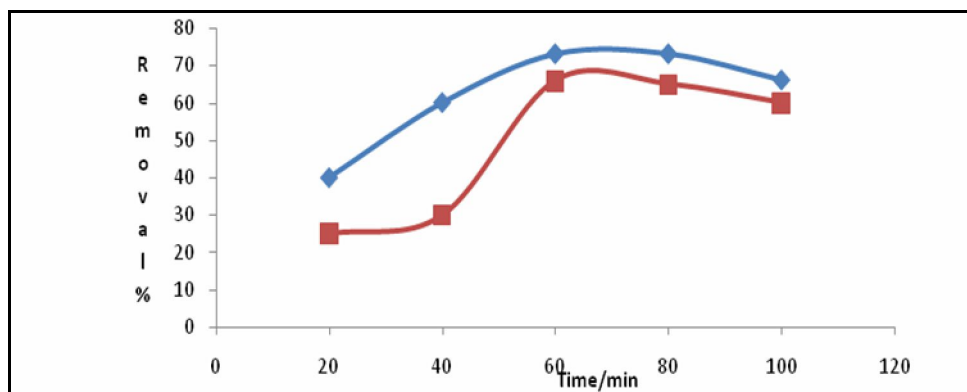
$\text{Fe}^{2+}$  ions. In low pH value, binding sites are generally protonated or positively charged (by the hydronium ions). Thus, repulsion occurs between the metal cation and the adsorbent at a higher pH value; binding sites start deprotonating, and makes different functional groups available for metal binding. In general, cation binding increases as pH increases<sup>5,46,47</sup>.



**Figure 4; Adsorption of  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$  by chitosan as a function of pH at initial concentration of 50mg/L and adsorbent dosage 0.1 g .**

### 3.3. Effect of contact time:

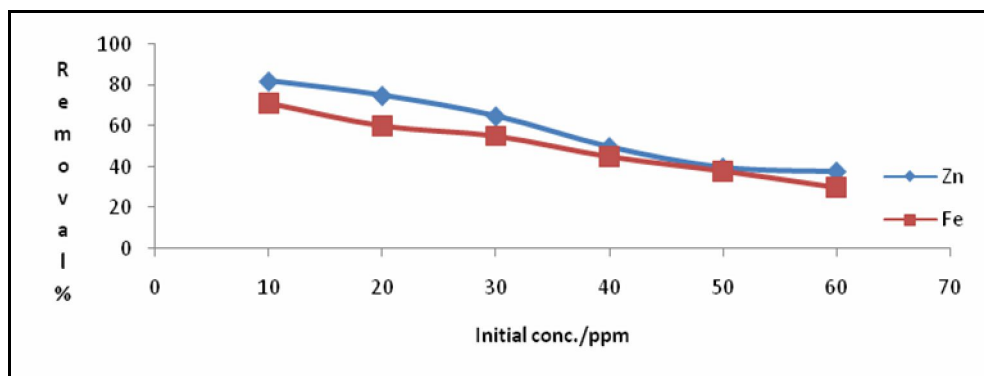
A 50ml of 50mg/L of  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$  was taken in conical flasks and treated with 0.1 gm chitosan (adsorbent) at several times (20, 40, 60, 80, 100, 120 and 140 min.). The variation in percent removal of  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$  with the time was shown in figure 5. It was found that the best time to remove these metal ions was 80 min. The results showed that the removal percentage was 73%  $\text{Zn}^{2+}$  and 65%  $\text{Fe}^{2+}$ , this due to saturation of active sites which do not allow further adsorption to take place<sup>48</sup>.



**Figure 5; Effect of contact time on  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$  adsorption(50mg/L) by 0.1gm chitosan.**

### 3.4. Effect of initial metals ions concentration

The effect of initial  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$  concentration on the percentage removal of the ions is shown in figure 6. The initial metals ions concentration was varied from 10 to 60 mg/L. A rapid initial adsorption of ions took place within the first 20 min, after which the adsorption slowed down and then almost reached equilibrium at 120 min. The percentage of ions removal evidently decreased with increasing initial ions concentration. The percentage removal was 82.05% for 10 mg/L initial concentration and only 30.26% for 60 mg/L after 120 min of adsorption (figure 6). This was caused by an increase in the mass gradient pressure between the solution and adsorbent<sup>44,45</sup>.



**Figure6;**The effect of variation of initial metal ions concentration on to their adsorption using chitosan.

#### 4. Conclusion

The synthesise of chitosan involved three main stages demineralization, deproteinization, and deacetylation., it characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid. Metal ions adsorption onto the chitosan depended highly on adsorbent dosage, initial ions concentration, solution pH and time.

#### References:

1. Matis K.A., Zouboulis A.I., Gallios G.P., Erwe T. and Blocher C., 2004. Application of flotation for the separation of metal-loaded zeolites, *Chemosphere*, 55: 65-72.
2. Clement R.E., Eiceman G.A. and Koester C.J., 1995. *Environmental-Analysis, Anal. Chem.*, 67: 221-255.
3. Saleh, J. M., , and Matloob, M.H. , 1974. Oxidation of titanium, tantalum, and niobium films by oxygen and nitrous oxide, *Journal of Physical Chemistry*, 78: 2486-2489.
4. Matloob, M. H., ,, 2011. Fluoride concentration of drinking water in Babil-Iraq, *Journal of Applied Sciences*, 11: 3315-3321.
5. Aljebori, A. M.; Alshirifi, A. N., 2012. Effect of Different Parameters on the Adsorption of Textile Dye Maxilon Blue GRL from Aqueous Solution by Using White Marble, *Asian journal of chemistry*, 24: 5813-5816
6. Al-Asheh, S.; Banat, F.; Al-Omari, R.; Duvnjak, Z., 2000. Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data, *Chemosphere*, 41: 659-665.
7. Seco, A.; Marzal, P.; Gabaldón, C.; Ferrer, J., 1997. Adsorption of Heavy Metals from Aqueous Solutions onto Activated Carbon in Single Cu and Ni Systems and in Binary Cu–Ni, Cu–Cd and Cu–Zn Systems, *Journal of Chemical Technology & Biotechnology*, 68: 23-30.
8. Avlonitis S. A., Poulis I., Sotiriou D., Pappas M., and Moutesidis K., 2008. Simulated cotton dye effluents treatment and reuse by nanofiltration, *Desalination*, 221: 259-267.
9. Chakraborty S., Purkait M. K., Das S., Gupta S., De S., and Basu J. K., 2003. Nanofiltration of textile plant effluent for color removal and reduction in COD, *Sep. Purif. Technol.*, 31: 141-151.
10. Gheju M., and Balcu I., 2011. Removal of chromium from Cr(VI) polluted wastewaters by reduction with scrap iron and subsequent precipitation of resulted cations, *Journal of Hazardous Materials*, 196: 131-138.
11. Vergili I., Kaya Y., Sen U., Gönder Z. B., and Aydiner C., 2012. Techno-economic analysis of textile dye bath wastewater treatment by integrated membrane processes under the zero liquid discharge approach, *Resources, Conservation and Recycling*, 58: 25- 35.
12. Hsu, H., , Chen, S., Tang, Y., and Hsi, H., 2013. Enhanced photocatalytic activity of chromium(VI) reduction and EDTA oxidization by photoelectrocatalysis combining cationic exchange membrane processes, *Journal of Hazardous Materials*, 248-249: 97-106.
13. Alrobayi E. M., Algubili A.M. , Aljeboree A. M. , Alkaim A. F. , and Hussein F. H. , DOI: 10.1080/02726351.2015.1120836. Investigation of Photocatalytic Removal and Photonic Efficiency of Maxilon Blue Dye GRL in the Presence of TiO<sub>2</sub> Nanoparticles, *Particulate Science and Technology*.

14. Alqaragully M.B., AL-Gubury H. Y, Aljeboree A.M., Karam F.F., and Alkaim A. F., 2015. Monoethanolamine :Production Plant, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 6: 1287-1296.
15. Alkaim A. F., Sadik Z., Mahdi D. K., Alshrefi S. M., Al-Sammarraie A. M., Alamgir F. M., Singh P. M., and Aljeboree A. M., 2015. Preparation, structure and adsorption properties of synthesized multiwall carbon nanotubes for highly effective removal of maxilon blue dye, Korean J. Chem. Eng., 32: 2456-2462.
16. Aljeboree A. M., Alkaim A. F., and Al-Dujaili A. H., 2015. Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon, Desalin. Water Treat., 53: 3656-3667.
17. Aljeboree A. M., 2015. Adsorption of methylene blue dye by using modified Fe/Attapulgite clay., Research Journal of Pharmaceutical, Biological and Chemical Sciences 6: 778-788.
18. Al-Gubury H. Y., Fairouz N. Y., Aljeboree A. M., Alqaragully M. B., and Alkaim A. F., 2015. Photocatalytic Degradation n-Undecane using Coupled ZnO-Co2O3, Int. J. Chem. Sci., 13: 863-874.
19. Hadi Z. A., Aljeboree A. M. and Alkaim A. F., 2014. Adsorption of a cationic dye from aqueous solutions by using waste glass materials: isotherm and thermodynamic studies, Int. J. Chem. Sci., 12: 1273-1288.
20. Alkaim A. F., Aljeboree A. M., Alrazaq N. A., Baqir S. J., Hussein F. H., and Lilo A. J., 2014. Effect of pH on Adsorption and Photocatalytic Degradation Efficiency of Different Catalysts on Removal of Methylene Blue, Asian Journal of Chemistry, 26: 8445-8448.
21. Aljeboree A. M., Radi N., Ahmed Z., and Alkaim A. F., 2014. The use of sawdust as by product adsorbent of organic pollutant from wastewater: adsorption of maxilon blue dye, Int. J. Chem. Sci., 12: 1239-1252.
22. Aljeboree A. M., Alshirifi A. N., and Alkaim A. F., 2014. Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon, Arabian J. Chem., 10.1016/j.arabjc.2014.01.020.
23. Karam F. F., Kadhim M. I., and Alkaim A. F. , 2015. Optimal conditions for synthesis of 1, 4-naphthaquinone by photocatalytic oxidation of naphthalene in closed system reactor, Int. J. Chem. Sci., 13: 650-660.
24. Alkaim, A. F., Dillert, R., and Bahnemann, D. W., 2015. Effect of polar and movable (OH or NH2 groups) on the photocatalytic H2 production of alkyl-alkanolamine: a comparative study, Environ. Technol., 36: 2190–2197.
25. Petrilkova A., and Balintova M., 2011. Utilisation of sorbents for heavy metal removal from acid minedrainage, Chemical Engineering Transactions, 25: 339-334.
26. Gong J., Feng J., Liu J., Jiang Z., Chen X., Mijowska E., Wen X., and Tang T., 2014. Catalytic carbonization of polypropylene into cup-stacked carbon nanotubes with high performances in adsorption of heavy metallic ions and organic dyes, Chem. Eng. J., 248: 27-40.
27. Srivastava, V. C.; Mall, I. D.; Mishra, I. M., 2009. Competitive adsorption of cadmium(II) and nickel(II) metal ions from aqueous solution onto rice husk ash, Chemical Engineering and Processing: Process Intensification, 48: 370-379.
28. Baccar, R.; Bouzid, J.; Feki, M.; , M., A., 2009. Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions, J. Hazard. Mater., 162: 1522-1529.
29. Lv, K.; Xu, Y., 2006. Effects of Polyoxometalate and Fluoride on Adsorption and Photocatalytic Degradation of Organic Dye X3B on TiO2: The Difference in the Production of Reactive Species, The Journal of Physical Chemistry B, 110: 6204-6212.
30. Ho, Y. S.; Wase, D. A. J.; Forster, C. F., 1996. Kinetic Studies of Competitive Heavy Metal Adsorption by Sphagnum Moss Peat, Environmental Technology, 17: 71-77.
31. Brunelle, J. P., 1978. Preparation of catalysts by metallic complex adsorption on mineral oxides, Pure Appl. Chem., 50: 1211-1229.
32. Djilani C., Zaghdoudi R., Djazi F., Bouchekima B., Lallam A., Modarressi A., and Rogalski M., 2015. Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon, Journal of the Taiwan Institute of Chemical Engineers, 53: 112-121.
33. H. Karaer, and I. Uzun, 2013. Adsorption of basic dyestuffs from aqueous solution by modified chitosan, Desalin. Water Treat., 51: 2294-2305.

34. Wang, S., Ng, C.W., Wang, W., Li, Q., and Li, L., 2012. A Comparative Study on the Adsorption of Acid and Reactive Dyes on Multiwall Carbon Nanotubes in Single and Binary Dye Systems, *J. Chem. Eng. Data.*, 57: 1563-1569.
35. Zhou, L.; Jin, J.; Liu, Z.; Liang, X.; , S., C., 2011. Adsorption of acid dyes from aqueous solutions by the ethylenediamine-modified magnetic chitosan nanoparticles, *J. Hazard. Mater.*, 185: 1045-1052.
36. Duran, C.; Ozdes, D.; Gundogdu, A.; Senturk, H., 2011. Kinetics and Isotherm Analysis of Basic Dyes Adsorption onto Almond Shell (*Prunus dulcis*) as a Low Cost Adsorbent, *J. Chem. Eng. Data*, 56: 2136-2147.
37. Auta, M.; , H., B. H., 2011. Optimized waste tea activated carbon for adsorption of Methylene Blue and Acid Blue 29 dyes using response surface methodology, *Chem. Eng. J.*, 175: 233-243.
38. Hassan, A. F.; Abdel-Mohsen, A. M.; Fouda, M. M. G., 2014. Comparative study of calcium alginate, activated carbon, and their composite beads on methylene blue adsorption, *Carbohydrate Polymers*, 102: 192-198.
39. Hajati, S.; Ghaedi, M.; Karimi, F.; Barazesh, B.; Sahraei, R.; , D., A., 2014. Competitive adsorption of Direct Yellow 12 and Reactive Orange 12 on ZnS:Mn nanoparticles loaded on activated carbon as novel adsorbent, *J. Ind. Eng. Chem.*, 20: 564–571.
40. Kaur, P., Singh, A. P., Prince, A. K. & Kushwaha, J. P., 2015. Optimization and evaluation of CBSOL LE red wool dye adsorption from aqueous solution onto commercial activated carbon, *International Journal of Environmental Science and Technology*, 12: 3755-3766.
41. Durán-Jiménez, G., Hernández-Montoya, V., Montes-Morán, M. A., Bonilla-Petriciolet, A., & Rangel-Vázquez, N. A., 2014. Adsorption of dyes with different molecular properties on activated carbons prepared from lignocellulosic wastes by Taguchi method, *Microporous and Mesoporous Materials*, 199: 99-107.
42. Maneerung, T., Liew, J., Dai, Y., Kawi, S., Chong, C., & Wang, C., 2016. Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: Kinetics, isotherms and thermodynamic studies, *Bioresource Technology*, 200: 350-359.
43. Hadi, A. G., , 2012. Study of heavy metal  $Mn^{2+}$  adsorption by synthesized chitosan, *BJS*, 6: 2-7.
44. Hadi, A. G., , 2012. Adsorption of Cd(II) ions by synthesized chitosan from fish shells, *British journal of science*, 5: 33-38.
45. Wang L., Zhang J., Zhao R., Li C., Li Y., and Zhang C. L., 2010. Adsorption of basic dyes on activated carbon prepared from *Polygonum orientale* Linn: equilibrium, kinetic and thermodynamic studies, *Desalination*, 254: 68-74.
46. Nassar, M. M., El-Geundi, M. S., & Al-Wahbi, A. A., 2012. Equilibrium modeling and thermodynamic parameters for adsorption of cationic dyes onto Yemen natural clay, *Desalin. Water Treat.*, 44: 340-349.
47. Errais, E.; Duplay, J.; Darragi, F.; M'Rabet, I.; Aubert, A.; Huber, F.; Morvan, G., 2011. Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters, *Desalination*, 275: 74-81.
48. Padilla-Ortega, E., Leyva-Ramos, R., and Flores-Cano, J. V., 2013. Binary Adsorption of Heavy Metals from Aqueous Solution Onto Natural Clays, *Chemical Engineering Journal*, 225: 535-546.

\*\*\*\*\*