

Fabrication of ultrathin graphene oxide-coated membrane with hydrophilic properties for arsenate removal from water

Reza Rezaee¹, Simin Nasseri², Amir Hossein Mahvi³, Ali Jafari⁴, Mahdi Safari¹, Behzad Shahmoradi¹, Mahmood Alimohammadi³, Mohammad Khazaei⁵, Mohammad Maroosi⁶

1 Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran

2 Center for Water Quality Research (CWQR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran

3 Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

4 Department of Environmental Health Engineering, Faculty of Health and Nutrition, Lorestan University of Medical Sciences, Khorramabad, Iran

5 Research Center for Environmental Pollutants, Qom University of Medical Sciences, Qom, Iran

6 Department of Public Health, Neyshabur University of Medical Sciences, Neyshabur, Iran

Original Article

Abstract

Terms and conditions of current drinking water quality standards, including reducing the maximum arsenic concentration from $50 \mu\text{g l}^{-1}$ to $10 \mu\text{g l}^{-1}$ and predicted stricter standards in future, reveals the necessity for development of new technologies. This study aimed to prepare and evaluate a new nanocomposite membrane using graphene oxide (GO) thin layer to remove arsenic (v) from water. To fabricate the membrane, initially GO was prepared using the modified Hummers' method and then to gain a narrow-dispersed GO dispersion, several times centrifugation and sonication were performed. Then resultant dispersed GO was coated on a microporous flat-sheet polyethersulfone support by coating/deposition and vacuum filtration process. Performance of the synthesized membrane was assessed using a dead end filtration system. The results showed that pure water flux decreased as the coated GO thickness increased. Among the three prepared membranes, the greatest flux was attributed to M₁ membrane with the value of $398.5 \text{ l m}^{-2} \text{ h}^{-1}$ and the minimum flux was for M₃ with a value of $131.3 \text{ l m}^{-2} \text{ h}^{-1}$ at 4 bar of pressure. Furthermore, by increasing the coated GO, rejection of arsenate ions increased significantly. With initial concentration of $1000 \pm 20 \mu\text{g l}^{-1}$, percentage of arsenate rejection for M₁, M₂ and M₃ membranes were 41.8%, 73.5% and 86.7%, respectively. Relatively high removal by this novel membrane can be due to the exceptional properties of GO nanostructure and the presence of hydrophilic functional groups.

KEYWORDS: Membrane, Nanocomposite, Drinking water, Arsenate

Date of submission: 15 Apr 2016, **Date of acceptance:** 12 Jun 2016

Citation: Rezaee R, Nasseri S, Mahvi AH, Jafari A, Safari M, Shahmoradi B, et al. **Fabrication of ultrathin graphene oxide-coated membrane with hydrophilic properties for arsenate removal from water.** J Adv Environ Health Res 2016; 4(3): 169-75.

Introduction

Arsenic is one of the hazardous inorganic contaminants in drinking water resources on a global scale. Tens of millions of people around the world are exposed to toxic

concentrations of arsenic consuming ground waters.^{1,2} High level of arsenic in ground waters is mainly geological originated; furthermore, man-made sources of arsenic include mining, pharmaceutical activities, glass and ceramics industries, pesticides and herbicides production, textile dyes, and wood industry.^{3,4} Generally, irreversible signs and

Corresponding Author:

Simin Nasseri

Email: naserise@tums.ac.ir

symptoms of arsenic poisoning through drinking water, appear during a 5 to 20 years period. In recent years, toxicological and epidemiological studies have revealed various diseases related to arsenic contamination from dryness in throat to cancers such as skin, lung, bladder, liver and kidney cancers.^{4,5} Accordingly, international agency for research on cancer (IARC) has classified inorganic arsenic compounds in group 1 (as human carcinogen).⁶ In recent years, strict standards and regulations have been established for arsenic in drinking waters. Therefore, World Health Organization (WHO) recommended maximum contaminant limit (MCL) of $10 \mu\text{g l}^{-1}$ for arsenic in drinking water instead of its previous guideline ($50 \mu\text{g l}^{-1}$).⁵⁻⁷ There are several proposed methods to reach the MCL of arsenic in drinking waters, including ion exchange, coagulation and flocculation, precipitation, adsorption and membrane technologies. Among the various available and applicable technologies, membrane filtration has known as a reliable method for removal of arsenic from water.^{8,9} Nowadays, polymeric membranes are widely used in various configurations for water purification due to the simplicity mechanism of pores formation, high flexibility, easy scale-up design, small footprints and relatively low cost compared to inorganic membranes.^{10,11} However, these types of membrane have still several drawbacks, including lack of selectivity and low resistance to fouling.^{12,13} Nanocomposite membranes are a new class of polymeric membranes made by blending nano-materials as a promising approach to solve the current addressed challenges.⁸ According to conducted studies, mixing nanomaterials in polymers not only improves the structure and physico-chemical properties of the membrane (such as hydrophilicity, porosity, mechanical, chemical, and thermal stability), but also results in inducing functional groups owning antibacterial and photocatalytic properties.^{14,15} Based on the membrane

structure and location of nano-materials, nano-composite membranes can be classified into four different types. The first type of nano-composites is common nanocomposites, in which nano-materials are distributed uniformly in membrane structure. The second type is thin film nano-composites (TFN) that only a thin film of nano-materials exists in the membrane structure. The third type is thin film composite (TFC) with nano-composite substrate that nanomaterials are present in sub layer substrate.¹⁵ In the fourth type of nano-composite membranes, nanomaterials are placed on surface of a substrate. In fact, these method is membrane structure modification in terms of improving the membrane hydrophilicity, pore size, density, surface charge, roughness and enhancement of membrane anti-fouling characteristics. The latter process of membrane fabrication (the fourth), can be used for a variety of membranes, due to the least effect on the main membrane structure, so they have the potential of commercial application for existing membranes. In this type, nano-composite can be placed on the membrane surface via self-assembly, electrostatic attraction, coating/deposition, layer-by-layer assembly, adsorption-reduction, and chemical grafting methods.^{15,16} Graphene and its derivatives have been of great interest among researchers for different fields including pololymeric membrane modification due to unique two-dimensional structure, such as diameter of one or more carbon atoms, theoretically very high surface area ($2630 \text{ m}^2\text{g}^{-1}$), good mechanical properties and low cost production.^{8,17} Graphene oxide (GO) is a very hydrophilic material due to the presence of oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl and epoxy.^{18,19} Several studies have reported that GO in various membranes enhanced the membrane efficiency with high resistance to fouling.²⁰⁻²²

The aim of this study was to prepare and evaluate a new nanocomposite membrane to remove arsenic (v) from aqueous solutions.

Nano-composite membrane was fabricated by coating a thin layer of GO on surface of a commercial ultrafiltration membrane as substrate via coating/deposition method. The efficiency of synthesized membrane was evaluated by measuring the water flux and arsenate removal.

Materials and Methods

In present study analytical grade chemicals were used for all experiments. Graphite was received from Merck (Germany) as a high pure powder (average particle size < 50 μm). A flat sheet UF membrane, polyethersulfone (PES, MWCO = 20000 dalton), was purchased from Septro (USA) and used as support media. For preparation of sample arsenate containing solution sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) (Sigma-Aldrich) was used. Furthermore the other chemicals used in this study were obtained from Sigma-Aldrich. In addition pure water flux (PWF) and solution preparation were performed using deionized (DI) water.

Graphene oxide-coated membrane synthesis

For fabricating the nano-composite membranes, initially GO was prepared by modified Hummer's method.²³ After that, to obtain a narrow-dispersed GO dispersion, several times centrifugation and sonication process were performed. To obtain a GO suspension, certain amount of GO (0.5 g) was placed in 100 ml of ethanol containing a defined amount of binder (ethyl acetate) and sonicated for 2 h at room temperature. To prepare membrane with different thicknesses of GO, volumes of 10, 20 and 30 ml of the suspension was coated on surface of a microporous flat-sheet polyethersulfone (PES) support membrane as the substrate. The substrate sheet was cut in 5 cm (diameter), rinsed and dried before employing. Then, GO was coated on the substrate by coating/deposition and vacuum filtration system. The synthesized membranes were kept for 24 hours at 40 °C vacuum oven. Membranes performance was

evaluated using a dead end filtration system. Nano-composite membranes were made based on volume of coated suspension namely 0, 10, 20 and 30 ml, called as pristine PES, M_1 , M_2 and M_3 , respectively. The fabricated membranes were placed in a desiccator for further use.

Characterization of the GO and fabricated membranes

To find out the functional groups on the membrane, attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) was used (ATR-FTIR spectroscopy, Tensor 27, Bruker Inc., Germany). The structure and morphology of surface and cross section of the GO modified membrane was studied by a field-emission scanning electron microscope (FE-SEM, S-4160, Hitachi, Japan). Furthermore, the changes in hydrophilicity properties of different fabricated membranes (membranes with different thicknesses of GO), was studied using the contact angle between the water and the top membrane surface via a contact angle measurement instrument (OCA 15 Plus, DATAPHYSICS, Germany).

Measurements of PWF and arsenate removal

A lab scale filtration set up was used to measure the permeability and arsenate rejection through the prepared membranes. The dead end set up consists of a flat sheet module (effective area = 9.6 cm^2). Before the experiments, each membrane was placed under a 5 bar pressure at 25 ± 0.5 °C for 15 min till the membrane got quite compacted and the flux reached to a constant value. Then, the pressure was immediately lowered to 4 bar and the flux was measured for 1 h by collecting the volume of permeate. Finally, following equation was used to calculate the membrane flux (Equation 1).

$$J_w = \frac{V}{A \cdot \Delta t} \quad (1)$$

Where, J_w is the PWF (lm^2h^{-1}), V is the volume of collected permeate (L), A is the

membrane effective area (m^2) over Δt (sampling time) (h). In the next step, arsenate solutions ($1000 \pm 20 \mu g l^{-1}$) was prepared based on a standards procedure²⁴ and the rejection of the membrane was investigated at 4 bar. Arsenic concentration was measured by inductively coupled plasma optical emission spectroscopy (HG-ICP/OES) (Model Spectro Arcos, SPECTRO Inc, Germany) connected to a hydride generator. Finally, equation 2 was used to calculate rejection of arsenic (R %).

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

Where, C_p is the concentrations of arsenate in the permeate and C_f is the concentrations of arsenate in the feed solution ($\mu g l^{-1}$). All the experiments were conducted in triplicate.

Results and Discussion

GO and GO-membrane properties

The IR spectroscopy was used to characterize synthesized GO. ATR-FTIR spectra of GO is illustrated in figure 1. As shown in the figure, a dominant absorption peaked at band 3411.94 cm^{-1} , that shows the typical property of GO spectra. This strong peak is assigned to stretching vibration of O-H bond and confirms the presence of hydroxyl functional group. Furthermore, the band at 1395.86 cm^{-1} can be attributed to O-H bending vibration.¹⁹ Absorption peak at band 1713.63 cm^{-1} represents the stretching vibration of carbonyl (C=O) and represents carboxyl functional group. The absorption peak observed at 1110.65 cm^{-1} is attributed to stretching vibration epoxy bond (C-O).²⁵ Therefore, with presence of oxygen-containing functional groups, the synthesized GO is effectively hydrophilic. Nearly similar results have been reported by other studies.^{18,22} Figure 2 depicts digital photographs of three types of membranes modified with GO.

As it is apparent, pale membranes contain thinner layer of GO on the surface (M_1), and darker ones contain thicker GO (M_3).

According to the characteristics of the substrate, the prepared membranes are quite flexible, capable of bending and cutting with scissors.

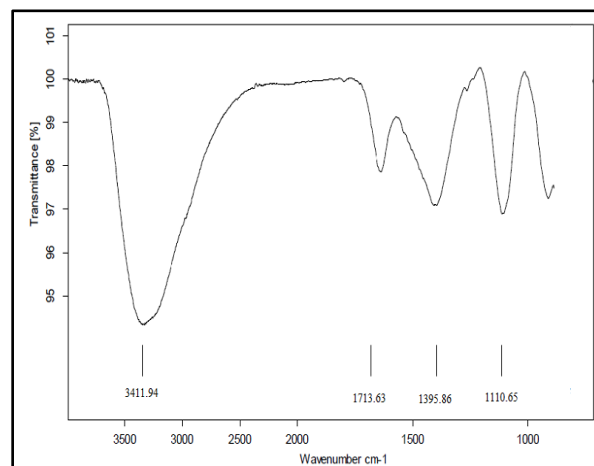


Figure 1. Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) spectrum of the prepared graphene oxide (GO)

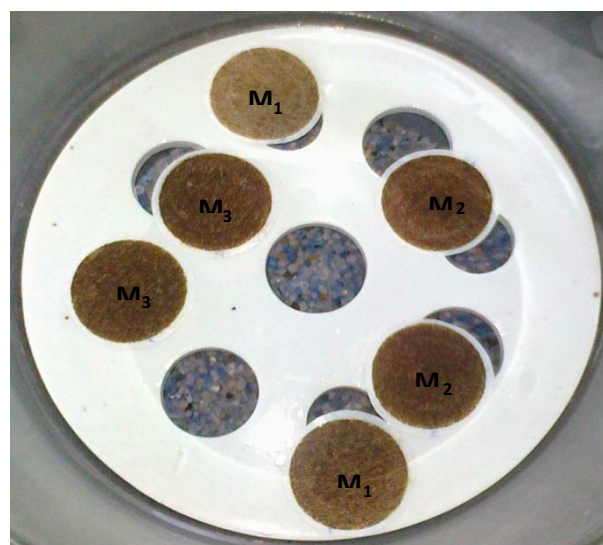


Figure 2. Digital photograph of graphene oxide-coated membranes

FE-SEM micrographs of the cross section is shown in figure 3 for M_2 membrane. As it is evident from the figure, a network structure has been created on the surface of the substrate by GO and accompanying binder, which has penetrated into the pores of the substrate and increased the porosity and mechanical strength of the membrane. Some factors such as characteristics of nano-

materials, nano-materials dispersion quality, and coating method affect synthesized membrane properties.¹⁵ Membrane surface hydrophilicity plays an important role in membrane flux, porosity and anti-fouling conditions. Basically, smaller contact angles reveals more hydrophilic surface.²⁶

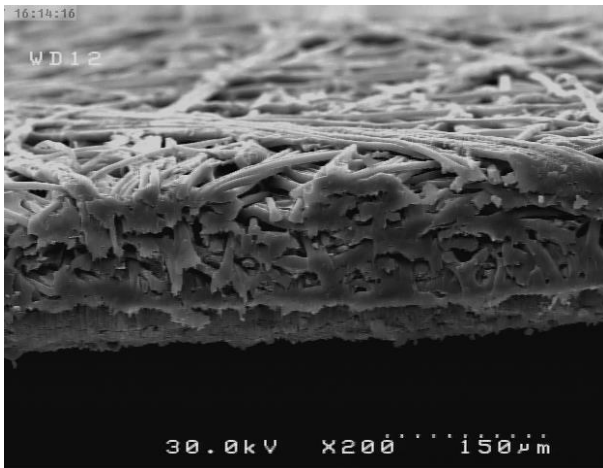


Figure 3. Cross sectional field-emission scanning electron microscope (FE-SEM) images of graphene oxide-coated membrane (M₂)

In figure 4, the contact angle of the synthesized membranes and substrate is provided. A contact angle of 75.5° for pristine membrane was relatively hydrophobic. While with GO coating on the surface, it became hydrophilic and the contact angle reduced. The hydrophilic functional groups on the GO, especially hydroxyl group (O-H) on the surface of the membrane improved the membrane hydrophilicity. Furthermore, density of the hydrophilic groups on the surface of the membrane reduces the interface energy to water.^{22,27} The positive results of GO addition on membrane hydrophilicity were consistent with other similar studies.^{19,21}

Membrane PWF and arsenate removal performance

Figure 5 represents the results of pure water flux for prepared membranes. As it is shown, by increasing the thickness of the coated GO, the pure water flux decreased. After the pristine membrane, M₁ and M₃ had the

maximum and minimum fluxes, respectively. Such decrease in flux is the result of the increase in thickness of coated GO which results in irregular arrangement of GO on surface of the substrate and consequent substrate pores blocking and porosity reduction.^{14,22}

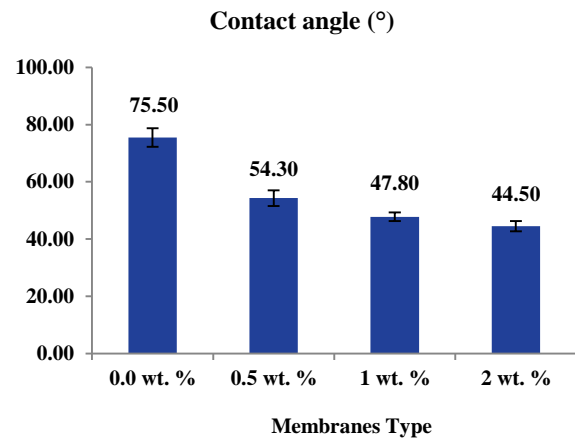


Figure 4. Effect of graphene oxide content on contact angle of the fabricated membranes

Several studies also showed no significant correlation between membrane flux and thickness of coated GO.^{28,29} This difference may be due to differences in the characteristics of the substrate and the binder used in the preparation of GO suspension in this study.

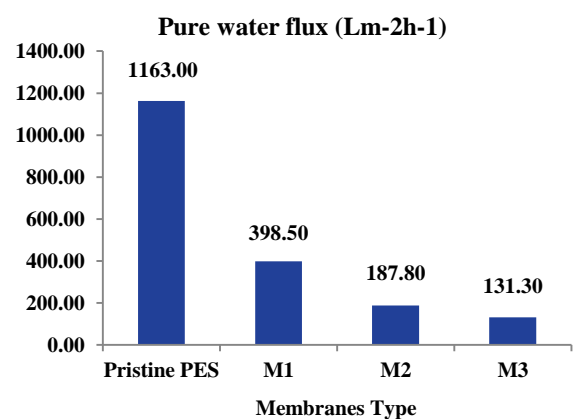


Figure 5. Pure water flux of the graphene oxide-coated membranes. Operating pressures = 4 bar, pH = 8.5 ± 0.2, initial arsenate concentrations = 1000 ± 20 µg/l, feed temperature = 25 ± 0.5 C°
PES: Polyethersulfone

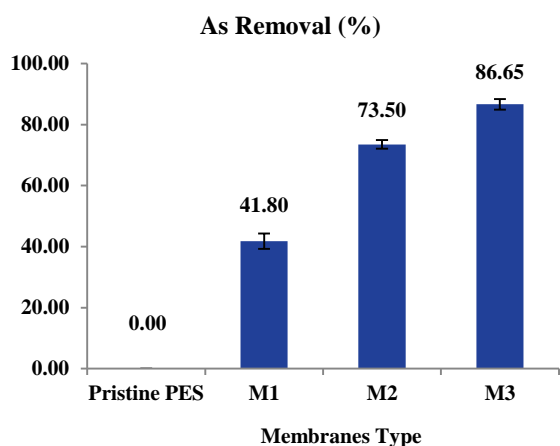


Figure 6. Arsenate rejection of the graphene oxide-coated membranes. operating pressures = 4 bar, pH = 8.5 ± 0.2 , Initial arsenate concentrations = $1000 \pm 20 \mu\text{g/l}$, feed temperature = $25 \pm 0.5 \text{ C}^\circ$
PES: Polyethersulfone.

The results of the four types of arsenate rejection by each membrane are presented in figure 6. From the figure, arsenate rejection for M₁, M₂, and M₃ membranes were 41.8%, 73.5%, and 86.7%, respectively. In contrast, the rejection for the substrate was negligible. As shown, the percentage of rejection dramatically improved by increasing the thickness of coated GO compared to net substrate. Negative hydrophilic functional groups such as hydroxyl and carboxylic in GO can induce a negative charge and cause a high zeta potential on the surface of the membrane. Negatively charged membrane surface and negative charge of arsenate increased the Donnan exclusion effect and the rejection.^{14,21} In addition, the membranes modified by GO provide several sites to form complex with metal ions. Functional groups (-OH and -COOH) on the surface of the membrane can also form complex with metal ions, so the rejection of metal ions by GO increased due to increase in number of active sites.^{17,30} However, relatively high removal of pollutants from water, low energy consumption and simple preparation of nano-composite membranes, showed a promising application of these technologies in the future. In contrast, some challenges still exist and need more studies. There is no

comprehensive understanding of nanomaterials effect and their role in large scale designs and applications. In particular, the proportion of hydrophilic surface, pore size, charge density and porosity on the membrane performance is still unknown. The potential effects of nanomaterials through the filter and their release into the environment, their health and toxicity effects have not been well understood and need to be systematically evaluated.¹⁵

Conclusion

This work revealed that by increasing the thickness of the coated GO on the surface of substrate, the pure water flux decreased due to irregular arrangement of GO on surface of the substrate and consequent substrate pores blocking and reduction of porosity. It was also shown that by increasing the membrane thickness, arsenate rejection increased significantly. Furthermore, GO due to owning oxygen-containing functional groups, can modify membrane surface morphology, create a negative charge, provide active sites for complexes with metal ions, and increase the rejection. Finally, further studies are needed to evaluate the cost-benefit of this type of membrane in the large-scale application and long-term health and environmental monitoring during its application.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

The present study was supported by the Center for Water Quality Research (CWQR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Iran (project number: 22716-46-02-92).

References

1. Joseph T, Dubey B, McBean EA. A critical review of arsenic exposures for Bangladeshi adults. *Sci Total Environ* 2015; 527-528: 540-51.

- Ebrahimi R, Maleki A, Shahmoradi B, Daraei H, Mahvi AH, Barati AH. Elimination of arsenic contamination from water using chemically modified wheat straw. *Desalin Water Treat* 2013; 51(10-12): 2306-16.
- Sato Y, Kang M, Kamei T, Magara Y. Performance of nanofiltration for arsenic removal. *Water Res* 2002; 36(13): 3371-7.
- Jain CK, Singh RD. Technological options for the removal of arsenic with special reference to South East Asia. *J Environ Manage* 2012; 107: 1-18.
- Saitua H, Gil R, Padilla AP. Experimental investigation on arsenic removal with a nanofiltration pilot plant from naturally contaminated groundwater. *Desalination* 2011; 274(1-3): 1-6.
- Ntim SA, Mitra S. Adsorption of arsenic on multiwall carbon nanotube-zirconia nanohybrid for potential drinking water purification. *J Colloid Interface Sci* 2012; 375(1): 154-9.
- Sabbatini P, Yrazu F, Rossi F, Thern G, Marajofsky A, Fidalgo de Cortalezzi MM. Fabrication and characterization of iron oxide ceramic membranes for arsenic removal. *Water Res* 2010; 44(19): 5702-12.
- Rezaee R, Nasserri S, Mahvi AH, Nabizadeh R, Mousavi SA, Rashidi A, et al. Fabrication and characterization of a polysulfone-graphene oxide nanocomposite membrane for arsenate rejection from water. *J Environ Health Sci Eng* 2015; 13: 61.
- Jafari A, Mahvi AH, Nasserri S, Rashidi A, Nabizadeh R, Rezaee R. Ultrafiltration of natural organic matter from water by vertically aligned carbon nanotube membrane. *J Environ Health Sci Eng* 2015; 13: 51.
- Pendergasta MT, Hoek EM. A review of water treatment membrane nanotechnologies. *Energy Environ Sci* 2011; 4(6): 1946-71.
- Ng LY, Mohammad AW, Leo CP, Hilal N. Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review. *Desalination* 2013; 308: 15-33.
- Shi X, Tal G, Hankins NP, Gitis V. Fouling and cleaning of ultrafiltration membranes: A review. *J Water Process Eng* 2014; 1: 121-38.
- Li N, Liu L, Yang F. Highly conductive graphene/PANi-phytic acid modified cathodic filter membrane and its antifouling property in EMBR in neutral conditions. *Desalination* 2014; 338: 10-6.
- Vatanpour V, Madaeni SS, Moradian R, Zinadini S, Astinchap B. Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polysulfone nanocomposite. *J Memb Sci* 2011; 375(1-2): 284-94.
- Yin J, Deng B. Polymer-matrix nanocomposite membranes for water treatment. *J Memb Sci* 2015; 479: 256-75.
- Han Y, Xu Z, Gao C. Ultrathin graphene nanofiltration membrane for water purification. *Adv Funct Mater* 2013; 23(29): 3693-700.
- Khazaei M, Nasserri S, Ganjali MR, Khoobi M, Nabizadeh R, Mahvi AH, et al. Response surface modeling of lead (II) removal by graphene oxide-Fe₃O₄ nanocomposite using central composite design. *J Environ Health Sci Eng* 2016; 14: 2.
- Zhao C, Xu X, Chen J, Yang F. Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes. *J Environ Chem Eng* 2013; 1(3): 349-54.
- Ganesh BM, Isloor AM, Ismail AF. Enhanced hydrophilicity and salt rejection study of graphene oxide-polysulfone mixed matrix membrane. *Desalination* 2013; 313: 199-207.
- Xia S, Ni M. Preparation of poly(vinylidene fluoride) membranes with graphene oxide addition for natural organic matter removal. *J Memb Sci* 2015; 473: 54-62.
- Zinadini S, Zinatizadeh AA, Rahimi M, Vatanpour V, Zangeneh H. Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates. *J Memb Sci* 2014; 453: 292-301.
- Wang Z, Yu H, Xia J, Zhang F, Li F, Xia Y, et al. Novel GO-blended PVDF ultrafiltration membranes. *Desalination* 2012; 299: 50-4.
- Hummers WS, Offeman RE. Preparation of graphitic oxide. *J Am Chem Soc* 1958; 80(6): 1339.
- Eaton AD, Franson MA. Standard methods for the examination of water & wastewater. Washington, DC: American Public Health Association; 2005.
- Lin Y, Jin J, Song M. Preparation and characterisation of covalent polymer functionalized graphene oxide. *J Mater Chem* 2011; 21(10): 3455-61.
- Zhao H, Wu L, Zhou Z, Zhang L, Chen H. Improving the antifouling property of polysulfone ultrafiltration membrane by incorporation of isocyanate-treated graphene oxide. *Phys Chem Chem Phys* 2013; 15(23): 9084-92.
- Sun M, Su Y, Mu C, Jiang Z. Improved antifouling property of PES ultrafiltration membranes using additive of silica? PVP nanocomposite. *Ind Eng Chem Res* 2010; 49(2): 790-6.
- Song JJ, Huang Y, Nam SW, Yu M, Heo J, Her N, et al. Ultrathin graphene oxide membranes for the removal of Humic acid. *Sep Purif Technol* 2015; 144: 162-7.
- Hu M, Mi B. Enabling graphene oxide nanosheets as water separation membranes. *Environ Sci Technol* 2013; 47(8): 3715-23.
- Shah P, Murthy CN. Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal. *J Memb Sci* 2013; 437: 90-8.