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Brackish water treatment with carbon nanotubes

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Abstract. The present work aims to experiment the action of carbon nanotubes (MWCNTs) in the removal of sodium chloride from aqueous systems, not using them as a membrane but dispersing them directly in solution, in order to evaluate possible applications in the desalination of brackish water. For this purpose, different aqueous systems have been prepared by varying the sodium chloride concentration and the amount of carbon nanotubes dispersed therein. The systems were stirred for scheduled times and then the amount of residual sodium chloride was measured by drying, after filtration, the systems and weighing the dry residue. In the final part of the experimentation, after having identified the best system, the tests were carried out directly on sea water and using different types of carbon nanotubes such as not oxidized (MWCNTs) and oxidized (MWCNTS-ox) ones.

1. Introduction

The water is a fundamental good for human health. However, the continuing industrial and demographic growth is threatening the quality and quantity of water available on our planet. Industrial and anthropogenic pollutants are creating problems for the entire ecosystem [1-4].

The pollutants released into the environment almost always end up moving into the water, therefore the safeguarding of this important asset must involve various research sectors, such as, chemical innovation processes [5-10] and eco-friendly materials [11-17] with low environmental impact and low pollutant production.

Particularly interesting are those materials which can be advantageously used for the degradation and adsorption of pollutants [18-25] with specific applications in water purification [26-37].

The rapid growth of the world population is causing an increasing demand for clean water. Furthermore, there are many countries where the presence of water is very scarce.

In this context, salt water represents a vast resource and a possible solution since, properly treated, it will be able to meet the needs of a growing population in the near future.

Today the research is focusing on the application of nanotechnology in the field of desalination through the use of nano-materials with interesting and efficient properties, such as graphene [38] and carbon nanotubes [39-42]. The introduction of nanotechnology allows for the creation of more

efficient materials, such as the so-called "new generation membranes" [43-46] that require less energy and chemical reagents and, therefore, a lower emission of pollutants into the environment.

In particular, in this work the possibility of using carbon nanotubes in water desalination was tested, not using them as a membrane but directly dispersing them in solution.

2. Materials and methods

2.1. Preparation of initial solutions
Initially three solutions of sodium chloride (NaCl) with different molar concentrations were prepared such as: [0.2], [0.5] and [0.75] M.

These concentration values were chosen because they fall more frequently in the molar concentrations of brackish waters.

2.2. Synthesis of multi walled carbon nanotubes
The carbon nanotubes (MWCNTs) used in the experimentation were prepared according to the methodology already reported in previous articles [47, 48].

In particular, they were synthesized using the Catalytic Chemical Vapor Deposition (CCVD) method, where the catalyst used was Co-Fe on a natural zeolite support and the carbon source was ethylene. The obtained nantotubes were characterized by a purity of 94%.

Oxidized nanotubes (MWCNTs-ox) were also used for the seawater tests, prepared according to the methodology already detailed in a previous article [48].

In particular, in order to oxidize the carbon nanotubes, they were treated with a hydrofluoric acid solution for 24 hours and then subsequently treated by a solution with HNO_3/H_2SO_4 ratio equal to 0.6 for 24 hours.

2.3. Experimental procedures
The different systems were prepared by varying the concentration of sodium chloride solutions, the amount of carbon nanotubes and the stirring time.

In particular, each system was prepared by taking 50 mL of each single sodium chloride solution of different concentration. Inside them different amounts of carbon nanotubes equal to 0.05 g, 0.15 g, 0.25 g, 0.5 g, 0.75 g were added.

Finally, each system was stirred using a stirring speed of 200 rev / min for different times of 2.5 min, 5 min, 10 min, 30 min, 60 min and 75 min. The tests were all conducted at room temperature. After the predefined stirring time, the samples were filtered on cellulose filters to remove the carbon nanotubes.

Subsequently the filtered solutions were dried at 200°C on a hot plate until a dry residue was obtained. Finally, the latter was weighed on a precision balance. The amount of obtained solid residue represented the amount of sodium chloride not retained by the carbon nanotubes.

The amount of NaCl retained by the MWCNTs was simply calculated as the difference between the weight of NaCl initially present in solution and the weight of the dry residue.

3. Results and discussions
The following diagrams show the percentages of sodium chloride removed as a function of the stirring time and the quantities of carbon nanotubes used in the different sodium chloride solutions.

Figure 1 shows that the percentages of removal of NaCl, from 50 mL of sodium chloride solution [0.2] M, vary between a minimum value of 5.017%, which occurs for a stirring time of 2.5 min and using 0.05 g of MWCNTs, at a maximum value of 8.28% which occurs for a stirring time of 30 min and using 0.5 g of MWCNTs.
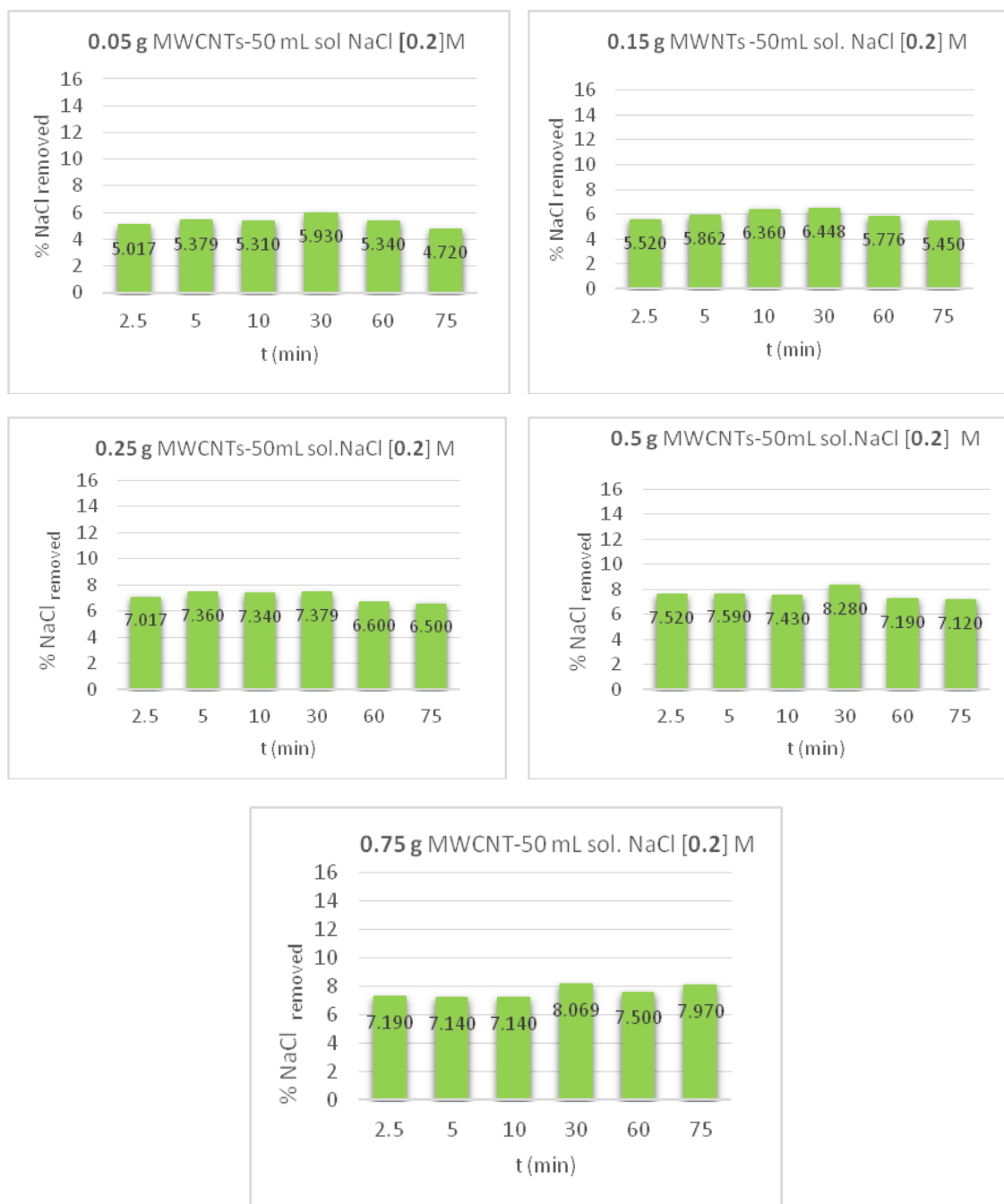
Figure 1. Percent grams of NaCl removed from 50 ml of a solution [0.2] M of NaCl at room temperature, as a function of the stirring times and the amount of MWCNTs.

The following Figure 2 shows the data obtained using an initial solution of sodium chloride with a concentration equal to [0.5] M.

The minimum reduction value is 4.65%, using 0.05 g of MWCNTs with a stirring time of 2.5 minutes, while the highest value is obtained using 0.5 g of MWCNTs for a time of 30 min, equal to 9.66%.

Figure 3 shows the data obtained using a starting solution of sodium chloride with a molar concentration of [0.75] M. In this case, the minimum percentage of NaCl percentage removal is 4.817%, for a quantity of MWCNTs equal to 0.05 g and for a time of 2.5 min, while the maximum

value is 11.662% and is obtained for a quantity of MWCNTs equal to 0.75 g and for a time of 30 minutes.
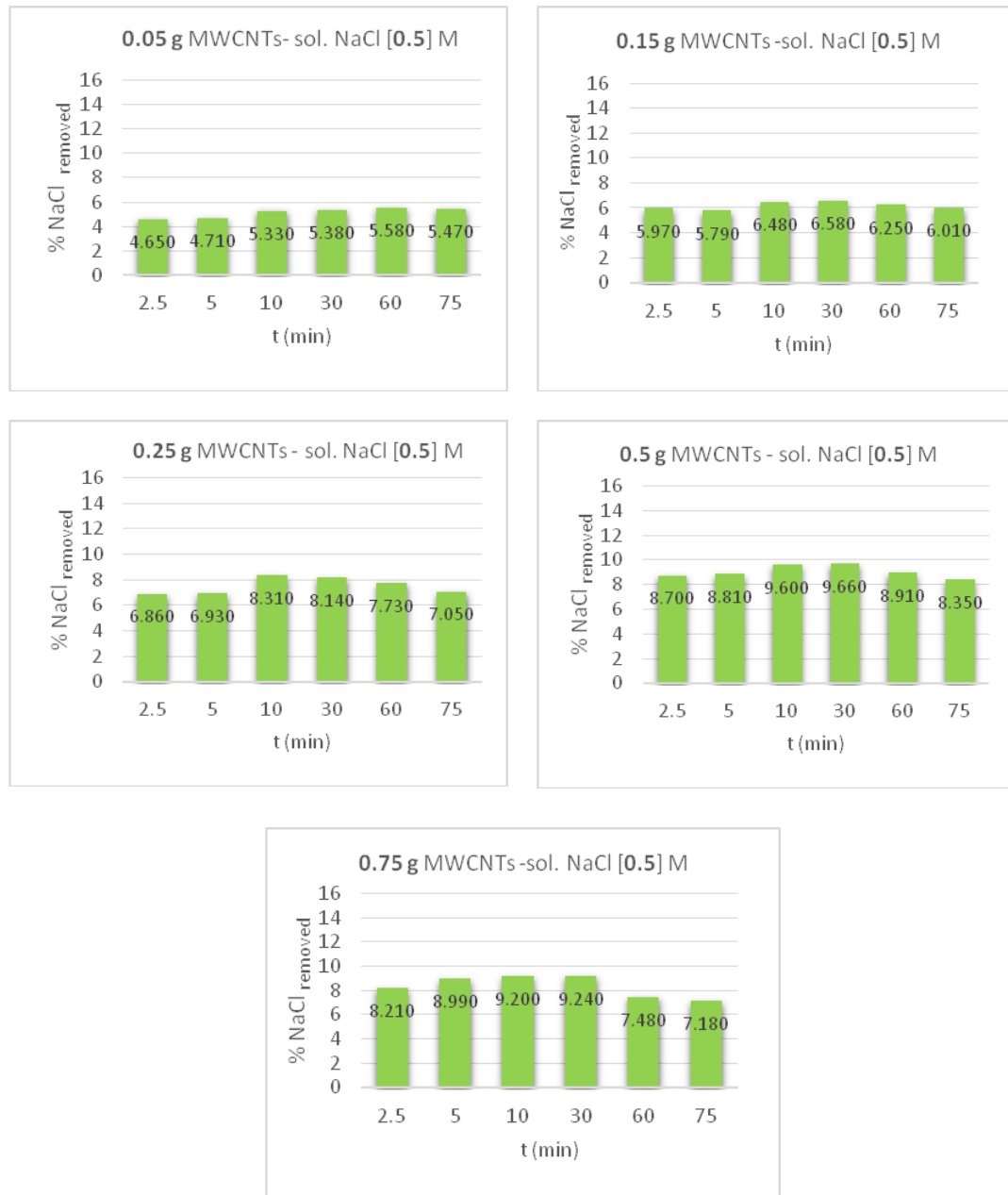

Figure 2. Percent grams of NaCl removed from 50 ml of a solution [0.5] M of NaCl at room temperature, as a function of the stirring times and the amount of MWCNTs.

Figure 4a shows the average removal values obtained by averaging the values obtained at different stirring times for each individual system. From the reported data it is clear that increasing the quantity of carbon nanotubes used, there is an increase in the average percentage of salt retained. However, in some cases, the experimental results showed a slight decrease in the percentage of removal for maximum amount of MWCNTs used, i.e. equal to 0.75 g. This can be justified by the fact that the

presence of many nanotubes in solution creates agglomeration phenomena between the nanotubes themselves with a consequent decrease in the removal capacity.
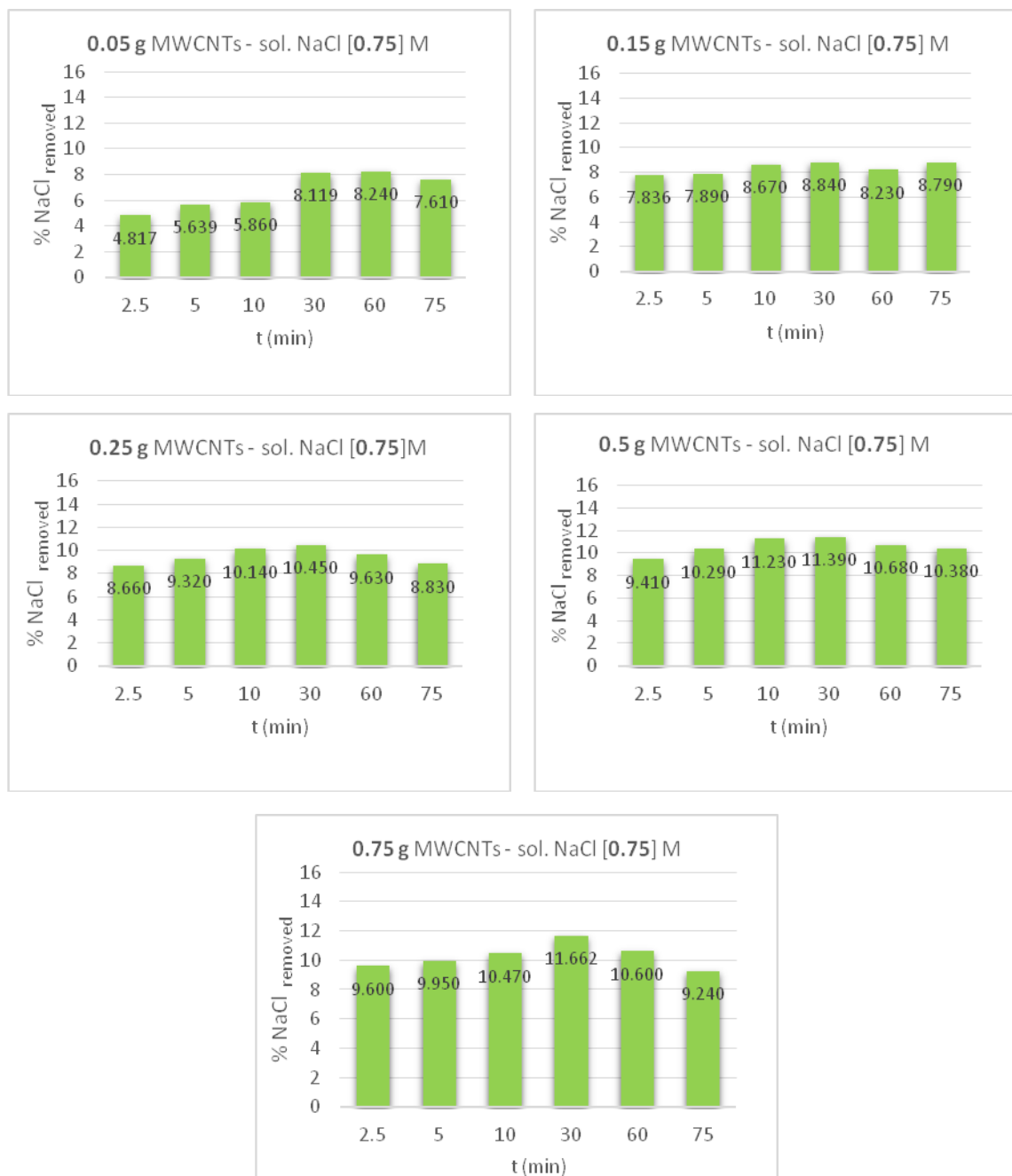

Figure 3. Percent grams of NaCl removed from 50 ml of a solution [0.75] M of NaCl at room temperature, as a function of the stirring times and the amount of MWCNTs.

Figure 4b compares the average percentages of removal obtained by averaging the values relating to different quantities of carbon nanotubes of each system.

The data obtained show that as a function of the stirring time, regardless of the quantity of nanotubes used, a NaCl removal trend is observed which reaches its maximum for times of 30 minutes.

Thus, among the different experimental conditions studied, the greater reduction in sodium chloride is obtained utilizing a solution of sodium chloride with concentration of [0.75] M, using 0.75 g of MWCNTs and stirring times of 30 minutes.
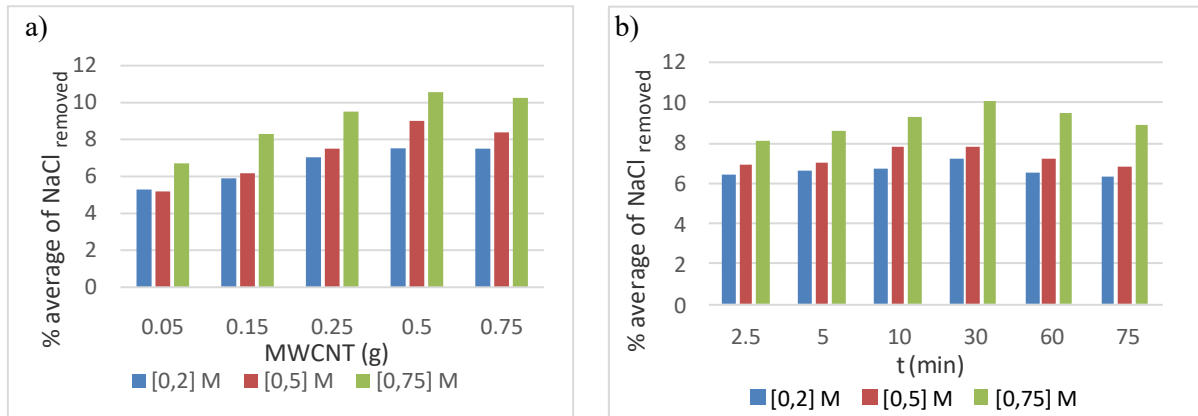

Figure 4. Average percentages of removal of NaCl: (a) as a function of amount of MCWNTs; (b) as a function of stirring time.

3.1. Identification of the optimal ratio $NaCl_{initial}$ (g) /MWCNTs (g)

Subsequently, the data obtained were processed as a function of the ratio $NaCl_{inital}$ (g) / MWCNTs (g), where the numerator represents the amount in grams of sodium chloride present in the initial solutions at concentration [0.2] M, [0.5] M and [0.75] M, while the denominator represents the quantity in grams of carbon nanotubes used.
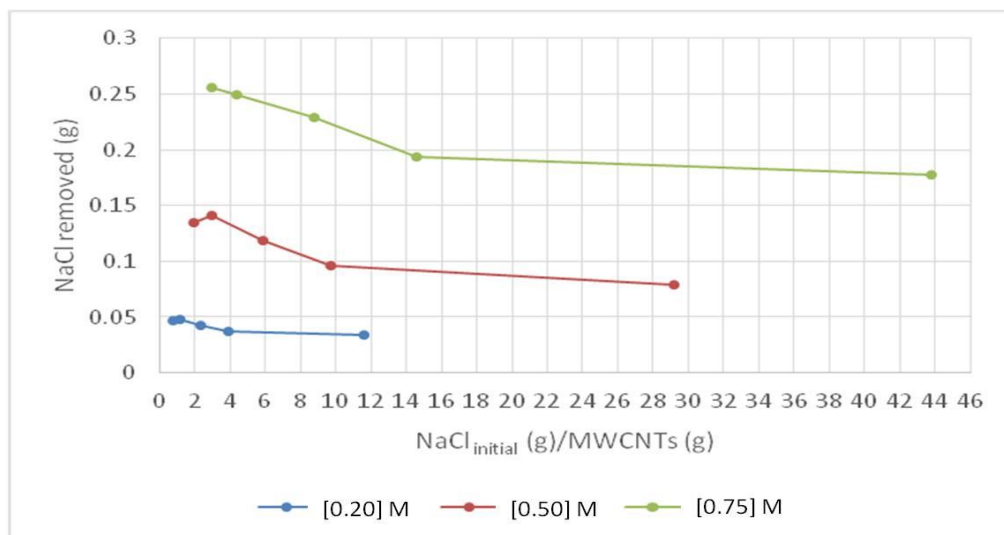

Figure 5. Variation of the NaCl grams removed as a function of the initial ratio $NaCl_{inital}$ (g)/MWCNTs (g) after a 30 minute treatment in the three systems with different salt concentration [0.2] M, [0.5] M, and [0.75] M.

Several graphs have been developed for each stirring time considered. In this context, for reasons of space, only the one relating to 30 minutes is reported (Figure 5). It is possible to observe that the values of the ratio $NaCl_{initial}$ (g) / MWCNTs (g), which allow the highest removal of sodium chloride fall at low values of this ratio between about 1 and 5.

3.2. Sea water sample test

Subsequently, the data obtained were compared with those made directly on a seawater sample. The sea water sample was initially characterized by determining the dry residue by drying it at 180 °C, which was found to be 33.6 g/L. Considering, by approximation, this as if it were all sodium chloride, the sample was found to have a molar concentration of 0.57M. Therefore the data of the sea water sample were compared with the data previously obtained relating to the 0.5 M solution, being concentrations very similar to each other. Furthermore the tests were also carried out with oxidized carbon nanotubes (MWCNTs-ox).
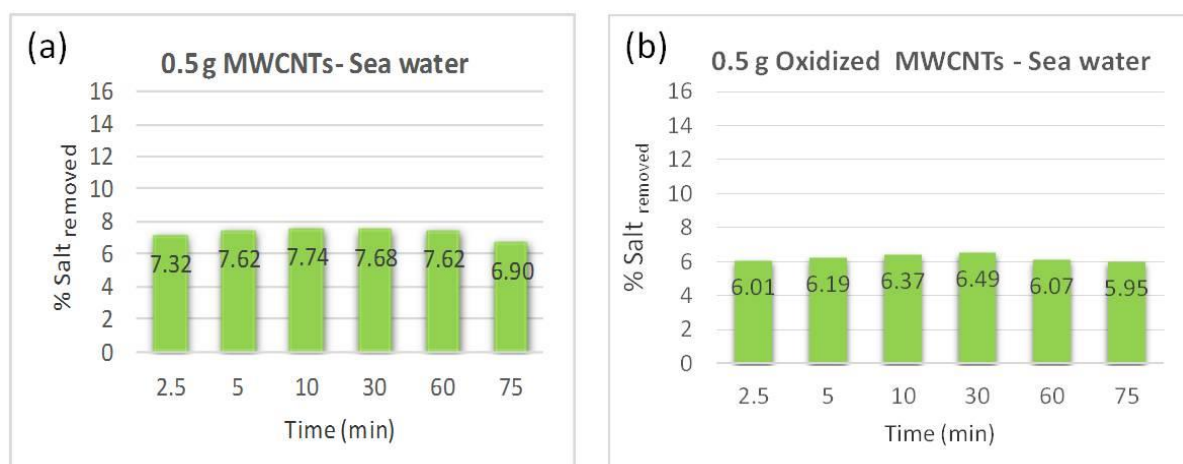

Figure 6. Removing percentage of salt removed as a function of the stirring time on a 50 mL sea water sample: (a) using 0.5g of carbon nanotubes; (b) using 0.5g of oxidized carbon nanotubes.

The data reported in Figure 6a show percentages of removal that are on average around 7.5% slightly lower, but still comparable to the data reported in Figure 2 and relating to the similar system characterized by 0.5 MWCNTs and concentration 0.5 M NaCl. No advantage was obtained with the use of oxidized carbon nanotubes which showed lower efficiency (Figure 6b).

4. Conclusions

The results obtained allow us to draw the following conclusions:

Of all the systems prepared in the laboratory by varying the quantity of nanotubes, the salt concentration of the solution and the stirring times, the maximum removal of sodium chloride recorded was around 11.5%.

The stirring time that allows to have the highest removal rate, with the same salt concentration and quantity of nanotubes used is 30 min

Tendentially, the removal of salt increases as the quantity of carbon nanotubes present in the samples increases, but for quantities of nanotubes greater than 0.5 g there is a slight decrease caused by agglomeration effects of carbon nanotubes.

As the molar concentration of the initial solutions increases, the percentage of salt retained by the carbon nanotubes increases.

The data obtained directly on a sample of sea water can be considered comparable with the data obtained from laboratory salt solutions. It has been shown that oxidized carbon nanotubes do not produce any advantage over unoxidized ones. The reduction of salt on the sea water sample, through a direct dispersion of the carbon nanotubes in the system, has reached an average value of 7.5%.

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