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The impact of rice husk, activated carbon, almond shell, and sand filters on some physical and chemical properties of aqueous salt solution

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ABSTRACT

In this study, the impact of rice husk, activated carbon, almond shell, and sand filters on some physical and chemical properties of saline water was investigated and compared. Salt solutions were collected downstream of columns filled with pure sand, sand plus rice husk, sand plus activated carbon, and sand plus almond shell, all with similar weights. The turbidity, water hardness, and the concentrations of chloride, sodium, potassium, magnesium, and calcium ions were measured over time. The results showed no effect of the pure sand on the adsorption of chloride (Cl^-), calcium (Ca^+), and magnesium (Mg^+) ions. However, the highest adsorption of Ca^+ (30.5%), Cl^- (20%), and Mg^+ (17.5%) ions and the maximum reduction of water hardness (23%) were achieved by passing saline water throughout a mixture of sand plus rice shell filters. The minimum adsorption of the ions was obtained with a mixture of sand plus almond shell filters. None of the filters had a significant impact on electrical conductivity of the saline water. In conclusion, combining sand filter with rice and almond shell filters were more effective in the desalinization of saline water.

Keywords: Activated carbon; Almond shell; Time impact; Rice husk; Sand

1. Introduction

With increasing population and the limited water resources, many countries in the world will suffer from the lack of freshwater and consequently increasing competition for freshwater by 2025 [1]. Shortage of freshwater over the past two decades has encouraged fundamental and applied researchers to investigate the use of unconventional water resources in many countries. Nowadays, one way to reduce the shortage of freshwater is to consume low quality waters or unconventional water resources such as saline and brackish waters that are abundant in the region facing freshwater scarcity.

Iran is a Mediterranean country with arid and semiarid climate, characterized by low mean annual precipitation and also non-uniform spatial and temporal distribution of rainfall. These factors have intensified the lack of water potential and increased the probability of drought, in particular during the last two decades. Therefore, the necessity of planning and managing both water consumption and freshwater resources limitation, and the utilization of unconventional water resources is highly considered by authorities and experts. The total volume of salt and brackish water in Iran is nearly 12.8 billion cubic meters,

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consisting 12% of potential renewable surface water resources. In addition, the total volume of ground water resources is approximately 1.74 billion cubic meters that comprises 5% of total volume of underground water resources [2].

Several chemical and physical techniques have been suggested and adopted by researchers to adsorb or control the level of salinity from salt or brackish waters. However, these methods are expensive, time-consuming, and result in high energy loss. Therefore, scientists are looking for low-cost methods of desalinization. The use of plant residuals or organic amendments is a rapid and inexpensive tool that was recently considered by scientists to remove harmful elements from water. For example, sawdust is one, which was used to eliminate heavy metal ions from water solutions [3]. This organic adsorbent consists of various organic compounds such as lignin, cellulose, hemicellulose, and polyphenols with various functional groups that are able to trap heavy metals by different mechanisms [4].

The first study on metal adsorption and ions separation from waste organic matter was performed on mercury by Friedman and Vayzer (1979) which was narrated by Motedayen Aval [5]. In another study, Aburdgab and Raji (1997) added polyacrylamide to sawdust and investigated its performance as a function of Pb concentration, pH, and temperature variables [6].

Rafatullah et al. [3] reported the adsorption of Cu, Cr, Ni, and Pb ions from water solutions using sawdust as adsorbent. They indicated the capability of sawdust to remove the ions from 1–200 mg/L. The maximum adsorption was achieved at pH 6. They also tried to remove Zn and Cd from water solutions using sawdust produced from the neem tree. Their findings showed that the sawdust had a high capacity to adsorb the ions from the water solution, when modified NaOH and H_2SO_4 were used.

Wheat shell, a byproduct of wheat-grinding industry, is also a good adsorbent to remove different heavy metal ions. The existence of a powerful dehydration agent such as sulfide acid in wheat shell may have a considerable adsorption surface area that in turn causes a better efficiency of adsorption of Cu ions. In another investigation, the effect of presence of multi-metals such as Na, K, Mg, and Ca on Cu adsorption by wheat stems was evaluated. The results showed that the effect of Na ions on Cu adsorption was negligible, but K, Mg, and Ca ions reduced Cu adsorption by 2.46, 5.27, and 13.34%, respectively. Based on these findings, the light metal ions with more positive charge and more atomic radius have more influence on Cu adsorption [7].

Sand is a cheap and accessible substance, but due to its limited surface area, the adsorption of pollutants such as heavy metals is limited. Although, sand has a low adsorption power, it can be used efficiently if it is applied simultaneously with other materials [8]. Yabe and Oliveira [9] used sand, silica, activated carbon, and aluminum oxide adsorbents to remove heavy metals from industrial fluids. They found that heavy metal concentrations were below the detection limit. Livingston [10] also showed that a combination of sand, soil, gravel, and compost as a filter was able to remove pollutants from sewage.

Different techniques are used to desalinate salt and brackish waters. However, it is important to find a cheap approach to desalinate unconventional water resources. In this research, the impact of rice husk, almond shell, activated carbon plus sand (bio-filters), and sand filters on some physical and chemical properties of saline water was investigated and compared.

2. Material and methods

This study was performed at Irrigation and Drainage Lab of Shahrekord University. Four filters including: (1) a mixture of sand plus rice husk, (2) a mixture of sand plus almond shell, (3) a mixture of sand plus activated carbon, and (4) pure sand (control) were used. Table 1 shows the physical characteristics of the adsorbents used in this experiment. The bulk density of substances (ρ_{b}) was calculated using the following formula:

$$\rho_{\mathrm{b}} = \frac{M}{V_t} \tag{1}$$

where M is the mass (g) and V_t (cm^3) is the total volume of substance. Particle density (ρ_{s}) was predicted using the Eq. (2):

$$\rho_{\mathrm{s}} = \frac{M}{V_s} \tag{2}$$

in which V_s (cm^3) is the volume of substance particles. The porosity of materials (η) was predicted applying the following equation:

$$\eta = \left(1 - \frac{\rho_{\mathrm{b}}}{\rho_{\mathrm{s}}}\right) \times 100 \tag{3}$$

Sieve analysis method was used to draw the particle size distribution curve and to obtain the mean particle

Table 1
Physical property of adsorbents

Row	Absorbent	Bulk density (gr/cm^3), ρ_b	Mean diameter, μ	Particle density (gr/cm^3), ρ_s	Porosity (%), η	Gradation coefficient, G
1	Rice husk	0.32	350–800	0.94	66	1.57
2	Almond shell	0.45	350–800	1.14	60	1.58
3	Activated Carbon	0.79	350–800	0.88	10	1.58
4	Sand	1.6	500–4,000	2.59	38	2.54

diameter. The following equation was also used to find the coefficient of gradation (G):

$$G = \frac{(D_{30})^2}{D_{60} \times D_{10}} \tag{4}$$

where D_{60}, D_{30}, and D_{10} are diameters of 60, 30, and 10% of particles which are smaller.

A PVC tube with 10 cm diameter and 150 cm length was used as a column for filtering. Two-holed caps were used to close both sides of the tube. As shown in Fig. 1, the distance between the two caps was divided into three sections. Sections were separated from each other by metal screens. The sections numbered 5 and 7 (Fig. 1) were filled with gravel and a mixture of sand plus adsorbent, respectively.

A water reservoir of 220 L was used to keep saline water for tests. The saline water used was collected from a drainage network located in the eastern Isfahan city, Iran. The selected chemical and physical properties of saline water used for the tests are given in Table 2. The following relationship was applied to relate total dissolved solids (TDS, mg/L) with electrical conductivity (EC, dS/m) of saline water.

$$\mathrm{TDS}_{\mathrm{mg/L}} = 640\mathrm{EC}_{\mathrm{ds/m}} \tag{5}$$

The calcium and magnesium hardness is the concentration of calcium [Ca^{2+}] and magnesium [Mg^{2+}] ions expressed as equivalent of calcium carbonate [$CaCO_3$]. Total permanent water hardness (TH, mg/L) expressed as equivalent $CaCO_3$ was calculated with the following formula:

$$\mathrm{TH} = [\mathrm{CaCO_3}] = 2.5[\mathrm{Ca^{2+}}] + 4.1[\mathrm{Mg^{2+}}] \tag{6}$$

Turbidity is a measure of the relative clarity or cloudiness of water. The turbidity of filtered water was measured in nephelometric turbidity units (NTU), using a turbidity meter device [11].

The adsorbents were crushed and milled using an electrical mill, and separated into 350 to 800 μ particles by applying sieve analysis method. Then, the chopped

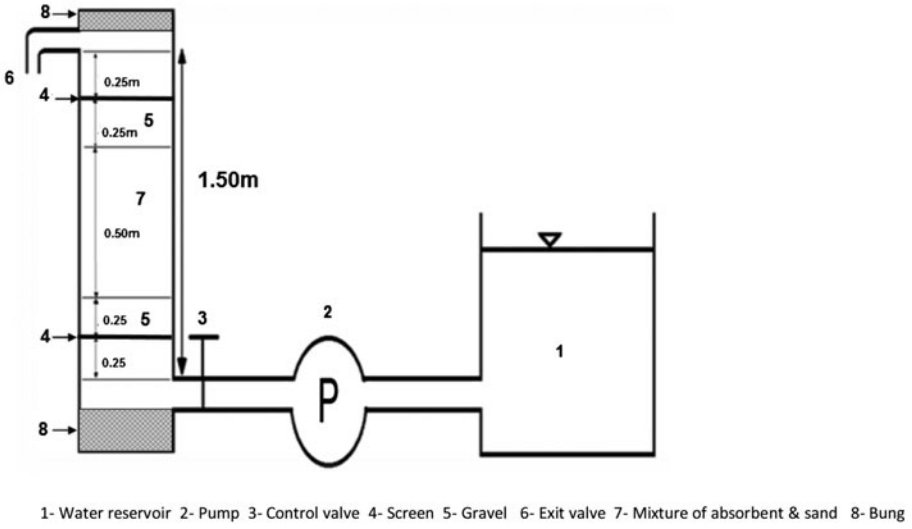

Fig. 1. A view of water reservoir, pump and the location of filter.

Table 2
Some of chemical and physical properties of salt water solution used for tests

Parameters	Values
Turbidity (NTU)	8.55
EC (ds/m)	8.76
Cl (ppm)	3,057
Mg (ppm)	54.23
Ca (ppm)	58.71
Na (ppm)	1,480
K (ppm)	4.6
TH (mg/L)	377
TDS (ppm)	5,760

adsorbent particles were washed with plenty of water and dishwashing liquid to remove surface pollutants. The adsorbent particles were dried in an oven at 70℃. Tables 3 and 4 present some chemical properties of almond shell and rice husk adsorbents cited from Bulut and Tez [12] and Chuah et al. [13].

A filter mixture with 30% dried adsorbent particles combined with 70% sand by weight was prepared as a bio-filter and was placed inside the filter unit. Four filters including pure sand, a mixture of sand plus activated carbon, a mixture of sand plus rice husk, and a mixture of sand plus almond shell were prepared to perform tests.

Saline water was pumped from reservoir through the filter units. During the experiment, samples were taken every 3 min from the outflow solutions in order to measure the parameters such as EC, turbidity, hardness, and Ca, Mg, and Cl ions. Titration method was used to measure Ca, Mg, and Cl ions.

The following equation was used to find the uptake efficiency of adsorbents (A_c):

$$A_c = \frac{C_o - C_f}{C_o} \times 100 \tag{7}$$

where C_o and C_f are the initial and final concentrations of saline water (ppm). According to Aydin et al., the adsorption equilibrium is different for different types of adsorbents and metals to be removed. For instance, it takes 30 min for acid removal onto walnut shell [14], and Pb adsorption onto hazelnut and almond shell was between 40 and 75 min [15]. As it will be illustrated later on in this study, the adsorption equilibrium was less than 30 min.

Table 3
Chemical properties of almond shell [12]

Components	Unit	Amount
Carbon	%	53.38
Hydrogen	%	6.26
Carboxylic	mmole/g	0.0415
Lacktonic	mmole/g	0.4298
Phenolic	mmole/g	0.9732

Table 4
Chemical properties of rice husk [13]

Components	Percent
Cellulose	2/32
Hemi cellulose	3/21
Linguini	4/21
Extractable material	8/1
Water	1/8
Mineral ash	15
SiO_4	3/96
K_2O	3/2
MgO	4/0
FeO_3	2/0
Al_2O_3	4/0
CaO	4/0

3. Results and discussion

3.1. Turbidity index

Fig. 2 shows the impact of four types of filters on turbidity index (T_o/T_i) of saline water samples over time, where T_o and T_i are turbidity of outlet and inlet salt solutions to and from the filter, respectively. Zero is the time at which the saline water starts to flow into the filters. In the first few minutes, the turbidity index increased and reached to a peak value and then declined over time in all four filters. This seems to be due to the colloidal particles, such as clay and organic particles, which may be fully washed out from the filter materials at the beginning of the test and water flow. However, the peak value for pure sand filter is

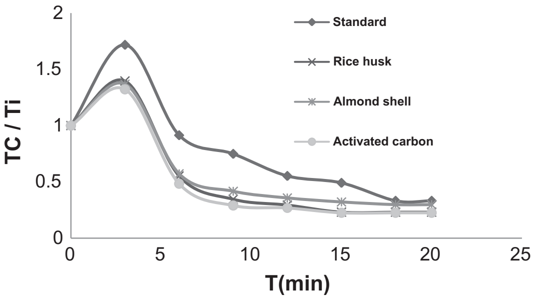

Fig. 2. The effect of different filters on turbidity index with time.

more than that for other filters (bio-filters). As indicated in Fig. 2, the turbidity index sharply declined to much less than its initial value then reached a fixed value and remained constant over the study time. This constant value, which was the lowest for activated carbon and rice husk, was reached as the filter was fully saturated. The reductions in turbidity index for activated carbon, rice husk, almond shell, and pure sand (standard) filters were 77.4, 77.2, 70.2, and 66.7%, respectively, which is nearly 10% more by bio-filters than pure sand filter. The equilibrium time of the three mixed filters was about 3 min less than the pure sand filter.

3.2. Electrical conductivity

Fig. 3 presents the impact of filters on EC of outlet solutions over time. As indicated, within the first few minutes, the EC curve increased and reached a peak value and then declined slowly and finally was parallel to time axis. The pure sand filter increased the salinity level to a value that is more than the initial value. This may be due to dissolution of different salt compounds from the sand surfaces. This measurement showed that the bio-filters did not reduce the EC value, as the saline water passed through the filter. The equilibrium time was around 15 min for bio-filters, except for sand filter.

3.3. Chloride adsorption

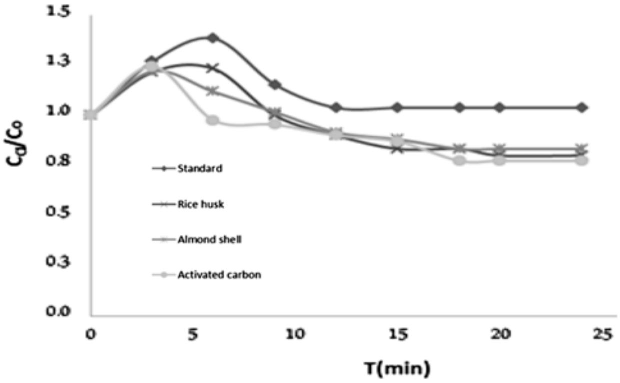

Fig. 4. The impact of filters on the chloride adsorption of output solutions.

Fig. 4 indicates the effect of tested filters on chloride concentration over time. Chloride concentration was increased within the first few minutes and then declined and subsequently remained unchanged in all the filters. However, the bio-filters reduced chloride concentration. The equilibrium time of chloride concentration through sand filter was 12, which was 5 min less than other filters.

3.4. Mg and Ca adsorption

The impact of four types of filters on Mg and Ca ions concentrations over time is shown in Figs. 5 and 6. The concentrations of Mg and Ca ions tended to increase slightly within the first few minutes, following a decline over time and ultimately attaining a constant value. The effect of four filters on desalination process was not the same. For instance, the pure sand filter did not affect Ca and Mg concentrations. This means that the final concentrations of Ca and Mg values were the same as the initial values. The equilibrium time of Ca concentration through sand filter was 12, showing 5 min less than that through other filters. However, this was different for Mg ions.

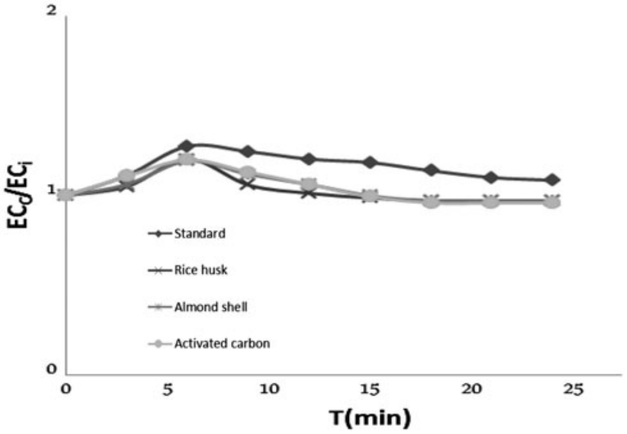

Fig. 3. Impact of filters on EC of output solutions.

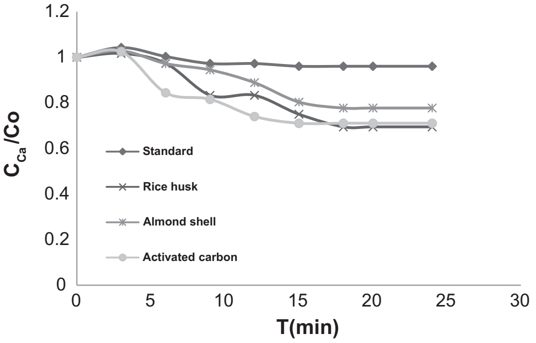

Fig. 5. The effect of filters on Ca removal from saline water.

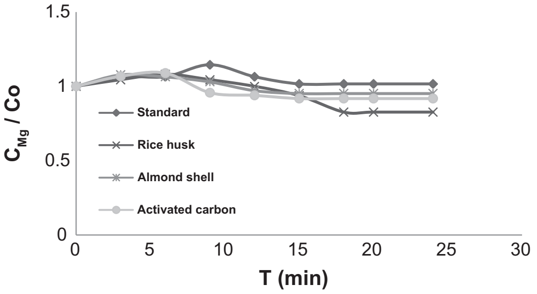

Fig. 6. The effect of filters on Mg removal from saline water.

3.5. Na and K adsorption

Figs. 7 and 8 show sodium (Na) and potassium (K) concentrations over time, as saline water flows through four filters. As indicated in these figures, the concentrations of Na and K initially increase and reach to peak values and then start to decline rapidly and ultimately remain constant over time. Fig. 7 shows pure sand, almond shell, and activated carbon filters do not adsorb Na, however, rice husk filter releases Na ions and increases its concentration in outflow. As shown in Fig. 8, sand filter releases a lot of K ions that causes K concentration to be increased, but other filters do not affect K concentration. In these experiments, the equilibrium time ranges from 6 to 12 min.

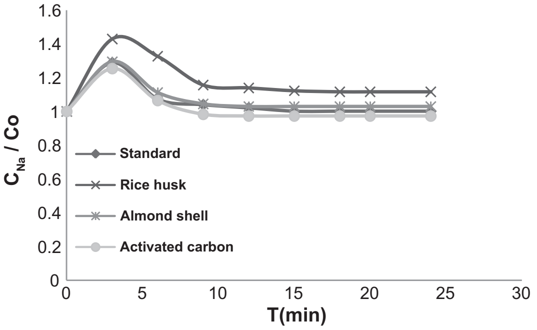

Fig. 7. The effect of filters on Na adsorption over time.

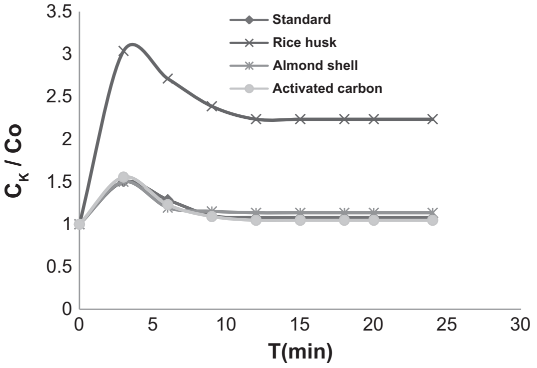

Fig. 8. The effect of filters on K adsorption over time.

4. Water hardness

Water hardness in pipe networks or irrigation systems may affect the performance of network tools. For instance, as mentioned in the previous section, water hardness may block the emitters in trickle irrigation systems. As shown in Fig. 9, after an initial increase, water hardness starts to decline and reaches a constant value at a time that is earlier than the end of experiments. Initial increase in water hardness is due to the desorption of cations by the adsorbents used in the filters. Sand, activated carbon, almond shell, and rice husk filters reduce water hardness, respectively, by 1.3, 18, 13.1, and 22% at the end of tests that are remarkably different from that of pure sand filter that is neutral.

As a whole, it can be seen in all Figs. 2–9, there is an initial increase in turbidity index, water hardness, EC, Cl, Mg, and Ca values in all tests. This increase may be due to the remaining salt ions on sand particles which are initially washed out in filtration process or due to desorption of ions by organic adsorbents.

5. Adsorption process

As already mentioned, the chemical properties of inlet waters to four filters were the same. Table 5 shows the percentage of chemical components reduction in outlet solutions collected from different filters. As indicated in this table, the bio-filters with sand reduced turbidity of outlet solutions by 10% more than sand filter. From this table, it can also be found that the sand filter is not only unable to reduce

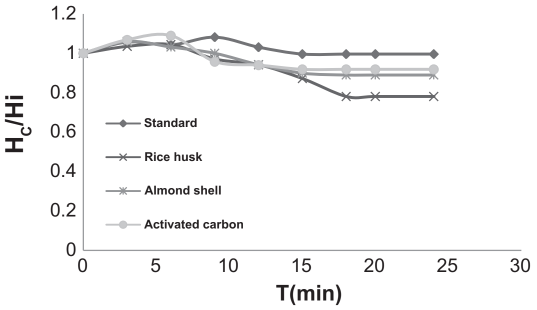

Fig. 9. The effect of filters on water hardness over time.

Table 5
Percentage of chemical components reduction in outlet solutions using different filters ("+" means adsorption and "–" desorption)

	Components							
Type of filter	Turbidity	EC	hardness	K^+	Na^+	Ca^+	Mg^{2+}	Cl^-
Pure sand	67.0	−8.5	0.44	−8	−0.2	4	−1.6	−4
Rice husk + sand	77.2	3	23.5	−123.4	−11.67	30.5	17.5	20
Almon shell + sand	70.2	3	13.1	−13.4	−3	22	5	16.7
Activated carbon + sand	77.4	4	18	−4.5	5.5	29	8.2	22.6

concentrations of existing ions such as Mg, Na, Cl, K, and EC from saline water, but it released some ions and increased the concentration of above-mentioned components. However, the impact of pure sand filter on the reduction of water hardness and Ca concentration is negligible. Regarding K and Na ions, bio-filters with sand (except activated carbon plus sand) released some ions and increased the concentration of K and Na ions in outlet solutions. However, these filters reduced the concentrations of Ca, Mg, Cl, water hardness, and EC in outlet solutions from 3.4% for EC to 30.5% for Ca.

Among the bio-filters, the highest adsorption value of Ca was related to rice husk plus sand that was 30.5% and the minimum value was 22% for almond shell plus sand filter. Regarding Mg and Cl ions, the maximum adsorption value, 22.6%, was related to activated carbon plus sand and minimum value, 5%, was related to almond shell plus sand. The highest reduction of water hardness was achieved by rice husk and sand filter that was 23.5% and lowest one was related to activated carbon plus sand that was 13.1%. The impact of three bio-filters on EC reduction was nearly the same and negligible.

What can be found from this study is the capability of rice husk, almond shell, and activated carbon plus sand filters (bio-filters) to adsorb Ca, Mg, Cl ions, and water hardness from 5 to 30.5%. None of these filters reduced the concentration of K in outlet solutions.

The past research results showed that the capability of adsorbents is different. For instance, a research indicated that the adsorbent coefficient of rice shell was nearly 90%. However, the magnitude of element that is adsorbed depends not only on the type of adsorbent, but also on the type and amount of substance exists in the aqueous solution [7]. The capability of pure sand to maintain surface adsorption is low [16], but a mixture of sand and organic adsorbents such as the above-mentioned filters in this research can adsorb ions and reduce the salinity [17].

6. Conclusions

The results of the current study provided evidence that:

(1) Sand filter is not able to reduce concentration of Mg, K, Na, and Cl ions, turbidity and EC indices of the saline water.
(2) A combination of organic adsorbent with sand (bio-filter) can reduce Mg, Ca, and Cl ions to different extents. Rice husk, almond shell, and activated carbon with sand as bio-filters reduce Ca concentration by 30.5, 22, and 29%, respectively. The percentage of Cl adsorption by rice husk, almond shell, and activated carbon are 20, 16.7, and 22.6%, respectively.
(3) A mixture of rice husk, activated carbon, or almond shell with sand can reduce water hardness by 23, 18, and 13.12%.
(4) What resulted from these tests are the reductions of 70 to 77% and 67% in turbidity index by bio-filters and pure sand (standard) filters, respectively. That is nearly 10% more than pure sand filter.

List of symbols

Symbols		Description	Unit
Ca^{2+}	—	concentration of calcium cations	ppm
C_f	—	final concentration of saline water	ppm
C_o	—	initial concentration of saline water	ppm
EC	—	electrical conductivity	ds/m
Mg^{2+}	—	concentration of magnesium cations	ppm
TDS	—	total dissolved solids	mg/L

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