International Journal of Chemical and Pharmaceutical Research Updates

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(RESEARCH ARTICLE)

A new adsorbent for removing Cu2+ and Fe2+ Ions from wastewater

Aamer A. Alhatem *

Department of Medical Devices Engineering Techniques, Al-Turath University College, Baghdad, Iraq.

International Journal of Chemical and Pharmaceutical Research Updates, 2023, 01(01), 029-037

Publication history: Received on 14 August 2023; revised on 12 October 2023; accepted on 16 October 2023

Article DOI: https://doi.org/10.53430/ijcpru.2023.1.1.0044

Abstract

Activated carbon derived from cheap sources showed good adsorption for the removal of most heavy metal ions from wastewater as it has an extended surface area, high adsorption capacity, and a certain degree of surface reactivity due to the presence of appropriate functional groups. Langmuir and Freundlish's adsorption isotherm models have been utilized to decipher the balance adsorption information. The pH, time of contact, and the dose of adsorbent have a great effect on the whole process. In this study, we aimed to demonstrate the adsorption characteristics of charcoal derived from municipal Olive seeds residues produced in the region of Mosul to remove heavy metal ions from wastewater.

Keywords: Olive seeds residues; Wastewater; Adsorption isotherm; Heavy metal removal; Charcoal

1 Introduction

A municipal Olive seed residue is considered food waste, it can be used as fodder, other parts of the waste can be used as a fertilizer, but most of these residues are dumped or burned, due to its expensive processing. However, Olive seed residues are carbonaceous and have the potential to be converted into adsorbents and this conversion could contribute in reducing the volume of waste. Wastewater from industry contains various contaminants such as colors, metal ions, acids, bases, and other substances that are thought to be carcinogenic when ingested by animals[1,2]. Heavy metals belong to the class of hazardous pollutants due to their toxicity even at low concentrations[3]. Various treatments have been carried out for the removal of metals from wastewater by chemical complexation [4], ion exchange[5], and adsorption[6]. Actuated carbon is generally utilized because of its viability and flexibility. In recent years, low coast adsorbents have been produced from by-products and their utilization for wastewater treatment has been attempted[7-10]. Pyrolusite has been used for the adsorption of Pb, Zn, and Mg ions from their aqueous solution[11]. Zeolites have been used for the removal of heavy metals from wastewater[12]. M.M.Rahman et.al [13] have also used adsorption techniques for the removal of heavy metals from polluted water. Adsorption of heavy metal ions from polluted water has been also used by activated carbon from date pits [14]. Scientific works present a wide possibility of models to deal with these situations, based on the information extracted from the scientific literature, six groups of risk methodologies are defined, analyzed, and characterized with methods that cover the standards, preventive, probabilistic, traditional, modern, and dynamic evaluation that are applied or could be used in industrial parks [15], chitosan [16], polyamine composites [17], polystyrene [18,19], mercerized cellulose and sugarcane bagasse [20], wood sawdust [21], rice husk [22], and biomass of baker's yeast [23] have been used as supports for EDTA functionalities.

In this study, we aimed to demonstrate the adsorption characteristics of charcoal from Olive seed residues to remove metals from wastewater.

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* Corresponding author: Aamer A. Alhatem

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2 Experimental

2.1 Synthetic polluted water samples

Synthetic polluted water samples containing a definite concentration of Iron and Copper ions were prepared by diluting stock solution (1000ppm Fe, Cu) with bidistilled water.

2.2 Adsorbent samples

The extracted residues of the Olive seeds were grounded and sieved through (~20) mesh and then divided into two portions, one of them called (Husk), which was washed with distilled water and dried at 110ºC for 48 hs., then stored in a desiccator until use. The other portion called (Ash), was dried until water content was reduced by more than 50%, then were manufactured to get the charcoal from the seed residues as follows:

First, seed residues were analyzed to study their composition, results are indicated in Table1.

Table 1 Indicative chemical composition of different olive seeds types

		% of dry matter			
Type	**Dry matter**	**Ash**	**Crude Protein**	**Crude Fibre**	**Ether Extract**
Crude olive seeds	75–80	3–5	5–10	35–50	8–15
Partly destoned olive seeds	80–95	6–7	9–12	20–30	15–30
Exhausted olive seeds	85–90	7–10	8–10	35–40	4–6
Partly destoned exhausted					
olive seeds	85–90	6–8	9–14	15–35	4–6
Fatty pulp	35–40	5–8	9–13	16–25	26–33

Sources: many authors.

Second, the preparation of activated carbon from the seed residues includes three stages: boiling, soaking, and a joined advance of carbonization of the residue. In the initial step, the residues were boiled in a pressure cooker for around three hours at three phases with a duration of one hour for each stage. Boiling water was replaced with new water toward the finish of every step. Then, at that point, the hot residues were dried in an electric oven at 110°C for 24 hours and squashed with a mallet followed by soaking the residues. The arrangement regularly utilized in the substance treatment interaction of delivering enacted carbon is phosphoric corrosive (H_3PO_4). During this stage, a concentrated phosphoric acid (85% H_3PO_4) was added cautiously into the compartments containing the grinded residues with an impregnation proportion of 1 g of residues to 2 ml of 85% H_3PO_4 at 25 ºC for 24 hours [24]. Then, at that point, the residues were left in the air for halfway dryness and afterward dried at 120ºC for 60 minutes. Finally, is the carbonization and activation of residues by putting {in a muffle furnace [(Naber therm .B170) at 800º C before use] [25]. Hot Distilled water was added to the Ash to get the desired pH(6.5). Afterward, the product was dried in an electric oven at 120ºC for 48 hours. furthermore, put away in a desiccator until use.

2.3 Standard solutions

Fe and Cu standard solutions (1000ppm) were prepared using $FeCl_2$ and $CuSO_4$ salts respectively, it was purchased from BDH Chemicals Ltd. Poole England.The ion-specific meters reagents were purchased by Hanna instruments.

2.4 Analytical measurements

The samples resulting from each treatment were analyzed spectrophotometrically for Fe^{2+} and Cu^{2+} [26] using wavelengths (575 nm and 525nm)respectively, using a spectrophotometer (300 Jenway).

3 Adsorption conditions

3.1 Effect of contact time

0.5 g of each Ash and Husk were treated separately with 10 ml of (5ppm) Fe^{2+} and Cu^{2+} standard solutions in conical flasks, the samples were shaken for time intervals (0,10,20,30,60,120,180 min.) on a shaker of speed 30 rpm. For obtaining correct results, each experiment was run in triplicates, and mean values were reported. After attainment of equilibrium, the content of the flask was filtered through Whatman filter paper, and the desired ion was then determined using the spectrophotometric method [26]. It was found out that one hour gives good results.

3.2 Effect of dose

(0.1,0.2,0.3,0.4,0.5,1.0,1.5,2.0,2.5,3.0 g) of each Ash and Husk were treated separately with 10 ml portions of (5ppm) standard Fe^{2+} and Cu^{2+} solutions. After one hour the content of the flask was filtered through Whatman filter paper, and the desired ion was then determined using the spectrophotometric method to find out the adsorption capacity. It was found out that(1.0 and 2.5 g) Ash and Husk respectively are the best adsorption treatment.

3.3 Removal of $Fe^{2+}$and Cu^{2+} ions from wastewater

10 ml of the synthetic wastewater sample was treated with 0.5g of each Ash and Husk adsorbent in a conical flask, pH was adjusted to (pH 7). After one hour of shaking time, the amount of metal ion concentration remaining was then determined photometrically.

3.4 Effect of pH on adsorption

0.5 g of the adsorbent (Ash or Husk) was treated with 50 ml of (5 ppm) Iron, Copper standards, and the pH of the adsorption mixture was adjusted to different pH values (3,7and 9) using 0.5 M NaOH or 0.5 M HCl.The remaining concentration of the metal was then determined spectrometrically.

4 Results and discussion

4.1 Effect of pH on heavy metals adsorption

pH is one of the crucial parameters influencing substantial heavy metals adsorption. In this way, the impacts of pH on heavy metals adsorption were assessed and the pH range for Iron and Copper expulsion was looked over 3 to 9. The work demonstrates that the most extreme adsorption of metal ions was seen to be at pH esteem < 7, and by surpassing this pH esteem the adsorption will in general diminish, which gives a decent concurrence with that announced in writing [27].

The dependence of metals removal on pH is related to the significant functional active sites which could attach with the pollutants to allow contaminant removal from water with high adsorption capacity during exudation of wastewater across the membrane. Generally, the physical adsorption needs a short interval of contact time for the adsorbed molecules, it is the opposite for the chemical adsorption due to strong chemical bonding of the adsorbent with adsorbate to achieve the attainment of equilibrium with longer contact time[28].

In general, the course of substantial metal expulsion is happened on the strong surface by adsorption, and the balance is gotten by accomplishing constant concentrations of the adsorbed heavy metals in water. The reliance of metals expulsion on pH is identified with the critical utilitarian dynamic locales which could connect with the poisons to permit foreign substance expulsion from water with high adsorption limit during exudation of wastewater across the adsorbent. The actual adsorption needs a short timespan time for the adsorbed ions, it is the inverse for the synthetic adsorption because of solid compound holding of the adsorbent with adsorbate to accomplish the fulfillment of balance with longer contact time[28]. Overall, the course of substantial metal expulsion is happened on the strong surface by adsorption, and the balance is acquired by accomplishing steady centralizations of the adsorbed weighty metals in water. Thus, the adsorbents for removal of heavy metals are nontoxic and friendly, they offer high adsorption capacity tothe low concentrations of pollutants and enable removal of pollutants from their surfaces easily, both factors, the surface functional groups present on the biomass and the chemistry of the metal in solution helping in the success of the adsorption process[29].

4.2 Adsorption evaluation

In the adsorption operation, the adsorption assessment depends on the measure of adsorbate at balance (qe; mg g^{-1}). It is commonly registered with the equilibrium of material during an adsorption operation, the vanished adsorbate from the arrangement, and the adsorbent mass [30] [Eq. (1)].

$$q_{e=}\frac{C_{o-}C_e}{m}\times V\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

$$R(\%)=\frac{C_{o-}C_e}{100C_O}\times V\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

where C_o (mg L^{-1}) is the initial adsorbate concentration, Ce (mg L^{-1}) is the equilibrium adsorbate concentration in the solution, V (L) is a volume of the adsorbate solution, and m (g) is the dried mass of employed adsorbent. The adsorption evaluation is referred to as the adsorbate removal efficiency (%R) from the solution [31], as shown in Eq. (2).

4.3 Adsorption isotherms

The relationship between the amounts of adsorbed heavy metal ions in water is termed an adsorption isotherm [32] at equilibrium and could be based on Langmuir and Freundlich's models. In the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent. Once adsorbates occupy the active sites, the adsorp tion is naturally terminated at this site. In the non-linear Langmuir model, its equation is presented in Eq. (3) [33], where qmax is the maximum adsorption capacity (mg g−1) of adsorbent, KL is the equilibrium constant (Lmg−1), Ce is the equilibrium concentration (mgL−1), and q is the amount of adsorbed metals at equilibrium (mg g−1). Moreover, the linear Langmuir model is stated in Eq.(4), where qm is the saturated monolayer adsorption capacity, and b is the adsorption equilibrium constant. The plot of Ce /qe vs. Ce provides a straight line. The maximum adsorption capacity and the bond energy of adsorbates are determined with the slope and intercept. In the Freundlich model, its equation is seen as an experienced model of multilayer adsorption on the adsorbent. The non-linear Freundlich model is shown in Eq. (5) [34]. The linear Freundlich model is described in Eq. (6), where qe is a loading of adsorbate on adsorbent at equilibrium (mg g−1), KF is an indicator of adsorption capacity (mg1−n Ln g−1), n is adsorption energetics, and Ce is the aqueous concentration of adsorbate at equilibrium(mg L−1).

$$\propto=\frac{q_{max}K_LC}{1+K_LC}\ \ldots\ldots\ldots\ldots 3$$

$$\frac{C_e}{q_e}=\frac{C_e}{q_m}+\frac{1}{b\,q_m}\ \ldots\ldots\ldots\ldots\ldots\ldots 4$$

$$q_e=\mathrm{KF}\ C_e^n\ \ldots\ldots\ldots\ldots\ldots\ldots 5$$

$$\mathrm{Logqe}=\mathrm{Log\ KF}+\frac{LogC_e}{n}\ \ldots\ldots\ldots\ldots\ldots\ldots 6$$

4.3.1 Langmuir adsorption isotherm

Longmuir equation was used as a model for adsorption, the adjusted equation in its linear form being[35]:

$$1/(x/m)=1/C\ b+1/a$$

where a is Langmuir bonding energy coefficient.
b (mg/kg) is the adsorption maximum.
C (mg/dm^3) is the concentration of adsorbate left in solution at equilibrium.
x/m is the amount of adsorbate adsorbed per unit mass of adsorbent.

The Langmiur isotherm can be explained through plotting 1/(x/m) against 1/C, if the data lie on a straight line then the Langmiur model can be considered to be appropriate. Using least square linear regression, the term b (reciprocal of the slope) and k (1/b) may be found.

4.3.2 Freundlish adsorption isotherm

Other model is the Freundlish isotherm, which is expressed as:

$$k/m=kc^{1/n}$$

Where x/m is the amount adsorbed per unit mass of adsorbent, c is the solution concentration at equilibrium, k and n are constants relating to adsorption capacity and intensity. From these adsorption models; the adsorption maximum, binding energy, adsorption capacity and can be calculated, and so the efficiency of the adsorbent for the removal of Iron and Copper can be obtained.

4.4 Removal of Fe^{2+} ions by adsorption on Olive seeds Husk

On using Husk for removing of Iron metal ions from wastewater,a good straight line was obtained indicating a good agreement with Freundlish isotherm model with correlation coefficient ($R^2 = 0.981$), Fig(1) compared to the Langmuir isotherm model with correlation coefficient ($R^2 = 0.863$)Fig(2).

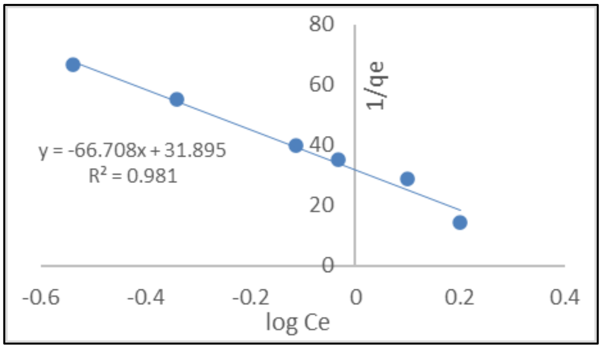

Figure 1 Freundlish isotherm for Iron.(Husk)

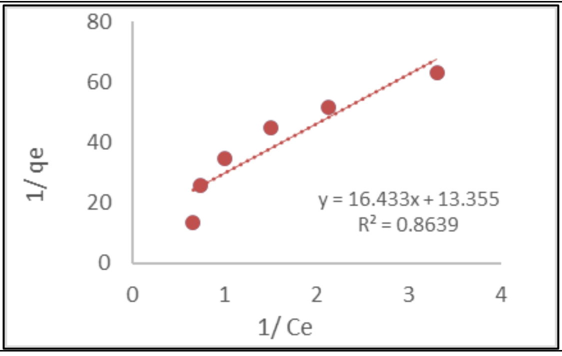

Figure 2 Langmuir isotherm for Iron(Husk)

The efficiency of adsorption was about 200% by using sample dose of 0.5 ppm, the adsorption was slowed down to 73.4 %, and by increasing the dose to 1.5 ppm, the percentage rises again to reach a maximum of % 98.18 when using sample dose of 3ppm.The same result was obtained by Parkman et al [36]who has reported that percent uptake of Sr on kaolinite was greatest at the highest initial Sr concentration.This increment may be due to the large surface area of the adsorbate as well as physical and chemical interactions between the solid surface of a substance and a dissolved metal species.

4.5 Removal of Fe^{2+} ions by adsorption on Olive seeds Ash

The efficiency of removing Iron ions using Ash exceeded 98% when using sample dose 1ppm, but it slowed down to 68.9% by decreasing the dose to 0.2 or 0.1ppm , this loss in adsorption capacity may be due to the low surface area of the Ash. Langmuir isotherm model yields better coincidence ($R^2 = 0.896$),Fig.(3)compared to Freundlish isotherm model ($R^2 = 0.851$),Fig.(4).

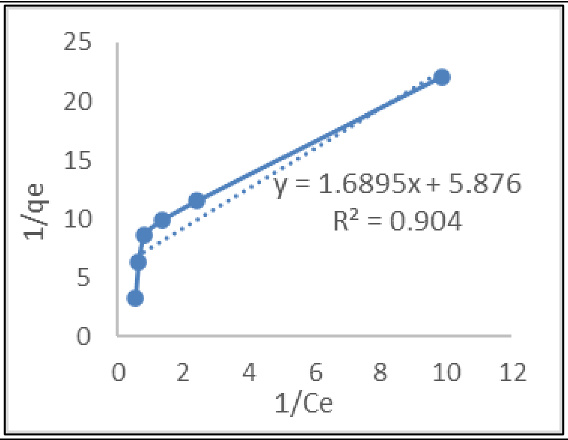

Figure 3 Langmuir isotherm for Iron (Ash)

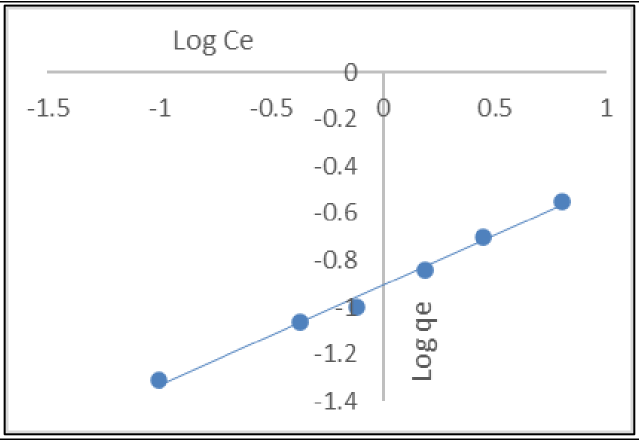

Figure 4 Freundlish isotherm for Iron.(Ash)

4.6 Removal of Cu^{2+} ions by adsorption on Olive seeds Husk

From Fig.(5) Langmuir isotherm model with ($R^2 = 0.657$) is not of great significance to the process of adsorption of Copper ions using Ash compared to that of Freundlish isotherm model Fig.(6) with ($R^2 = 0.995$). The straight line of Freundlish isotherm was applied in the range of 2-3ppm.

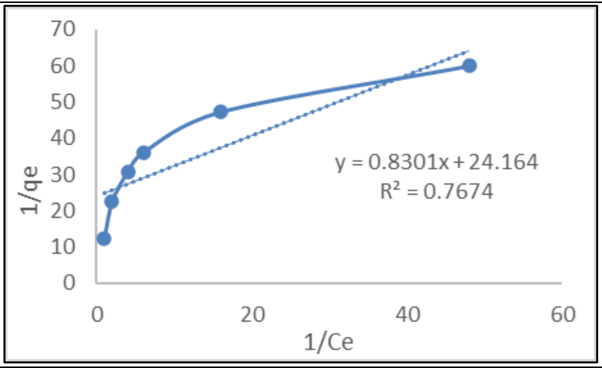

Figure 5 Langmuir isotherm for Copper (Ash)

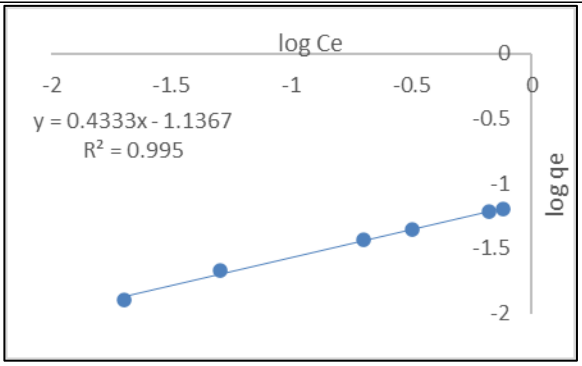

Figure 6 Freundlish isotherm for Copper (Ash)

It can be concluded that the amount of Copper adsorbed on the Husk was about 0.081mg/g, which seemed to be a low value compared to the percentage of recovery which reached 81.54% by using 0.5ppm and 99.88% when using sample dose 3ppm.

4.7 Removal of Cu^{2+} ions by adsorption on Olive seeds Ash

The results of adsorption of Cu^{2+} ions on Olive seeds Ash, indicates that100% removal of Cu^{2+} ions was obtained by using sample dose 1ppm.The least removal percentage obtained by using Ash was 95.98% when the chosen dose was 0.1ppm which gave an adsorbent amount equal to 0.479mg/g of the Ash.

Table 2 Adsorption of Cu2+ ions on Olive seeds Ash

Dose (C_{ppm})	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**1**
eq.conc.($C_{e\ ppm}$)	0.201	0.131	0.076	0.027	0.006	0
Adsorbate[mg/g]	0.479	0.243	0.164	0.118	0.099	0.05
% Adsorption	95.98	97.38	98.48	99.46	99.88	100

4.8 Effect of time on the adsorption of Fe^{2+} and Cu^{2+}ions

The time of adsorption in case of Iron ions is of a great importance, according to Fig.(7) it was clear that Ash gives an adsorption capacity about (91.1%)at a time intervals not exceeding 1 hr, while in case of Husk the adsorption shows very low efficiency, it reaches equilibrium value by a percentage recovery not exceeding (71.1%)within about 40 min. after that it showed a steady state.In case of Copper ions,as shown in Fig.(8), the adsorption capacity of Ash increases by increasing contact time intervals reaching a maximum value of recovery (100%)after 55 min. while in the case of Husk it reaches the equilibrium state after 10 min. with a percentage recovery(82.88%). The high efficiency of the Ash compared to the Husk in the case of Fe^{2+} and Cu^{2+}ions, may be due to the high surface area of the Ash molecules which gives a great contact with the Iron and Copper ions in the sample solution.

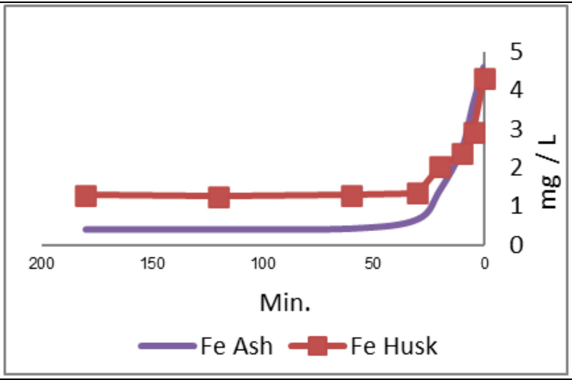

Figure 7 Effect of time on adsorption of Iron ions on Husk and Ash

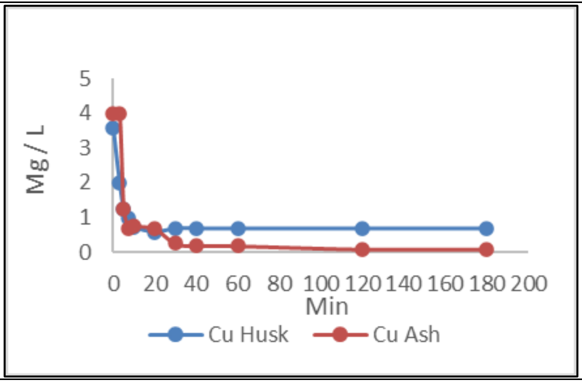

Figure 8 Effect of time on adsorptrion of Copper ions on Husk and Ash

According to the results obtained from the experiments carried out in the presence of different adsorbent quantities, it was reported that the adsorbent dose was of great importance in this direction. According to Fig.(9), 2.5 g of Husk causes the removal of 90% of Iron ions in solution, while the same amount of Husk causes the removal of more than 99.88% of Copper ions in solution. The presence of 0.3g of Ash gives 100% removal of Copper ions compared to 68% of Iron ions while 1g of Ash gives a maximum of 98.06% removal of Iron Fig.(10).

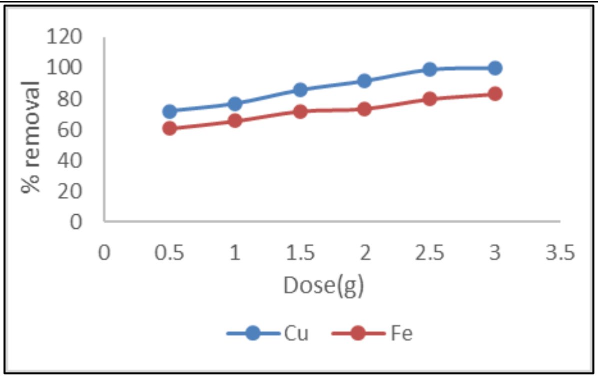

Figure 9 Effect of dose of Husk on the adsorption of Iron and Copper.

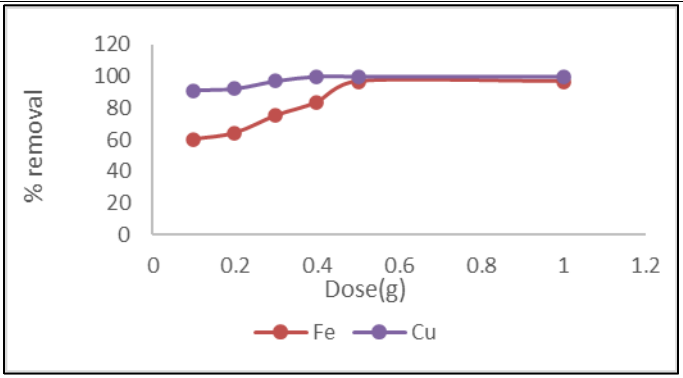

Figure 10 Effect of dose of Ash on the adsorption of Iron and Copper

5 Conclusion

Husk and Ash of Olive seeds residues were very effective in removing Iron and Copper ions from wastewater .The results indicate high efficiency for Ash compared to Husk especially in case of removing Copper ions from sample solution(Table 2),which is related to the high adsorption capacity and a certain degree of surface reactivity due to the active sites located on the Ash and the presence of appropriate functional groups which causing chemical interaction between the adsorbent and the metal ions in the bulk solution. The process can be influenced by changing pH, time of contact, and adsorbent dose.

Table 3 Comparison between Freundlish and Langmuir isotherm models

Adsorbent and Adsorbate	**Freundlish isotherm model**		**Langmuir isotherm model**	
	linear eq. (Y)	**R^2**	**linear eq. (Y)**	**R^2**
Cu^{2+} on Husk	y = 0.433x - 1.1367	0.995	y = 0.8301x + 24.164	0.7674
Cu^{2+} on Ash	y = 0.151x −1.298	0.605	y = 0.0020x + 35.56	0.389
Fe^{2+} on Husk	y = -66.708x +31.895	0.981	y = 16.433x + 13.355	0.8639
Fe^{2+} on Ash	y = 0.4248x - 0.9065	0.9919	y = 1.6895x + 05.876	0.904

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