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The Effect of Magnetic Nanoparticles along with Magnetic Experimental Modeling for the Desalination of the Caspian Sea Water

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ABSTRACT

In this study, samples of coastal waters of Kiashahr port were collected. Magnetic desalination involves exposing the sample to a magnetic field and putting the water in physical contact with magnetic nanoparticles which were synthesized with the co-precipitation method. X-ray diffraction, Fourier transform infrared spectroscopy and field-emission scanning electron microscopy were used for the characterization of nanoparticles. The results showed that nanoparticles have a spherical shape and a diameter of less than 20 nm. After modifying the surface of Fe_3O_4 nanoparticles with SiO_2, they maintained their uniform distribution and spherical shape but their size increased by 20 nm. The salinity and electrical conductivity of the sample was measured prior to and following the magnetic treatment. Maximum reduction in the level of salt and electrical conductivity was achieved when 0.1 g of nanoparticles was placed in contact with sea water for 2 h and also when sea water at a flow of 50 ml/min was introduced to a magnetic field of 30 mT for 20 s. The amount of salt in the sample was reduced to 9.65 g/l using the above-mentioned method -having an initial value of 11.6 g/l.

Keywords: Water purification; Magnetic field; Nanomaterials; Caspian Sea; Salinity

1. INTRODUCTION

Water is the basic substance of life on earth. Water shortages affect 88 developing countries that are home to half of the world's population. In today's world, finding freshwater supplies the prevention of water pollution and treatment of water resources to be used in living environments and desalination are among the serious challenges faced by human societies. Owing to a decrease in the level of ground waters and the resulting increase in salinity of agricultural waters and also overpopulation and the increasing need for water, the focus of this study is on methods of facilitating the desalination of sea water for needed applications [1-4].

The techniques in water purification can be classified into eight methods: distillation processes, adsorption, biotechnology, catalytic processes, membrane processes, ionizing radiation processes, magnetically assisted processes and nanomaterials based processes which will be dealt with in this study [5]. When water is passed through a magnetic field, its physical and chemical properties are improved, this water is called "magnetic water". When obtaining magnetic water by applying force on ions of salts in water –most of which are soluble dicarbonates - they are transformed from ions into molecules.

One of the other changes that occur in magnetic water, is the configuration of the

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electrical changes of the water molecules. Given that there is little difference in the amount of forces existing between molecules of water, their configuration is completely coincidental. If a magnetic object approaches molecules of water with one of its poles, water molecules with the opposite pole facing the object are attracted to it and those with the same pole facing it are repelled. In these circumstances, positive hydrogens obtain more power and consequently, the electrical charge of the water molecule will be different from normal water resulting in a decrease in the size and therefore an increase in the number of molecules per volume unit and also in the solubility of the water [6]. In irrigation of farmland with magnetic water, the device generating magnetic field is placed in the outlet of water from wells or where river water enters the access channel and as water passes through the magnetic field, changes occur in water molecules and ions. The water becomes more active and is able to flow and also prevent harmful metals such as Lead or Nickel from being absorbed by the roots of plants [7, 8].

In a study using magnetic fields with different intensities and modes, on a lake in Jeddah, Saudi Arabia, Alkhazan et al. (2010) magnetized the lake water and studied its physical and chemical properties and the existing bacteria. They found that the intensification of the magnetic field results in the clarity of water, a relative increase in pH and a remarkable decrease in the electrical conductivity of the lake water. There was also a fall in the number of Lead ions and bacteria [9].

The unique properties of the reacting surface of nanoscale materials, lead to the development of magnetic separation models at nanoscale, when dealing with nanosized magnetic materials, different magnetic behaviors are shown toward magnetic material bodies as the design of the magnetic separator changes. Fe_3O_4 magnetic nanoparticles have presently attracted researchers' attention considerably as a result of their unique properties such as very small size, high surface to volume ratio, surface modification capabilities, excellent magnetic properties and their high bio compatibility. They have reverse spindle structure properties and at nanometer scale, they show superparamagnetic properties [4, 5].

Functionalized magnetic nanoparticles were selected as adsorbent in methods that are a combination of adsorption and magnetic separation due to the following benefits: a) magnetic nanoparticles can be prepared with high quality and through a simple procedure. b) Their adsorption capacity is higher because of their high surface area. c) These particles are superparamagnetic, i.e. the metal coating on the absorber can easily be separated from the water by applying external magnetic field [10].

The use of magnetic nanoparticles in water treatment to remove pollutants is divided into two categories:

1)The technologies that use magnetic nanoparticles as a deterrent absorbent or carrier to promote an effective removal.

2)Those who apply magnetic nanoparticles as a photocatalyst to break down pollutants or convert them into a less toxic form [4].

In recent years, application of nanoscale irons-which are strong ferromagnetic- for water purification, has been widely studied. These nanoparticles are effective in changing the shape and detoxification of a wide variety of environmental pollutants such as chlorinated organic solvents, organochlorine pesticides, trinitrotoluenes, phenols, and herbicide molinate, amino carboxylic acids and p-hydroxybenzoic acid. It has been proven that in addition to organic contaminants, inorganic anionic contaminants such as NO_3^- , $Cr_2O_7^{2-}$, can be broken down using iron nanoparticles [4, 5].

2. MATERIALS AND METHODS

The most common way for quantitative description of the salinity of water is measuring the electrical conductivity [7]. Experiments in this study, were carried out on the coastal waters of the Caspian Sea. The Caspian Sea is a unique and closed water environment and also the largest on Earth, located in Asia and Europe and is considered to be specially important both globally and in the countries around it. The volume of this sea is 78000 km^3 with an area of about 400000 km^2**.**

One of the most important abiotic factors of the Caspian Sea is its salinity. Compared with oceans and seas, the average amount of the Caspian Sea salt is about one third of the seas [11]. Not only that the salt water of the Caspian Sea is different from other seas, but the composition of its salt is also different. The relative concentration of Calcium, Magnesium and sulfate ions in the Caspian Sea is more than the average existing in the oceans [12]. Salinity of the Caspian Sea increases from the north to the south. Salinity of the southern region is usually between 12 -13.5 gr/lit and is variable. Changes in the salinity of the Caspian Sea from north to south is an indication of an input of fresh water in the northern region and the values of 12.5 to 13.5 gr/lit are in the central and southern parts of the Caspian Sea and seasonal variations of salinity are less than 0.2-0.4 gr/lit. The average annual salinity of the Caspian Sea in the deep water in the southern region increases as much as 0.1-0.3 gr/lit from the surface to the bottom [13].

According to studies carried out on the salinity of the Caspian Sea and considering that the average salinity of the Caspian Sea has been reported to be 12.85 gr/lit, samples were collected from coastal waters of Kiashahr Port that is the input fresh water of Sefidrood River. The position of sampling is specified using GPS (GARMIN-model76csx) with alatitude of 37° 26′ and a longitude of 49° 57′.

Chemicals

All chemicals used were of analytical grade were used without further purification. Sodium chloride, iron sulphate, iron nitrate, ammonium solution (25wt. %), poly-ethylen-glycole (M.W.6000), hydrochloric acid, trichlorooctadecylsilane all of which were purchased from Merck (Germany) and absolute ethylalcohol was purchased from Bidestan (Iran). The deionized water used in all experiments was produced with a Milli-Q unit (millipore) with a resistivity of 18 MΩ/cm. All of the above substances were used for preparing nanoparticles.

Experimental

The tests include two parts: physical contact of water with magnetic nanoparticles and exposing water to a magnetic field.

Method of preparing magnetic nanoparticles

In preparing the magnetic nanoparticles in order to obtain a pure product, the ratio of Fe^{3+} to Fe^{2+} should be two to one. The major factor that disturbs this ratio is oxygen that oxidizes Fe^{2+} and transforms it into Fe^{3+}. Therefore, to obtain relatively pure product, oxygen should be removed from all the stages of the synthesis [14, 15].

First, 1000 ml of deionized water was placed on the nitrogen flow for 30 min to be deoxygenized. This water was used to dissolve the salts and wash magnetic nanoparticles. The amounts of 8.1 g of iron nitrate and 2.8 g of iron sulfate were weighed and put into a two neck flask with 100 ml of deionized water and stirred on a heater at a temperature of 60° C under helium gas for half an hour. A 2 g of poly-ethylene-glycole, was stirred in 15 ml of deionized water on the heater at a temperature of 60° C for half an hour and added to the first solution and mixed for half an hour. Then, 20 ml of ammonia solution was added to the solution. The color of the solution quickly turned from orange to black. After half an hour, the contents of the flask were moved into a beaker and a magnet was put under a beaker. A black sediment was deposited and separated from the solution. The sediment was washed several times with water and ethyl alcohol to pH=6. Figure 3 shows the magnetic nanoparticles synthesized. To modified surface of magnetic nanoparticles, 200 µl of trichlorooctadecylsilane, and 10 µl of hydrochloric acid were poured in 20 ml of ethylalcohol and 0.5 ml of deionized water was added and put on the heater at a temperature of 50°C to be stirred for half an hour. A 50 ml of ethylalcohol was poured on the black clot on the heater at a temperature of 60°C for 10 min. Then the previously-mentioned solution was added to this and stirred for half an hour. It was then washed with water to pH=7. Then the sediment was put in the oven for 8 h to dry [15, 16].Thereafter, nanoparticles were sent to an instrumental analysis laboratory to determine the morphology, crystal structure and composition and for the identification of functional group.

Subsequently, the salinity and the electrical conductivity of a sodium chloride solution with salinity of 12.85 g/l and a sample of sea water was measured (by conductivity meter model 914 Metrohm, Switzerland). Thereafter, the nanoparticles -with the weights of 0.025, 0.05, 0.075 and 0.1 g-were added to 50 ml of sodium chloride solution and each was put in a shaker with a speed of 250 rpm for half an hour, an hour, two hours and three hours. Again salinity and their electrical conductivity were measured.

According to Figures 9 and 10, an amount of 0.1 g of nanoparticles was added to 50 ml of sea water and was put in the shaker for two hours. The salinity and the electrical conductivity were measured again. Then according to the results in Figures 1 and 2, the water that was in contact with the nanoparticles was exposed to a magnetic field with an intensity of 30 mT and a flow rate of 50 ml/min for 20 s and once again, the two factors were measured.

Experimental model

The experimental model included a beaker with a volume of 2 L as the water tank, a varistaltic pump that is used for sending water with different flow rates into the magnetic field, silicone hoses and four magnets with intensities of 30, 150, 250 and 430 mT. Because electrical conductivity depends greatly on temperature, a bath-circulator was used to maintain a constant temperature of 25°C. Then, it was passed through a filter paper to separate its sand and silt particles. Sea water with three flow rates of 50, 100, 150 ml/min for durations of 20, 40, 60s was sent in triplicate into each of the magnetic fields and its salinity and electrical conductivity were measured again.

Fig. 1. Experimental model with magnetic field intensities of 150, 250, 430 mT.

In this way, the effect of intensity of a magnetic field, the change in flow rate and the time of exposure to a magnetic field were investigated and the results were analyzed using SPSS software.

3. RESULTS AND DISCUSSION

In this section, we first review the results of the statistical analysis of magnetic water using SPSS and then the features of synthesized nanoparticles were explained.

Figure 2 shows that changes in the salinity of the Caspian Sea in different magnetic field strengths, different flow rates, and different times were significant. Also, the lower the intensity of the magnetic field, the flow rate and the exposure time, the higher the amount of reduction in salinity. The greatest decrease in the salinity of the Caspian Sea was in magnetic field with a30 mT intensity and a 50 ml/min flow rate for a duration of 20 s.

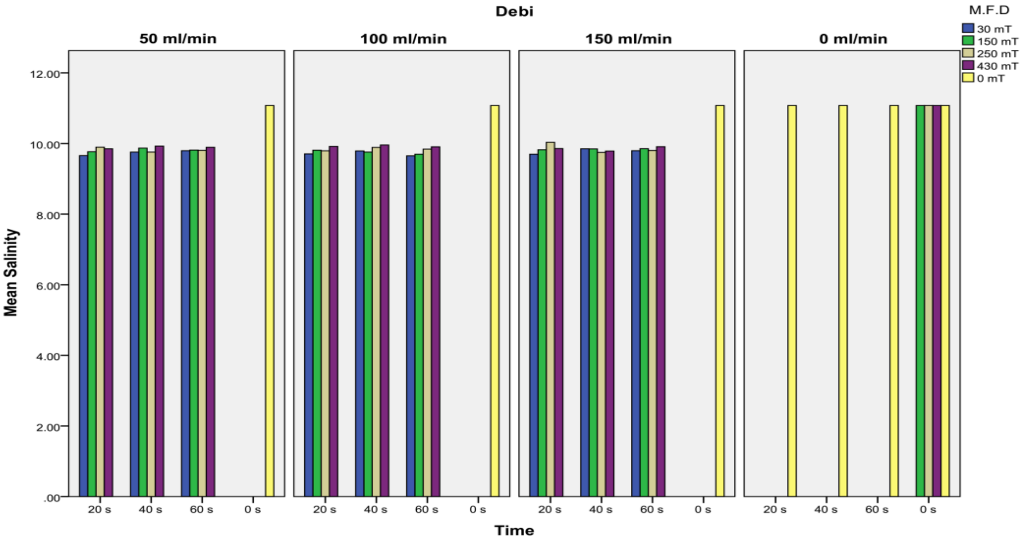

Fig. 2. The amounts of salinity of the Caspian Sea in Kiashahr port for flow rates of 50, 100, 150 ml/min, times of 0, 20, 40, 60 and magnetic field intensities of 0, 30, 150, 250, 430 mT.

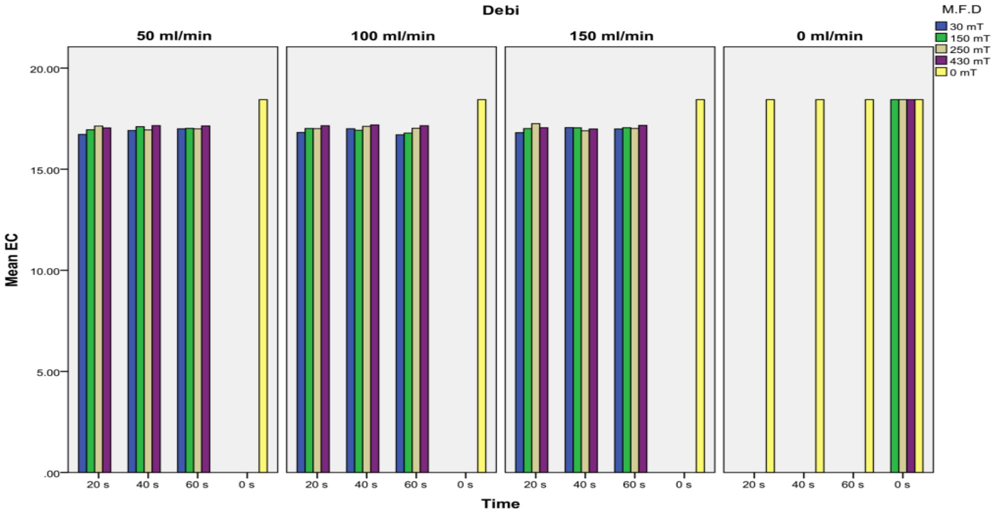

Fig. 3. The amounts of electrical conductivity of the Caspian Sea in Kiashahr port for flow rates of 50, 100, 150 ml/min, times of 0, 20, 40, 60 and magnetic field intensities of 0, 30, 150, 250, 430 mT.

Figure 3 shows that changes in the electrical conductivity of the Caspian Sea in different magnetic field strengths, different flow rates, and different times were significant and also, the lower the intensity of the magnetic field, the flow rate and the exposure time, the higher the amount of reduction in electrical conductivity. The greatest decrease in the electrical conductivity of the Caspian Sea was in magnetic field with a30 mT intensity and a 50 ml/min flow rate for duration of 20 s.

The FT-IR (model Nexus 870 by Nicolet) spectrum of synthesized nanoparticles can be seen in Figures 4 and 5.

In the FT-IR spectrum of synthesized nanoparticles of Fe_3O_4, the absorption band seen in the range of 566 cm^{-1} belongs to the link between iron and oxygen (Fe-O) indicating the formation of ironoxide. In Figure 6, this band is covered with the band of 669 cm^{-1} which is the proof of a successful bond coating of Fe_3O_4 by a SiO_2 group.

In the FT-IR spectrum of synthesized nanoparticles of Fe_3O_4 /SiO_2, the numbers 1388.73 and 1636.71 cm^{-1} indicate the absorption of SiO_2 on Fe_3O_4 nanoparticles.

XRD spectrum of synthesized nanoparticles can be seen in Figures 6 and 7.

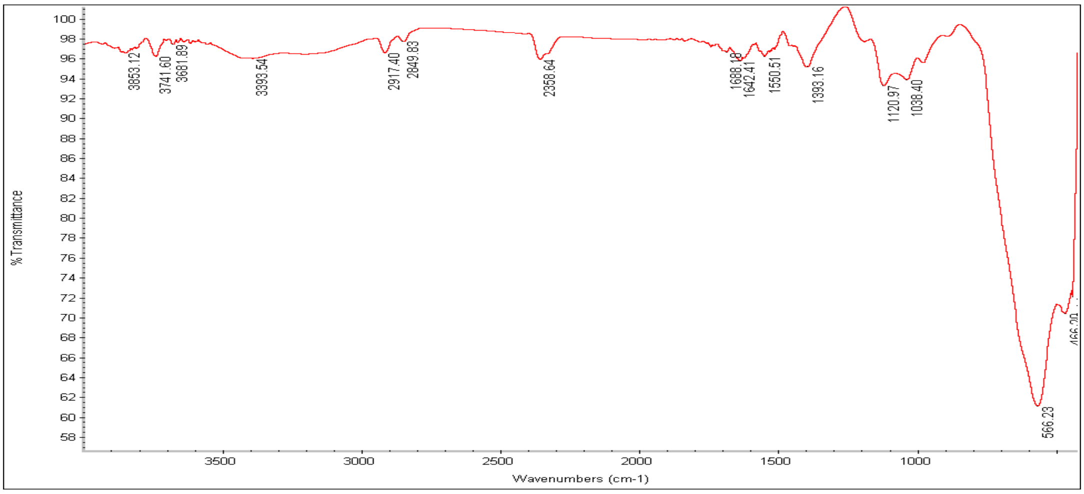

Fig. 4. FT-IR spectrum for nanoparticles of Fe_3O_4.

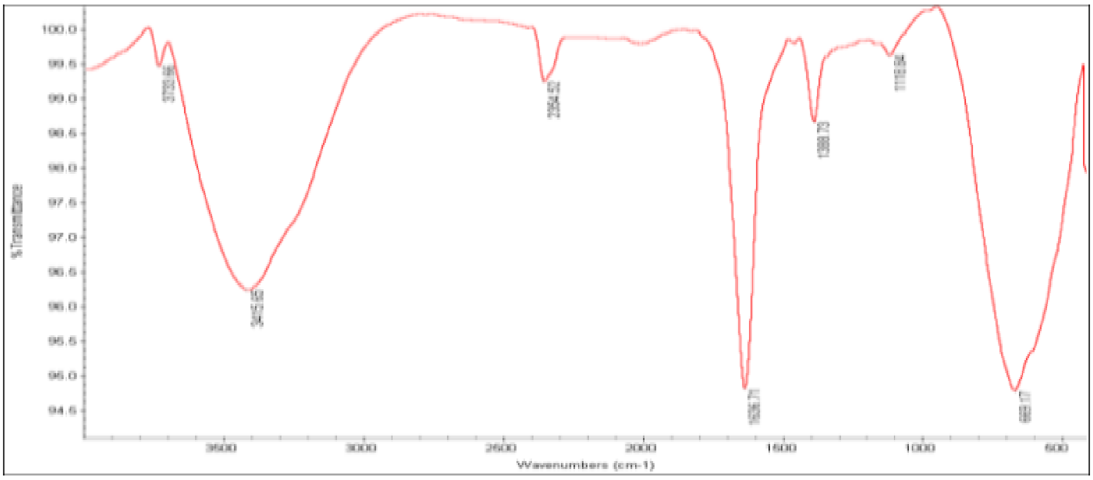

Fig. 5. FT-IR spectrum for nanoparticles of Fe_3O_4/SiO_2.

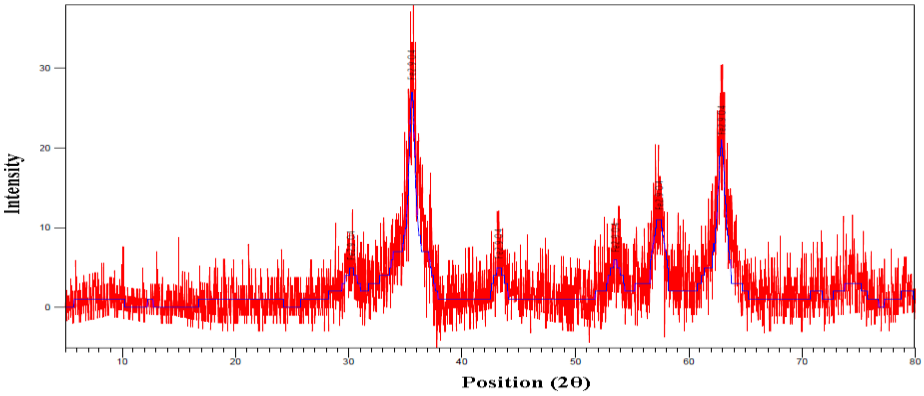

Fig. 6. XRD spectrum for nanoparticles of Fe_3O_4.

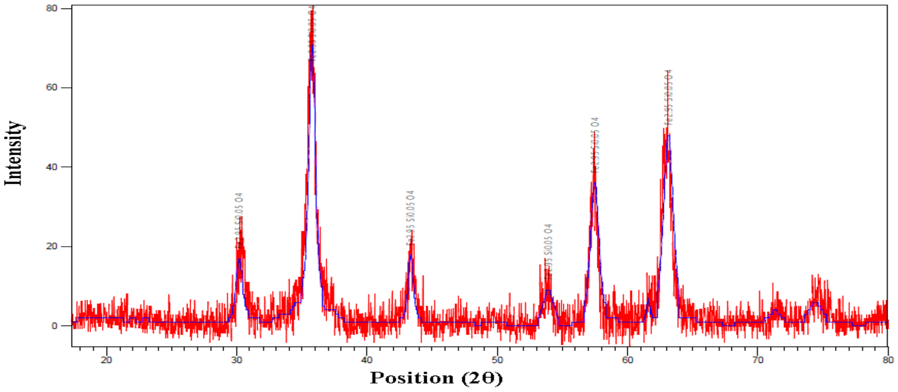

Fig. 7. XRD spectrum for nanoparticles of Fe_3O_4/SiO_2.

XRD (model 3003PTS by Seifert) spectrum of synthesized nanoparticles of Fe_3O_4 shows specific spectra that correspond with standard card number 01-087-0246 and as seen in Figure 6, $Fe_{2.9}O_4$ nanoparticles is formed. Figure 7 shows XRD spectrum for surface modified nanoparticles that correspond with standard card number 00-052-1140 and contains $Fe_{2.95}\ O_4Si_{0.05}$, these peaks indicate the stability of the crystal network of nanoparticles during the synthesis process.

Figures 8 and 9 show the FE-SEM (Mira3-XMU model by Teskan) images of synthesized nanoparticles. These images show that nanoparticles have spherical shapes and their size is below 20 nm. After modifying the surface of the Fe_3O_4 nanoparticles with SiO_2, they retained their uniform distribution and their spherical shapes and size increase slightly larger than 20 nm indicating being covered with SiO_2.

Magnetic nanoparticles were placed in physical contact with sodium chloride solution. The results of which can be seen in Figures 10 and 11 and according to Figures 10 and 11, the optimal amount of 0.1 g of nanoparticles was placed in physical contact with Caspian Sea water.

4. CONCLUSION

Changes in the salinity and electrical conductivity of the Caspian Sea at different magnetic field intensities, different flow rates, and different times were significant and also the lower the intensity of the magnetic field, the flow rate and the exposure time, the higher the amount of reduction in salinity. The maximum reduction in salinity and electrical conductivity occurs when 0.1 g of the nanoparticles are placed in contact with Caspian Sea water for 2 h and also when the sea water is exposed to a magnetic field of 30 mT intensity with a flow rate of 50 ml/min for 20 s. With the methods used in this study, the salinity of the water sample was reduced from11.6 to 9.65 g/lit making it suitable for the cultivation of plants resistant to salt. It was also noted that the effect of a magnetic field on the salinity and electrical conductivity is relative to exposure time and flow rate of the passing flow.

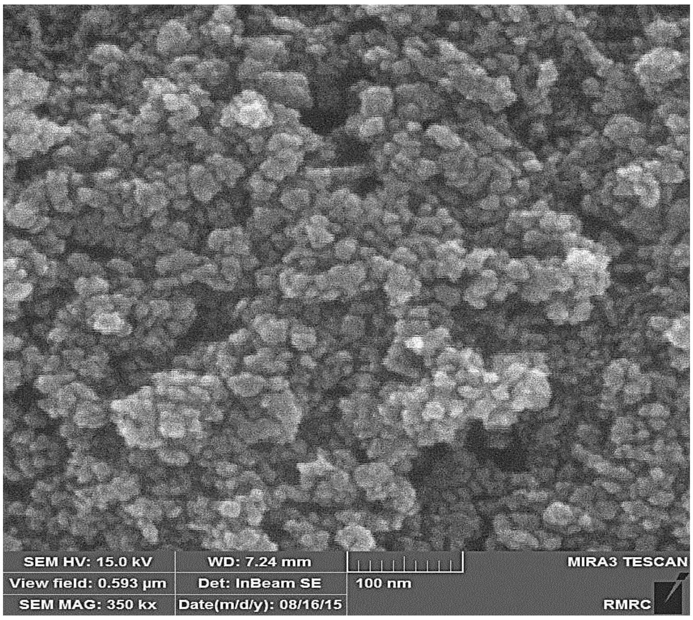

Fig. 8. FE-SEM image of Fe_3O_4 nanoparticls.

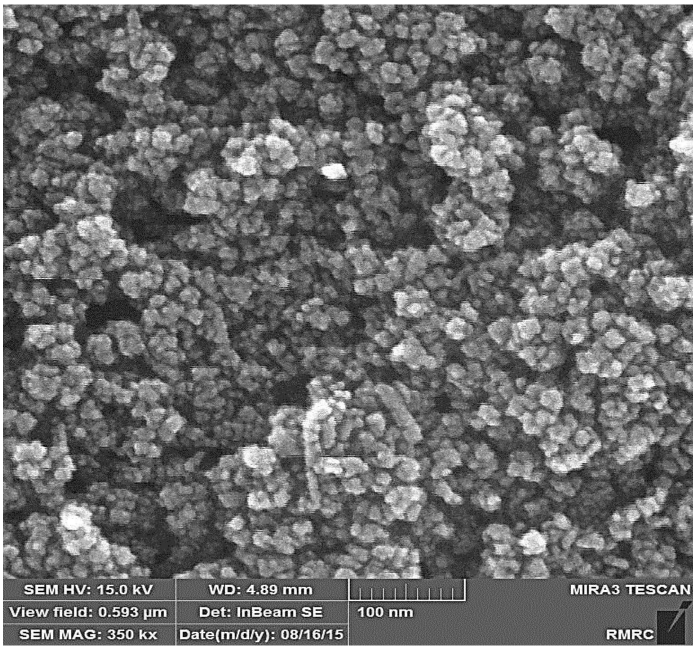

Fig. 9. FE-SEM image of Fe_3O_4/SiO_2 nanoparticles.

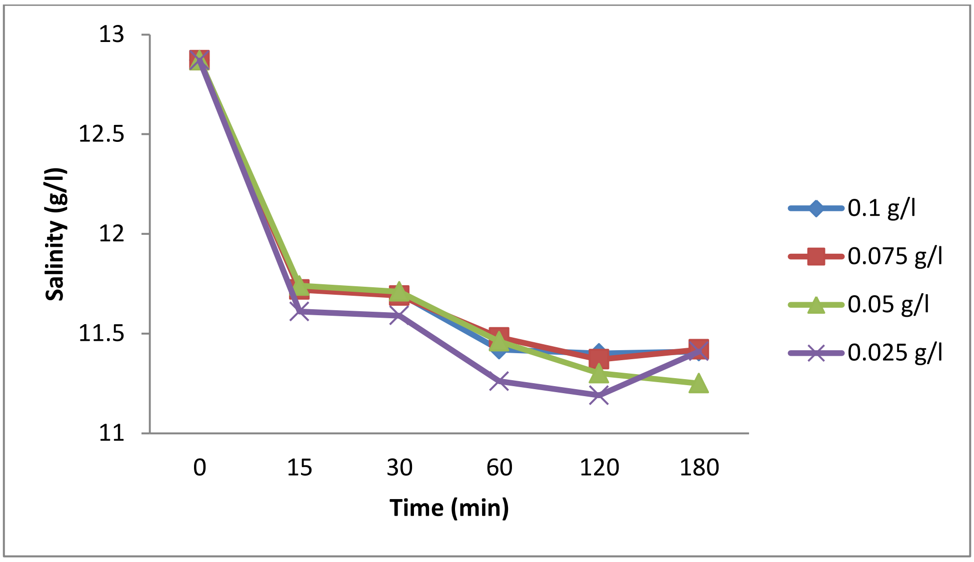

Fig. 10. Comparing the effect of different amounts of magnetic nanoparticles at salinity of NaCl solution during different times.

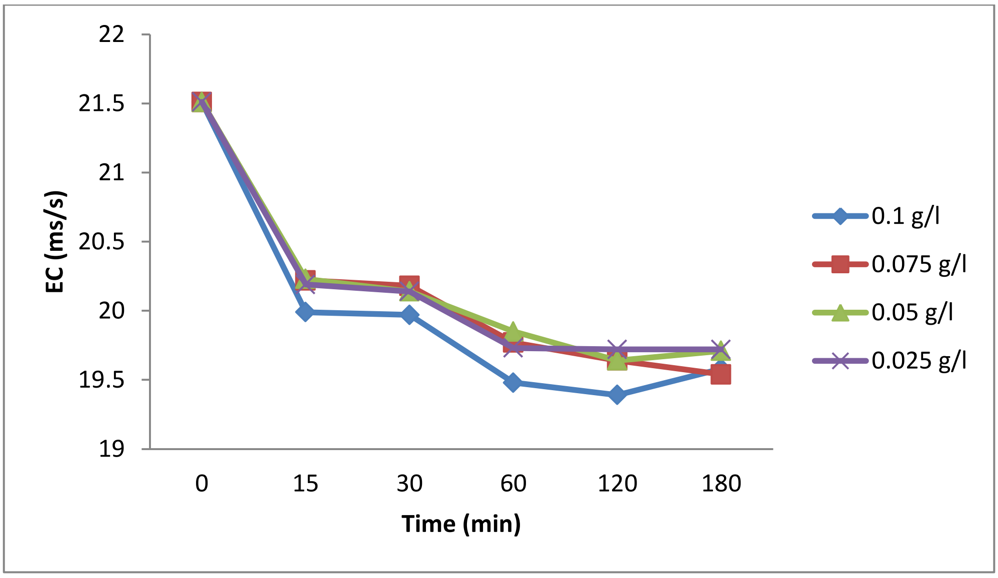

Fig. 11. Comparing the effect of different amounts of magnetic nanoparticles at electrical conductivity of NaCl solution during different times.

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