INTRODUCTION

Development of industrial activities in the last decade endangered environment and threaten human with different kinds of anthropogenic contaminants. Water is one of the vital aspects of human life which can solve, contain, and carry different components with it. The increase in anthropogenic pollution of surface water results in bioaccumulation and biomagnification of heavy metals and organic matters in the environment and in the food chain.\[1] Environmental...
pollution with different toxic substances, some with a very long biological half-life in the body, has been recognized as a public health hazard in all over the world.\[^2\] During water treatment, several processes have been utilized for removal these kinds of material from water. Many of the unit processes which currently implemented are sand filtration, oxidation and reduction, chemical precipitation, electrocoagulation, solvent extraction, carbon adsorption, ion exchange, and membrane treatment.\[^{[3,4]}\]

One of the novel techniques is electrosorption with different carbon material electrodes for removing dissolved inorganic contaminants from aqueous solutions such as radionuclides, metal ions, and anions.\[^{[5]}\] Carbon is one of the most popular materials for manufacturing electrodes which possess satisfying electrical, chemical and thermal properties, relatively high capacity, and high surface area. Different type of carbon nanostructures including multi-walled carbon nanotubes (CNTs) and single-walled CNTs (SWCNTs) and graphenes have recently drawn much attention.\[^{[6]}\] Among these types of CNTs, SWCNTs have an excellent mechanical property which can make a fixed bed in removal of contaminants.\[^{[6]}\] One of the promising fabrication techniques for producing electrodes coated with CNTs is the electrophoretic deposition (EPD) procedure, which is mainly a combination of electrophoresis and deposition methods.\[^{[5]}\] During EPD after voltage applied on both electrodes, ions in the water solution can move toward the oppositely charged electrode under the imposed electric field.\[^{[5]}\] Deposition occurs only on conducting surfaces and the advantages of the method are: Low cost, simplicity of the process, uniformity of deposits, control of deposit thickness, and microstructural homogeneity.\[^{[7]}\] The major limitation of EPD is that the deposition only occurs on conductive surfaces.\[^{[8]}\] Dispersing CNTs homogeneously in a suitable solvent is a necessary step for controlled deposition of CNTs. Various solvent have been used to prepare CNTs suspension for EPD, including distilled water,\[^{[9]}\] mixture of acetone and ethanol,\[^{[7,8]}\] dimethylformamide (DMF), etc.\[^{[6,7,9]}\] There are lots of studies that have used different solvent in electrodes fabrication through EPD. Table 1 summarizes some of these studies.

Based on the previous studies, DMF was chosen as the solvent to obtain a stable SWCNT suspension and it was used to make an electrode coated with SWCNTs for removal chromium from aqueous solutions.\[^{[4]}\] Besides coated electrodes, another study used DMF as a solvent to prepare solid-phase microextraction fiber coated with SWCNTs by EPD.\[^{[9]}\] However, as it is shown in Table 1 different studies preferred to use water for making electrodes through EPD. For example, Tomas et al., used water for deposit CNTs on metallic surfaces.\[^{[10]}\] Besides making a good dispersion, some other characteristics are important in solvent selection, including the ability of dissolving electrolytes, and making a constant conductivity for EPD. In this study for the 1st time in a sole experiment, we aimed to compare two different solvent, distilled water and DMF as an organic solvent, in various aspects including dispersion of CNTs, electrical conductivity (EC), and dissolving of reagents.

### MATERIALS AND METHODS

#### Reagent and materials

The reagents utilized in this study were sodium hydroxide (NaOH), sulfuric acid (H\(_2\)SO\(_4\)), nitric acid (HNO\(_3\)), and sodium sulfate (Na\(_2\)SO\(_4\)) which all purchased from Merck Co., N,N-dimethylformamide (≥99%) was purchased from Aldrich Co., and SWCNTs with 1-2 nm diameter were obtained from Research Institute of Petroleum Industry, Tehran, Iran. The scanning electron microscope image of SWCNTs is shown in Figure 1. Stainless steel net (SSNs) of 100 meshes was purchased from the local store.

#### Determination of the electrical conductivity

First, 30 ml of distilled water and 30 ml of DMF prepared separately and then <0.1 mol (350 mg) Na\(_2\)SO\(_4\) was added to each of the liquids. Both of them were placed on the stirrer for 15 min and, therefore, their ability of dissolving electrolyte was compared.

In the second step, EC of both solutions was determined by using an EC meter (Senceion 5, Hach Co., Germany)

![Figure 1: Scanning electron microscope image of single-walled carbon nanotubes](image-url)

#### Table 1: Overview of used solvents for EPD of CNTs

| CNTs type   | Solvent type                  | References |
|-------------|-------------------------------|------------|
| MWCNTs      | Water                         | [5,10,12]  |
| SWCNTs      | N,N’-dimethylformamide        | [4,6,9,13] |
| SWCNTs      | 1,2-dichloroethane            | [14]       |
| SWCNTs      | Methanol                      | [13]       |
| MWCNTs      | N-methylpyrrolidone + methanol| [15]       |
| Carbon      | N,N’-dimethylformamide        | [16]       |
| nanofibers  |                               |            |

CNTs: Carbon nanotubes, EPD: Electrophoretic deposition, SWCNTs: Single-walled carbon nanotubes, MWCNTs: Multi-walled carbon nanotubes
and EC of distilled water and DMF after dissolving the added electrolyte was compared. For accuracy, the test was repeated; therefore 0.35 g of Na$_2$SO$_4$ mixed completely with DMF, and after 15 min stirring the salts were settled at the bottom of the beaker. The sedimentation was separated and dried at 100°C for 15 h. They were perfectly dried and then weighted.

**Preparation of single-walled carbon nanotubes and electrophoretic deposition**

In case of fictionalizing SWCNTs, 100 mg of them were added to 10 mg of the mixture of H$_2$SO$_4$: HNO$_3$ (3:1) and placed in an ultrasonic bath (BANDELIN, DT 156, Germany) for 2 h. After this period of time, the suspension was washed with pure water to remove any residual acidic solution from SWCNTs. Washing continued until pH was reached to 7 using a pH meter (Cyberscan pH1500-Thermo Fisher Scientific Inc., Netherland). Then, SWCNTs were put in an oven for 48 h in a constant temperature about 50°C. During this process, the carboxylic functional groups were added to the defect and end sites of SWCNTs. These functional groups were determined using FT-IR test.

In the next step, 4 suspensions of SWCNTs were prepared. The solvent for these 4 trials were different, including: DMF, distilled water, a mixture of DMF with 30% distilled water and a mixture of DMF with 60% distilled water. The experiments were done from 1 to 5 min and were triplicate. Hence, the sample size was approximately 60 trials.

After 15 mg of functionalized SWCNTs were added to each solution, they ultrasonically dispersed. Subsequently, after 4 h a suspension of 0.5 mg/mL of SWCNTs was obtained. During all steps, pH was adjusted on 10 by adding 1 M NaOH solution. Consequently, two pieces of clean SSNs (6 cm$^2$ × 1 cm$^3$), one used as cathode and the other as anode, were parallel immersed into each suspension of SWCNTs. However, only parts of them (2 cm$^2$ × 1 cm$^3$) were placed in the suspension. The distance between the two SSNs was kept at 1 cm. A direct current voltage of 30 V was applied. The experiment was done in different periods of times ranging from 1 to 5 min. During the first experiment in the 1st min, no amount of electrolyte was added. However, for the next tests which were carried out from 2 to 5 min, a constant amount of electrolyte was added to each suspension. The test was done for all suspensions and the produced current was illustrated and compared. The amount of deposited SWCNTs was determined by weighting the SSN anode before and after each trial.

For the last experiment with DMF, another suspension of 0.5 mg/mL SWCNTs was prepared after 4 h dispersion. The solution of 10 g/L Na$_2$SO$_4$ was prepared. Optimum time was determined after the first experiment with DMF, and the experiment carried out in that time for several times. Before EPD, 10 ml of Na$_2$SO$_4$ solution was added to the suspension and the changes in amount of deposits and also electrical current was recorded. The experiment repeated for 3 more times and during each test, 2 ml of Na$_2$SO$_4$ solution was added to the suspension and the changes were compared.

Experiment with DMF repeated for 23 times in constant voltage and different amount of electrolytes. The difference and changes in amount of deposit was recorded in each step.

**RESULTS**

During the first step of the experiment, it was determined that DMF cannot dissolve the electrolyte (Na$_2$SO$_4$) completely. After the test was repeated and dried salts weighted, it was illustrated that 0.346 g of 0.35 g Na$_2$SO$_4$ was remained and was not dissolved. EC was measured before and after dissolving the reagent. The result of the experiment and measuring is shown in Table 2. The test showed that DMF has the ability of dissolving salt in a very little amount, which is responsible for making low electrical field in the slurry.

In the next step of the experiment, after all the suspensions were ultrasonically dispersed for 4 h, all of them showed a good dispersion similarly. It should be noted that, if the sonication occurs for a shorter time, for example for 30 min, DMF will show a better dispersion than distilled water with no agglomerated particle in the suspension.

During the EPD process in a constant voltage of 30 V, as it is mentioned in the method, the experiment took place in five stages in different time intervals. The results of all the tests are presented in Table 3. According to this table, the test for water did not complete in all mentioned deposition times. The reason is that when the electrolyte was added to the DMF, no great change in the electrical field was appeared and it was <0.1 mA. Besides, the suspension remained dispersed after the test was terminated. However, after adding electrolyte in the suspension with water, the electrical current rose up and had an ascending rate, however after the current turned off, the dispersion turned to an agglomerated situation. In addition, any amount of SWCNTs did not deposit on the SSN anode. The electrolyte weight was less than it was prior to the test and the yield was negative. The photo of distilled water and DMF just after the second trial is shown in Figure 2.

| Table 2: Results of adding electrolyte to both solvents |
|-------------|---------------|---------------|
| Solvent    | EC (1)* (ms/cm)| EC (2)** (ms/cm)|
| DMF        | 0.0022        | 13.21         |
| DW         | 0.0018        | 0.0027        |

*Before adding electrolyte. **After adding electrolyte. DMF: Dimethylformamid, EC: Electrical conductivity, DW: Distilled water
The results of the experiment with a different mixture of DMF and distilled water are also presented in Table 3. It can be understood from the table that in comparison with DMF and the amount of deposits through the experiment with the other used solvents, other mixtures were not successful in making an electrode.

Consequently, after the EPD process was accomplished, the suspension with DMF had a better deposition. Figure 3 shows the results of the test with DMF in different deposition times. As it is illustrated in Figure 3, the best time interval for EPD process was known as 4 min which showed a better deposition of SWCNTs on the SSN anode. This time was chosen as the optimum time for the last test. During the last test, electrolyte was dissolved in water and then added to the suspension. There was no change in the amount of deposits on the anode. The result of this experiment was similar with the trial of DMF and 60% water.

| Solvent       | Time (min) | Electrolyte (g) | Yield (mg/cm²) |
|---------------|------------|-----------------|----------------|
| DMF           | 1          | 0               | 0.15           |
|               | 2          | 0.3             | 0.30           |
|               | 3          | 0.6             | 0.25           |
|               | 4          | 0.9             | 0.40           |
|               | 5          | 1.2             | 0.25           |
| DW*           | 1          | 0               | 0.7            |
|               | 2          | 0.3             | -2.4           |
| 60% DMF + 30% DW* | 1        | 0               | 0              |
|               | 2          | 0.3             | -0.05          |
|               | 3          | 0.6             | -0.05          |
|               | 4          | 0.9             | -0.05          |
|               | 5          | 1.2             | 0              |
| 30% DMF + 60% DW* | 1        | 0               | 0              |
|               | 2          | 0.3             | -0.25          |
|               | 3          | 0.6             | -4.25          |
|               | 4          | 0.9             | -8.6           |

*DW: Distilled water, DMF: Dimethylformamid

As experiment showed, for having a homogeneous deposit on the electrode, a good dispersion is needed, but water is not able to have a good dispersion in a shorter time.

**DISCUSSION**

During EPD process, the applied voltage should make a good current in the suspension and consequently results in migration of charged particles to the opposite electrode. However, it has been said that the deposition rate is not simply related to the current. If there was no EC, no particle movement would appear. In addition, different studies demonstrated that conductivity of the suspension is a key factor and needs to be taken into account in EPD process. Randall and Van Tassel have proved in their study that for electrophoretic migration in the suspension, electrical fields should exist. It is illustrated from the results that DMF, as an organic solvent, and water have some advantages and disadvantaged in comparison to each other. Water is cheaper, healthy, and environmental friendly and produces a constant electrical field during the EPD. However, using water as the sole solvent will cause a number of problems. Electrochemical reaction in the electrodes when an electrical current is passed through is one of the main problems, which seriously affects the efficiency of the process and the uniformity of the deposit. Electrolysis of water comes about at low voltages and results in gas evolution at the electrodes; therefore, to prevent such changes, deposition time should be shortening enough. It is an emphasis on Besra and Liu study, in that study they acclaimed that when the current density is high, Joule heating of the suspension occurred and the deposit will electrochemically attacked. In the other hand, in metallic electrodes the normal potential of the electrode is largely overpassed. This phenomenon causes oxidation of the electrodes and metallic impurities and so their migration in the slurry. In most cases, these impurities are retained in the deposit. On the other hand, adding more electrolyte will cause an intensive electrical field in the suspension, whereas the existence of charger salts can play a significant role in improving the adhesion of CNTs the surface and in aggregating the deposition rate. The salts will associating a charge to the CNT surface and, therefore, make the suspension to be stable.

As experiment showed, for having a homogeneous deposit on the electrode, a good dispersion is needed, but water is not able to have a good dispersion in a shorter time.
Another problem in using water as the solvent is that, water cannot get used for several times in the EPD process. The experiment showed that water solely or in a mixture with organic solvent will oxidize the electrode and after adding more electrolytes the fabricated deposits will completely demolish. During the tests which had water as solvent the electrolyte weight after the experiment was even less than before the trial. This is an emphasis on Besra and Liu study which assert that EC of the suspension is not simply related to the EPD process.\[11\] However, Boccaccini et al., utilized water for EPD process. In that experiment, they acclaimed that after EPD and when the electrodes were dried EPD can repeated to make a thick film.\[10\] Nevertheless, the present study showed that, if the thicker film on the anode is needed, the new suspension should be used. It is better to avoid adding electrolyte because the electrolysis of water will speed up and consequently not only the deposits but also the electrode will damage.

For EPD process and for having a better dispersion, organic liquids are preferable. Using DMF reduced electrolytic gas evolution, joule heating, and electrochemical attack of the electrodes and in lower deposition times omit these adverse effects. Different studies have mentioned DMF as the best solvent for EPD of SWCNTs.\[4,6,7,9\] In another study, DMF solution compared to ethanol and acetonitrile for electrodeposition of carbon nanofiber. In that study, the suspension with DMF showed a better dispersion and stability.\[19\]However, for having an electric field in the bulk suspension a higher voltage is required. Likewise flammability, cost, and toxicity of organic solvents should be considered. Besides, with respect to all these facts, some studies tended to use more healthy and environmental friendly liquids as a solvent.\[11\]

In case of deposition of SWCNTs by using DMF, the EC was very low. However, it did not affect the migration of particles. As the experiment showed and as it can be illustrated from the Table 3, the yield of SWCNTs on the anode was better when DMF was used as the only solvent. This is probably due to the low EC of the solvent. As the DMF cannot dissolve the salt, therefore, no electrical field appeared in the slurry and so electrolysis of the solvent did not occurred. Therefore, the structure of the electrode was not damaged and the deposit in different stages remained stable.

In different experiments with water as the only solvent and deposition time of 30 min, after adding enough electrolyte a relatively higher EC appeared. In the end of EPD time, a great deposit conducted on the electrode. However, the deposition was not homogeneous at all and the opposite electrode was oxidized. In contrary, in the same experiment with DMF electrical field remain constant and the deposit was not thick but it was homogenous. The test which was repeated for 23 times had the same result; a homogeneous thin film, but constant in amount in all the intervals. Furthermore, evaporation in the suspension with water is higher and the temperature increase faster but it is more controllable in the organic solvent.

**CONCLUSION**

With respect to the mentioned facts, for making an electrode with a homogeneous deposition through EPD process, having a good dispersion, preventing of electrode’s oxidation, and better temperature control DMF is recommended. However, it is suggested that electrodes with different dielectric constant should be tested with DMF to obtain the better deposit on the anode.

**ACKNOWLEDGMENTS**

This article is the result of MSc dissertation, No 393263; approved and funded by vice chancellery of research of Isfahan University of Medical Sciences.

**Financial support and sponsorship**

Isfahan University of Medical Sciences.

**Conflicts of interest**

There are no conflicts of interest.

**REFERENCES**

1. Papagiannis I, Kagalou I, Leonardos I, Petridis D, Kalfakakou V. Copper and zinc in four freshwater fish species from Lake Pamvotis (Greece). Environ Int 2004;30:357-62.
2. Rubio C, Hardisson A, Reguera JI, Revert C, Lafuente MA, González-Iglesias T. Cadmium dietary intake in the Canary Islands, Spain. Environ Res 2006;100:123-9.
3. Lowe J, Hossain MM. Application of ultrafiltration membranes for removal of humic acid from drinking water. Desalination 2008;218:343-54.
4. Liu XY, Yuan DX, Yan JM, Li QL. Ouyang T. Electrochemical removal of chromium from aqueous solutions using electrodes of stainless steel nets coated with single wall carbon nanotubes. J Hazard Mater 2011;186:473-80.
5. Kang J, Wen J, Jayaram SH, Wang X, Chen SK. Electrochemical characterization and equivalent circuit modeling of single-walled carbon nanotube (SWCNT) coated electrodes. J Power Sources 2013;234:208-16.
6. Kim SK, Lee H. Fabrication of patterned single-walled carbon nanotube films using electrophoretic deposition. Ultramicroscopy 2008;108:1005-8.
7. Boccaccini AR, Cho J, Roether JA, Thomas BJ, Minay EJ, Shaffer MS. Electrochemical deposition of carbon nanotubes. Carbon 2006;44:3149-60.
8. Fu L, Yu A. Carbon nanotubes based thin films: Fabrication, characterizatin and applications. Rev Adv Mater Sci 2014;36:40-61.
9. Li Q, Wang X, Yuan D. Preparation of solid-phase microextraction fiber coated with single-walled carbon nanotubes by electrophoretic deposition and its application in extracting phenols from aqueous samples. J Chromatogr A 2009;1216:1305-11.
10. Boccaccini AR, Chawla KK, Koopman M, Thomas B, Shaffer M, Freeman S. Electrophoretic deposition of carbon nanotubes on metallic surfaces. Key Eng Mater 2006;314:141-6.

11. Besra L, Liu M. A review on fundamentals and applications of electrophoretic deposition (EPD). Prog Mater Sci 2007;52:1-61.

12. Randall CA, Van Tassel JJ. Mechanisms of electrophoretic deposition. Key Eng Mater 2006;314:167-74.

13. Corni I, Ryan MP, Boccaccini AR. Electrophoretic deposition: From traditional ceramics to nanotechnology. J Eur Ceram Soc 2008;28:1353-67.

14. Yang YJ, Zhao GJ, Hu S. Direct current electrodeposition of carbon nanofibers in DMF. Electrochem Commun 2007;9:2681-5.

15. Singh BP, Samal S, Nayak S, Māhi SM, Besra L, Bhattacharjee S. The production of a multi-walled carbon nanotube/hexamethylene diisocyanate nanocomposite coating on copper by electrophoretic deposition. Surf Coat Technol 2011;206:1319-26.

16. Gao B, Yue GZ, Qiu Q, Cheng Y, Shimoda Y, Fleming L, et al. Fabrication and electron field emission properties of carbon nanotube films by electrophoretic deposition. Adv Mater 2001;13:1770-3.

17. Shen L, Low JE, Wong SY, Li X, Tjiu WC, Liu Y, et al. Multi-walled carbon nanotube/polyimide composite film fabricated through electrophoretic deposition. Polymer 2010;51:2155-60.

18. Neirinck B, Fransaer J, Van der Biest O, Vleugels J. Aqueous electrophoretic deposition in asymmetric AC electric fields (AC-EPD). Electrochem Commun 2009;11:57-60.

19. Thomas B, Boccaccini A, Shaffer M. Multi-walled carbon nanotube coatings using electrophoretic deposition (EPD). J Am Ceram Soc 2005;88:980-2.