



Synthesis of Fe-Ag/f-MWCNT/PES nanostructured-hybrid membranes for removal of Cr(VI) from water



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ABSTRACT

This work describes the synthesis of Fe-Ag/functionalized-multiwalled carbon nanotube (f-MWCNT)/polyethersulphone (PES) nanostructured-hybrid membranes via a modified phase inversion method and its permeability properties. As-synthesized MWCNTs were first treated with acid and then Fe and Ag nanoparticles (Fe-Ag NPs) were uniformly dispersed on the surface of the f-MWCNTs using a microwave-assisted polyol method prior to addition to the PES polymer matrix. The addition of Fe-Ag/f-MWCNTs into the PES polymer increased the surface roughness of PES membranes and resulted to a higher hydrophilicity. Thermal stability and crystallinity properties of PES were significantly improved. The Fe-Ag/f-MWCNTs enhanced the surface charge density of the PES membranes and were found not to leach from PES. Performance evaluation studies revealed that the addition of Fe-Ag/f-MWCNTs into the PES polymer matrix increased water flux from 26.5 to 36.9 L/m² h and improved the rejection of Cr⁶⁺ ions (up to 94%) in a cross-flow system. Furthermore, the addition of Fe-Ag/f-MWCNTs improved fouling resistance of PES membranes. The improved properties of these hybrid membranes make the ideal for use as either point-of-use or end-of-use water purification system for production of potable water.

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1. Introduction

Environmental pollutants originating from industrial and/or anthropogenic activities have been reported to increase along with escalating industrialization and urbanization. Heavy metals such as Pb, Hg, Cr, Ni, Cd and Zn are of primary environmental concern even at low concentration due to their high toxicity and non-biodegradability nature in the aquatic environment [1–3]. The principal anthropogenic sources of heavy metals in the aquatic environment include metal extraction, metal fabrication and surface finishing, paints and pigments, as well as batteries manufacturing industries [1]. Among the heavy metals, chromium (Cr) tops the priority list of toxic pollutants defined by the United States Environmental Protection Agency (US-EPA) [4]. Chromium ion, which commonly found in both trivalent (III) and hexavalent (VI) forms (Cr(III) and Cr⁶⁺), is usually present in the effluents of the electroplating, tanning, mining and fertilizer industries [5–7]. Cr(III) is relatively immobile and innocuous while Cr⁶⁺ is reported

to be a group “A” human carcinogenic and to be toxic [8]. Thus the presence of Cr⁶⁺ in the aquatic environment poses a serious public threat and is of environmental concern. The US-EPA and World Health Organization (WHO) have set the maximum contaminant level (MCL) for Cr⁶⁺ at 0.1 ppm in drinking water [9]. The heightening concern with Cr⁶⁺ notably prompt the investigation, examination and development of new and improved materials to remove and recover Cr⁶⁺ from the water.

A number of technologies have been developed over the years for the removal and recovery of Cr⁶⁺, including electro-chemical precipitation, complexation, filtration membrane, ion exchange and reduction. The principal setbacks of some of the methods include high operation and maintenance costs, low efficiency and toxic sludge generation [3,4,8,10]. Membrane technology is the most popular method among the physico-chemical technique due to its ease of operation, flexibility in design, high efficiency, and has been effectively applied to removal of heavy metals including Cr⁶⁺ [11].

Nanostructured-hybrid membranes are one of the rapidly growing types of membranes used in separation science. These new types of membranes have been shown to exhibit excellent

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properties such as mechanical and thermal stability, permselectivity and fouling resistance, which are usually absent in pure membrane systems [12,13]. Materials used in membrane fabrication could either be hydrophilic or hydrophobic. The interaction of membranes with water is determined by their chemical compositions and corresponding surface chemistry. Hydrophilic membranes have high affinity for water relative to hydrophobic membranes. Hydrophilic membrane backbones include chitosan (CTS), cellulose acetate (CA) and polyaniline (PAN), while the latter group consists of polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polysulfone (PSf) and polyethersulfone (PES), to name a few [14].

PES is a widely used membrane separation material since it possesses desirable physical and chemical properties including good-heat-aging resistance, good dimensional stability and environmental endurance as well as ease of processing [15]. Other desirable properties of PES include creep resistance and inherent flame resistance [16]. However, its inherent hydrophobicity, due to its structure leads to low membrane flux and poor anti-fouling properties, which greatly impact or limit its application in water treatment. Since fouling is known to reduce membrane performance, many studies have focused on modifying the PES membranes to reduce the hydrophobicity in order to reduce their fouling propensity [15].

Inorganic nanomaterials have been used in the modification of PES membranes. Hybrid membranes containing inorganic nanoparticles (NPs) to form a polymer matrix are attractive because of their enhanced properties such as high permselectivity, higher hydrophilicity and enhanced fouling resistance [13,17]. Inorganic NPs that have been blended with polymers include but not limited to CNTs [13], nano- Al_2O_3 [8], ZrO [18] and Ag NPs [12]. Recently, the blending of polymers with bimetallic NPs has attracted increased research interest because of the enhanced properties of the bimetallic system, which is due to the synergistic effect of the two distinct metals [19,20]. This work sought to form bimetallic NPs of Ag and Fe. Ag NPs are well-known for their antibacterial properties. On the other hand, Fe NPs are widely used bimetallic NPs due to their high reactivity, low cost, ease of availability (scrap metal) and nontoxicity *i.e.* can be oxidized to naturally occurring soil mineral components [21,22]. Weng and co-workers used CTs stabilized Fe/Ni bimetallic NPs for the removal of mixed contaminants such as amoxicillin and Cd(II) from water. The study showed a removal efficiency of 68.9% and 81.3% of amoxicillin and Cd(II), respectively, when co-existing in solution, while 93.0% and 90.9% removal efficiencies were observed when the NPs were used individually with an initial concentration 60 mg/L within 60 min [23].

Although, bimetallic NPs perform extremely well in water treatment technologies due to their high reactivity compared to their bulk counterparts, they tend to agglomerate, thus reducing their surface area and their efficiency to remove pollutants. Because of their small sizes, surface corrosion and magnetic interactions of NPs show surface area reduction and inhibit electron transfer for redox reactions [24–27]. In order to overcome this problem, the nanomaterials are supported onto other systems such as polymers, membranes, inorganics and fibers, among others. This enhances their dispersion, stability and their long term removal efficiency. Amongst the different supporting materials, CNTs have received great attention. CNT properties such as high specific surface area, thermal conductivity and chemical stability render them very attractive candidates for use as templates for the dispersion and stabilization of metal NPs [28,29]. A study conducted by Mphahlele et al., showed high dispersion and stability of Fe-Ag bimetallic NPs on the walls of nitrogen doped CNTs [30].

To the best of our knowledge, Fe-Ag NPs supported on functionalised-multi-walled carbon nanotubes (f-MWCNTs) have

not yet been used as fillers and additives for PES membranes. The objective of the present study is therefore to synthesize and characterize Fe-Ag/f-MWCNT/PES nanostructured-hybrid membranes with antifouling properties and test their effectiveness in rejecting Cr^{6+} ions from water.

2. Experimental

2.1. Synthesis and functionalization of MWCNTs

MWCNTs were synthesized and acid treated according to a procedure reported by Mhlanga et al. [31]. Typically, acetylene (C_2H_2) was used as a source of carbon and was decomposed at a temperature of 700 °C in nitrogen (N_2) atmosphere on a Fe-Co/ CaCO_3 catalyst system. The obtained MWCNTs were treated with a mixture of H_2SO_4 and HNO_3 in a composition of 3:1 by volume. The MWCNTs (2 g) were added into 200 mL of the mixture of the acids and then placed in a closed Teflon vessel. The mixture was heated at 150 °C for 20 min in an Anton Paar Multiwave 3000 Industrial Microwave operating at 800 W power [32,33]. This process resulted to purified functionalized MWCNTs (f-MWCNTs) that were separated from the acids by an Eppendorf centrifuge 5430, and then washed with deionized water until a pH of 7 was attained. The samples were then dried in the oven at a temperature of 110 °C overnight. The f-MWCNTs were used in the subsequent synthesis of membranes.

2.2. Microwave-assisted synthesis of Fe-Ag/f-MWCNT nanocomposite

Fe and Ag NPs (5 wt.%) deposited on f-MWCNTs were prepared using a modified method reported by Mphahlele et al. [30]. Typically, 15 g of f-MWCNTs were dispersed in 100 mL ethylene glycol solution by sonication. In a separate beaker, a solution containing AgNO_3 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was prepared in ethylene glycol, respectively. Then, 20 mL of each of the solutions of Ag and Fe in ethylene glycol solutions were added to 40 mL solutions of f-MWCNTs (*i.e.* 15 g in 100 mL ethylene glycol). To the resulting solutions 4 mL of 0.4 M KOH was added as a precipitating agent while sonicating. These solutions were then placed in reaction vessels of an Anton Paar Multiwave 3000 Industrial Microwave and irradiated at a temperature of 200 °C for 5 min after which they were separated from the solvents using an Eppendorf centrifuge 5430. The residue was washed with acetone to remove the ethylene glycol and finally washed with distilled water until a pH of 7 was attained. The black material obtained was then dried in the oven at a temperature of 110 °C for 12 h.

2.3. Preparation of nanostructured-hybrid membranes

PES based hybrid/blend membranes were fabricated by a modified phase inversion method (immersion precipitation/coagulation method) using a casting solution containing 16 wt.% PES, 0.5 wt.% SDS, NMP and varying concentrations of Fe-Ag/f-MWCNT NPs [18] (Fig. 1). The compositions of the casting solutions for all the membranes prepared in this work are presented in Table 1. The NMP was used as a solvent due to its good interaction with PES and its miscibility in water, while SDS was used as an additive. The presence of SDS in the organic phase is known to increase permeation and rejection capacity of membranes [35].

The specific percentages of Fe-Ag/f-MWCNTs (0.1 and 1 wt.%) were sonicated in SDS for 3 h. The casting solutions were prepared by dispersing solutions Fe-Ag/f-MWCNTs with SDS into NMP solvent relative to casting solution to disperse the composite materials. Thereafter, PES was dissolved in a dope solution by continuous stirring for 10 h to make 16% PES solution. Then, the polymer mixture solutions or casting solutions were left at room temperature

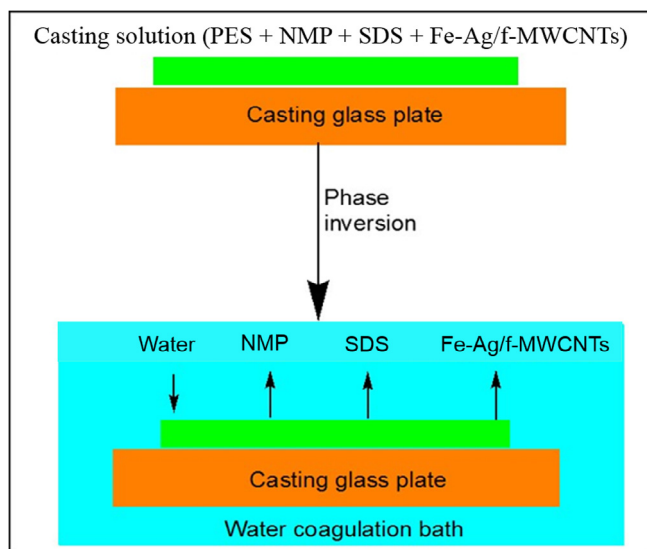


Fig. 1. Illustration of the phase inversion process used to synthesize membranes.

for 48 h to remove air bubbles. The solutions were then cast on a clean glass plate using a 250 μm thickness Elcometer 3545 Adjustable Bird Film applicator casting knife. Subsequently, the glass plate was horizontally immersed for 2 min into distilled water, which induced phase inversion. The formed membranes were washed and stored in distilled water for 24 h and then sandwiched between paper towels for 24 h at room temperature for drying.

2.4. Characterization techniques

MWCNTs and Fe-Ag/f-MWCNTs were characterized using a FEI Tecnai T12 transmission electron microscopy (TEM) and a Malvern Zetasizer Nano-ZS Nano series. The thermal stability and crystallinity properties of the membranes were determined using a Perkin Elmer 4000 thermogravimetric analyzer (TGA) and an Ultima-IV X-ray diffractometer (XRD). The surface morphology and roughness properties of the membranes were studied using the Dimension 3 100 Veeco atomic force microscopy (AFM) and VEGA3 TESCAN scanning electron microscopy (SEM). The hydrophilicity of the membranes was evaluated by contact angle measurements (Data Physics Optical Contact Angle OCA 15 EC GOP) using the sessile drop method. A Surpass electrokinetic analyser (Anton Paar GmbH) was used to determine the zeta potential surface charge of the membranes.

Porosity and swelling were measured using a dry-wet-weight method and calculated respectively using the following equations [36]:

$$\varepsilon = \frac{W_1 - W_2}{A \times l \times d_w} \quad (1)$$

Swelling percentage was expressed

$$\text{Swelling (\%)} = \frac{W_1 - W_2}{W_2} \times 100 \quad (2)$$

W_1 and W_2 are weights in g of swollen and dry membranes, respectively, d_w is density of water (0.998 g/cm³), A is the membrane effective area (m²) and l is membrane thickness. Porosity is an important factor in membrane technology because it has an impact on flux [37].

The Guerout-Elford-Ferry equation (Eq. (3)) was used to determine the membrane mean pore radius (r_m) based on the pure water flux and porosity data [37].

$$r_m = \sqrt{\frac{(2.9 - 1.7\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \quad (3)$$

where η is the water viscosity (8.9×10^{-4} Pa s), Q is the volume of the permeate pure water per unit time (m³/s), and ΔP is the operation pressure (0.5 MPa).

2.5. Leaching studies

Leaching tests were carried out on the Fe-Ag/f-MWCNT/PES membranes in order to ascertain any possible leaching of the NPs into solution during their use. In these tests, 50 mg of each of the Fe-Ag/f-MWCNT/PES membranes were sonicated in 25 mL of distilled water at different time intervals (30, 60, 720 and 1440 min). After sonication, the membranes were separated from the solvent, and the resulting filtrates were then analyzed for the presence of either Ag or Fe using inductively coupled plasma (ICP) ICP 6000 series spectrometer thermos Fisher-Scientific.

2.6. Performance of the membranes

The performance of the membranes was studied by measuring the pure water flux and rejection of Cr⁶⁺ ions. The experiments were carried out using the cross-flow filtration system (Sterlitech) with a membrane area of 14.6 cm² at room temperature. The membranes were preconditioned by compacting them at 5 MPa. Water flux ($J_{w,1}$) was measured in the pressure range of 1–5 MPa and then calculated using Eq. (4) [38];

$$J_{w,1} = \frac{V}{At} \quad (4)$$

where V (L) is the volume of the permeation water at time t (h) and A (m²) is the area of the membranes. The rejection was measured by filtrating a Cr⁶⁺ solution. The concentration in the feed and permeate was measured using Shimadzu AA-6200 atomic absorption spectrophotometer (AAS). The rejection (%R) was calculated using Eq. (5) [38].

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (5)$$

where C_p and C_f are Cr⁶⁺ concentrations in permeate and feed, respectively. After filtration of Cr⁶⁺ solution, the membranes were washed with distilled water and this was followed by evaluation of flux of cleaned membranes ($J_{w,2}$). The flux recovery (FR) was calculated using Eq. (6) [38].

$$\%FR = \frac{J_{w,2}}{J_{w,1}} \times 100 \quad (6)$$

Table 1

Composition of the casting solutions used for the preparation of blend membranes.

Membranes	Materials			
	PES	SDS	NMP	Fe-Ag/f-MWCNTs
PES	16	0.5	84.5	0.0
0.1% Fe-Ag/f-MWCNT/PES	16	0.5	83.4	0.1
1% Fe-Ag/f-MWCNT/PES	16	0.5	82.5	1.0

Higher FR values indicate the antifouling properties of the membranes. Fouling can be expressed by the resistance that is formed during the filtration process. Total fouling ratio was defined and calculated as using Eq. (7) [38].

$$\%R_t = \left(1 - \frac{J_{Cr}}{J_{w,1}}\right) \times 100 \quad (7)$$

where J_{Cr} is flux of Cr^{6+} solution. R_t is a degree of total flux loss caused by total fouling. The reversible (R_r) and irreversible (R_{ir}) fouling ratios were also calculated using Eqs. (8) and (9), [38] respectively.

$$\%R_r = \left(\frac{J_{w,1} - J_{Cr}}{J_{w,1}}\right) \times 100 \quad (8)$$

$$\%R_{ir} = \left(\frac{J_{w,1} - J_{w,2}}{J_{w,1}}\right) \times 100 \quad (9)$$

3. Results and discussion

3.1. Characterization of MWCNTs

Fig. 2 illustrates the surface morphology of pristine MWCNTs (p-MWCNTs), f-MWCNTs and Fe-Ag/f-MWCNTs. The nanotubes had an average diameter of 30 nm as observed previously. Fig. 2A demonstrates nanotubes tangled together in a spaghetti-like arrangement containing impurities *i.e.* the catalyst used during the synthesis. After acid treatment these catalyst NPs were removed due to the process of oxidation by strong mixture of H_2SO_4 and HNO_3 (Fig. 2B). The acid treatment process did not only remove the impurities but introduced carboxylic functional groups on the MWCNTs resulting in increases specific surface area and crystallinity of MWCNTs. Fe and Ag NPs were uniformly dispersed on the surface of f-MWCNTs with no agglomeration. The carboxyl functional groups on the f-MWCNTs groups provided a platform for the deposition of Ag and Fe-Ag NPs. The mean particle size distribution for Fe-Ag NPs was 5 nm (see Fig. 2 insert).

Zeta potential measurements were performed to investigate the change in surface properties of p-MWCNTs after treating them with acid. The zeta potential values of the MWCNTs decreased from -17.89 to -36.11 mV after acid treatment. This change in surface charge was ascribed to the presence of highly electronegative carboxylic groups. The zeta potential was then increased to -32.64 mV after deposition of NPs due to the enhanced interaction between the walls of f-MWCNTs and the metal NPs. The zeta potential was also used to evaluate the stability of the MWCNTs

in solvent such as ethanol and water. In addition, the zeta potential indicated the degree of repulsion between adjacent, similarly charged particles in dispersion. For example, for molecules and particles that are small enough, a high zeta potential will confirm stability, *i.e.*, the solution or dispersion will resist aggregation. When the zeta potential is low, this means that attraction exceeds repulsion and dispersion and thus the particles tend to break and flocculate. Therefore, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate [39]. The results showed that p-MWCNTs had a lower stability, hence they were more tangled as seen on TEM images (Fig. 2).

3.2. Characterization of the membranes

3.2.1. Surface characterization

The influence of the Fe-Ag/f-MWCNTs on the roughness and antifouling properties of the hybrid nanostructured membranes was determined by AFM. Fig. 3 presents AFM topographies of the PES membranes blended with Fe-Ag/f-MWCNTs. In the images, the brighter areas indicate the highest point of the membrane surface and the dark region show the valleys or pores of the membrane surface. Surface roughness is an important characteristic of the membranes which influences the adsorption and/or desorption of species on the surface of the membranes and therefore affects membrane fouling propensity [40]. The surface roughness of the membrane containing Fe-Ag/f-MWCNTs ($R_a < 11$) was high compared to pure PES membranes ($R_a = 6.9$). This was due to the fast exchange of solvents (NMP) and non-solvent (water) occurring during phase inversion because of hydrophilic nature of Fe-Ag/f-MWCNTs. An increase in the addition of Fe-Ag/f-MWCNTs into the polymer matrix from 0.1 to 1% increased surface roughness of the membranes. The hybrid nanostructured membranes are anticipated to have enhanced antifouling properties.

SEM images indicated that the Fe-Ag/f-MWCNTs blend PES membranes exhibit asymmetric structure defined by a dense layer and a highly porous sub-layer (Fig. 4). This dense layer was due to the instantaneous liquid-liquid demixing between the deionized water in the coagulation bath, SDS and the NMP in matrix during the phase inversion process.

The surface charge of the bare PES and nanostructured Fe-Ag/f-MWCNT/PES membranes are shown in Fig. 5. The bare PES membranes possessed slightly negatively charged surface throughout the tested pH value range, auto-titrated from pH 3–10. On the other hand, the zeta potential of the nanostructured membranes were positive at the low pH ranges and became negative across their respective isoelectric point, which is in the pH range of 4–5. This was due to the presence of f-MWCNTs and Fe-Ag NPs which

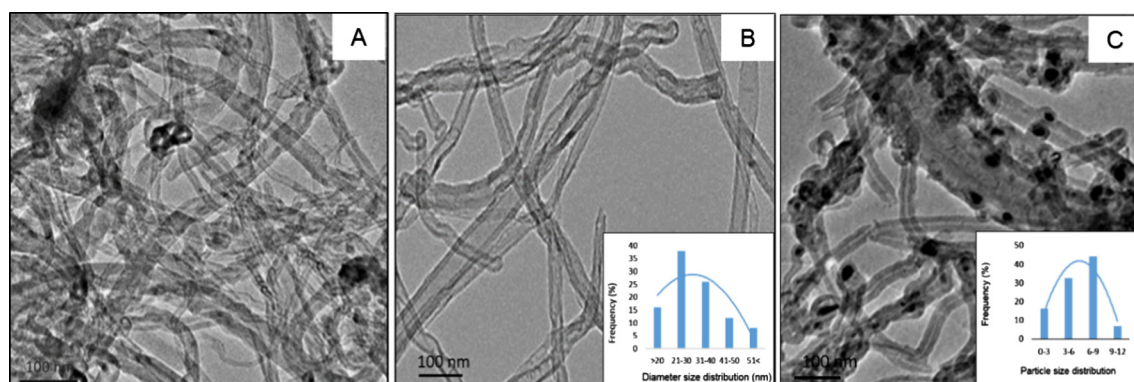


Fig. 2. TEM images of p-MWCNTs (A), f-MWCNTs (B) and Fe-Ag/f-MWCNTs (C).

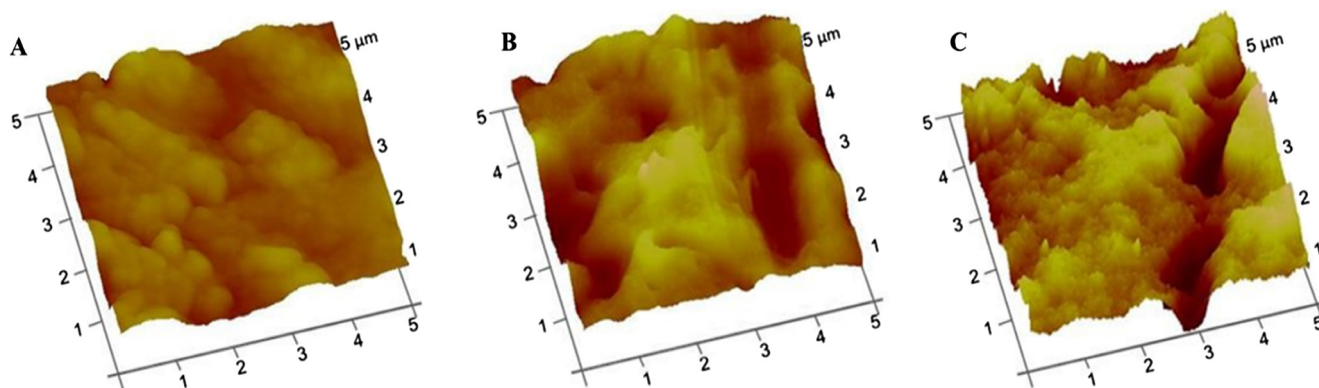


Fig. 3. AFM images bare PES (A), 0.1% Fe-Ag/f-MWCNT/PES (B) and 1% Fe-Ag/f-MWCNT/PES NPs (C) membranes.

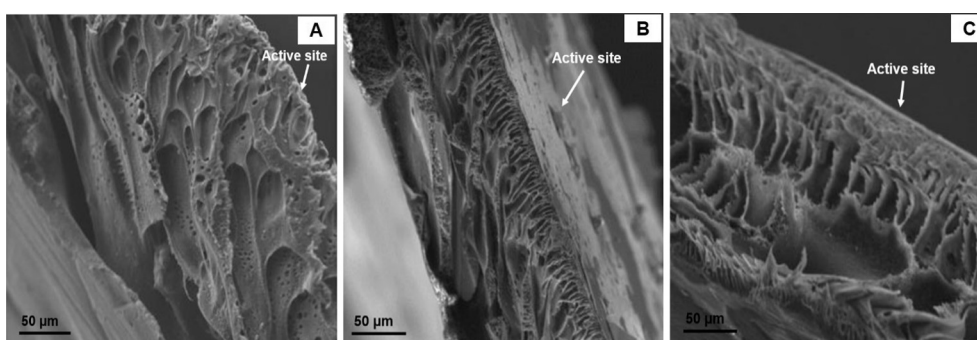


Fig. 4. SEM images of bare PES (A), 0.1% Fe-Ag/f-MWCNT/PES (B) and 1% Fe-Ag/f-MWCNT/PES (C) membranes.

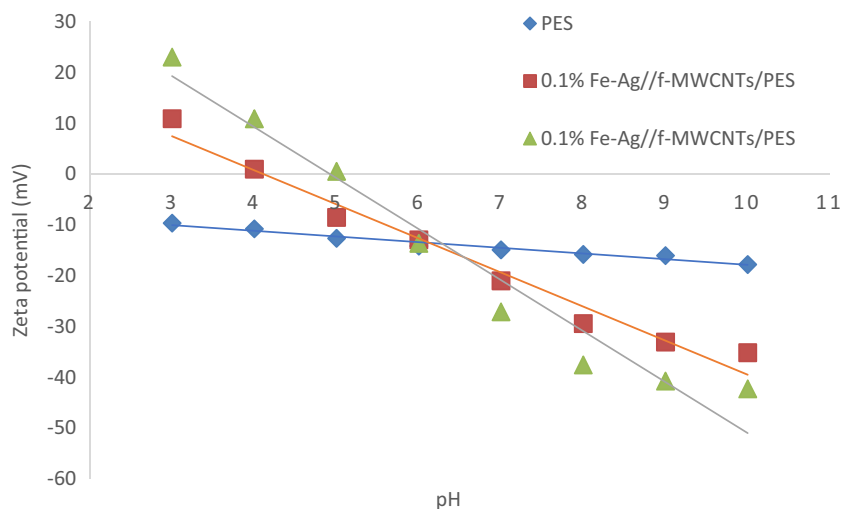


Fig. 5. Zeta potential measurements of bare PES and nanostructured hybrid PES membranes.

are negatively charged, thus increasing the charge density of the PES membranes.

The porosity, swelling and contact angles of the nanocomposite membranes are presented in Table 2. The results of the porosity measurements revealed that Fe-Ag/f-MWCNT/PES membranes possessed porosities in the range of 51.7–1.0 to 65.4–0.8% relative to 46.2–0.4% for bare PES membranes. Generally, porosity increased slightly with increase in the content of metal/f-MWCNTs. This was due to the fast exchange of NMP solvent and water of coagulation bath in a phase inversion process

Table 2

The porosity, water uptake (swelling capacity) and contact angles of pristine PES and PES loaded with ratio of metal/f-MWCNTs.

Properties	PES	0.1% Fe-Ag/f-MWCNTs	1% Fe-Ag/f-MWCNTs
Porosity (%)	46.2 ± 0.4	52.3 ± 2.2	65.4 ± 0.8
Swelling (%)	50.1 ± 0.0	53.2 ± 0.1	58.7 ± 0.0
Contact angle (°)	75.0 ± 3.0	55.2 ± 3.1	43.6 ± 3.1
Mean pore radius	3.07 ± 0.9	3.00 ± 1.6	2.78 ± 1.1

(Fig. 1). Instantaneous demixing leads to the formation of microvoids and it was promoted by the presence of f-MWCNTs which introduced the hydrophilicity of PES [40]. However, the mean pore radius decreased with an increase in loading of the nanomaterials. This decrease in mean pore radius of the membranes was due to blockage of the pores in the membrane, especially on the upper layer of the membranes (see Fig. 4). Generally, the mean pore radius for all membranes was 3 nm, which was big enough to let water molecules (radius = 0.27 nm) to pass through.

Furthermore, the contact angle of the PES membranes decreased with an increase in loading of metal/f-MWCNTs while the water uptake increased with increase metal/f-MWCNTs (Table 2). Lower contact angles and higher water uptake means high hydrophilicity. The bare PES membranes had the highest contact angle ($75.0 \pm 3.0^\circ$). Fe-Ag/f-MWCNT/PES (1%) blend membranes had the lowest contact angle, which indicated the surface hydrophilicity enhancement of PES membranes by addition of Fe-Ag/f-MWCNT/PES. This was due to spontaneous migration of hydrophilic Fe-Ag/f-MWCNT/PES to membrane/water interface to reduce interface energy [41]. The migration of the metal/f-MWCNTs was confirmed by the formation of a dense layer on the surface of the membranes (shown in Fig. 4). According to Vatanpour et al., the hydrophilicity plays an important role in water permeation of membranes. High hydrophilicity of membranes favours enhanced flux [38].

3.2.2. Thermal and crystallinity properties

Fig. 6 shows the TGA and DTA profiles of bare PES and Fe-Ag/f-MWCNT/PES hybrid membranes. The membranes generally exhibit a standard decomposition trend which begins around 500 °C. The initial decomposition was attributed to the loss of the sulfone groups which originated from the PES structure, whereas the second decomposition step was analogous to the degradation of the polymer chains [34,41]. The TGA and DTA profiles also indicated that when the Fe-Ag/f-MWCNT nanomaterials were used there was no significant impact as these materials were added in small amounts. The XRD patterns of the Ag/f-MWCNT and Fe-Ag/f-MWCNT nanocomposite membranes with different loadings between 0.1 wt.% and 1 wt.% are shown in Fig. 7. It can be seen that the bare PES polymer is mainly amorphous and presents one prominent peak at around $2\theta = 19^\circ$ [42]. The results also revealed the change in amorphous phase of PES due to embedment of Fe-Ag/f-MWCNTs. The new peaks are at $2\theta = 27^\circ$ (003), 32° (111) and 48° (211) are due to carbon, Ag and Fe, respectively. The intensities of the peaks increased with increasing load of Fe-Ag/f-MWCNTs. Therefore, the addition of Fe-Ag/f-MWCNTs into the PES matrix improved the crystallinity of PES polymer.

3.2.3. Leaching studies

Due to their small size and solubility, nanomaterials can easily leach out and find their way into the environment. This can induce

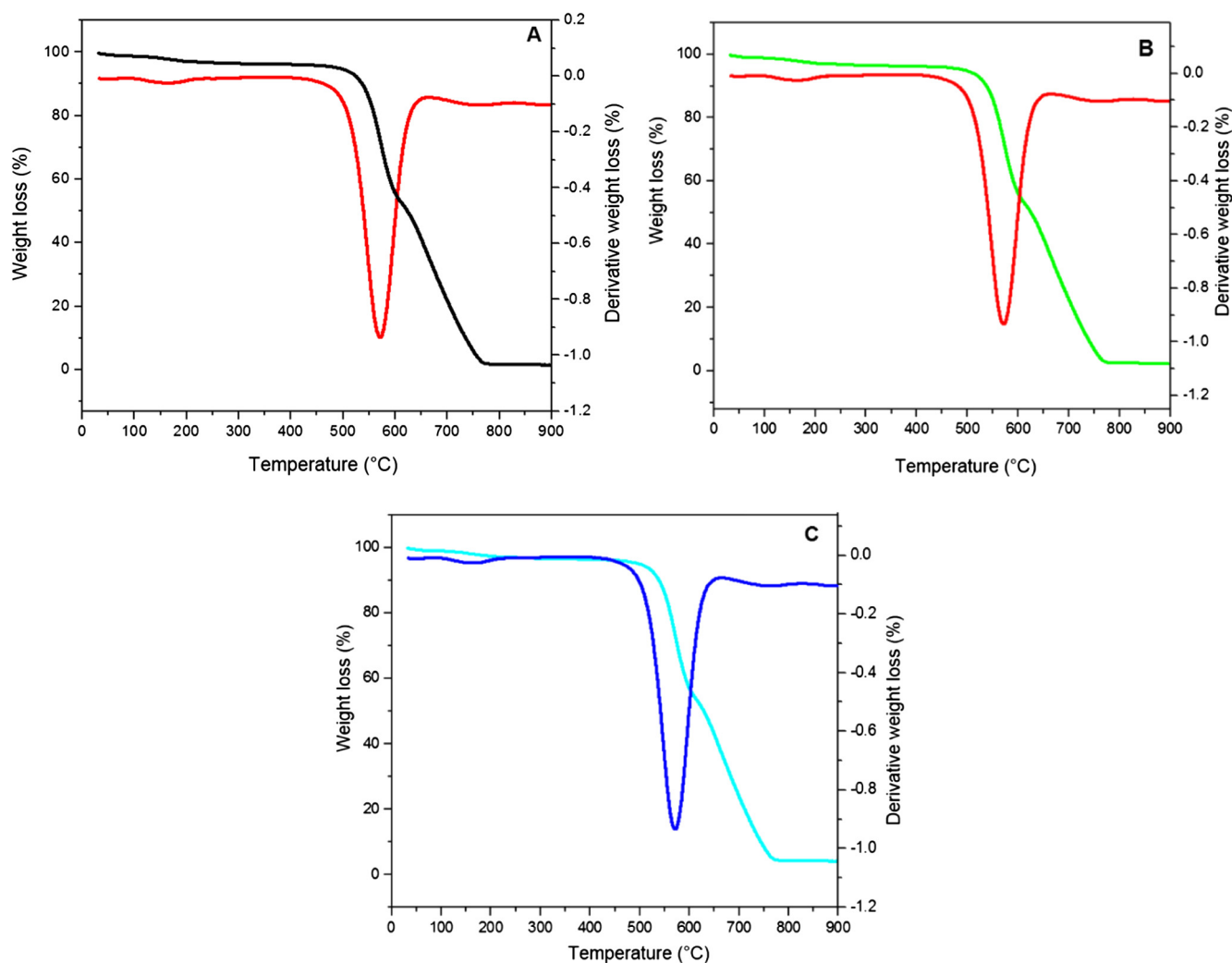


Fig. 6. TGA and DTA profiles of PES (A), 0.1% Fe-Ag/f-MWCNT/PES (B) and 1% Fe-Ag/f-MWCNT/PES (C) membranes.

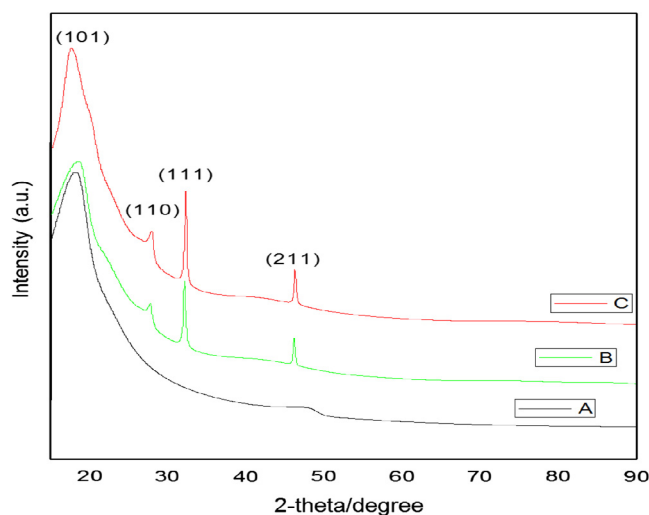


Fig. 7. XRD patterns of PES (A), 0.1% Fe-Ag/f-MWCNT/PES (B) and 1% Fe-Ag/f-MWCNT/PES (C) membranes.

the risks of high exposures, hence posing adverse health effect on human and animals. According to World Health Organization (WHO), the allowed concentrations of Fe and Ag in drinking water are 0.3 ppm and 0.1 ppm, respectively [43]. Table 3 presents the concentrations of Fe and Ag respectively after sonicating the Fe-Ag/fMWCNTs/PES membranes at different time intervals. The results show that the leaching of Ag and Fe ions were below the ICP-OES detection limits and below recommended limit for no risk. This was in line of the results reported by Mphahlele and coworkers [30]. Hence the materials were found suitable for water purification applications. This also suggested that the NPs were compatible with the f-MWCNTs due to the presence of the carboxyl functional groups, which assisted in holding the Ag and Fe NPs within the MWCNTs.

3.3. Performance of the membranes

Fig. 8 shows the effect of different pressures on the pure water flux. Generally, the flux increased with increasing operating pressure up to 5 MPa. The pure water permeability was measured using 4 different applied pressures and a good linear relationship between the water permeability and applied pressure was observed ($R^2 \approx 0.98$). The Fe-Ag/f-MWCNT/PES membranes showed enhanced pure water flux than bare PES membranes, and flux increased slightly from 26.5 to 32.8 L/m² h with increase in loading of Fe-Ag/f-MWCNT NPs. This improvement in pure water flux was assigned to increase in membrane porosity and hydrophilicity by the NPs. The Fe-Ag/f-MWCNT membranes had improved hydrophilic surface properties and this enhanced the water permeability by attracting water molecules inside the matrix of the membranes and facilitated them to pass through the

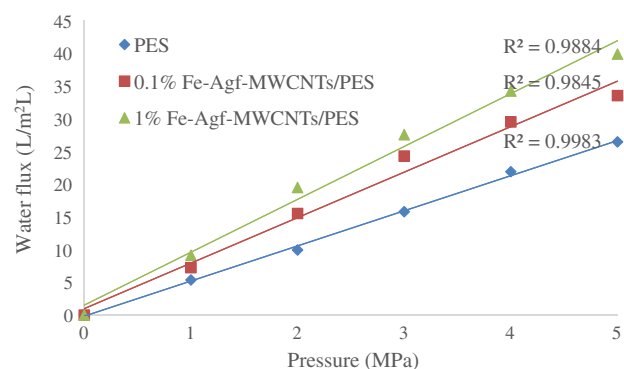


Fig. 8. The pure water flux of PES and PES loaded with different ratio of Fe-Ag/f-MWCNTs.

membranes [40]. PES membranes with 1% NPs had higher flux (36.9 L/m² h) than membranes with 0.1% NPs. This is because an increase in the amount of NPs added into PES polymer increase the porosity and hydrophilicity of the membranes.

Fig. 9 shows rejection capacity of Fe-Ag/f-MWCNT/PES blend membranes for Cr⁶⁺ at different pH (pH 2–10). The retention of Cr⁶⁺ higher at low pH values for all the materials. The retention measurements showed that the rejection behavior of the Fe-Ag/f-MWCNT/PES blend membranes could be classified as Donnan exclusion mechanism. Fe-Ag/f-MWCNTs which are negative charged (−32.64 mV) improve the charged exclusion mechanism for the rejection of negatively charges Cr⁶⁺ (Cr₂O₇^{2−}) from 9.34% to 93.74% rejection capacity.

The fouling resistance (FR) depicted in Fig. 10 present the suitable reusing properties of the PES modified membranes. It was observed that the FR of hybrid nanostructured membranes was higher than the bare PES membranes. The FR value of pristine PES membranes was 64% indicating poor antifouling properties. This was due to low hydrophilicity of pristine PES membranes. The FR was increased to 81.94% and 94.98% when 0.1% and 1% Fe-Ag/f-MWCNTs were added respectively. This suggested that the hybrid nanostructured membranes had excellent antifouling properties due to the improvement in hydrophilicity of PES by Fe-Ag/f-MWCNTs.

The R_f , R_r and R_{ir} values for hybrid nanostructured membranes are presented in Fig. 10. Pristine PES membranes had the highest R_f and R_{ir} , which was caused by lower hydrophilicity. The R_f decrease with increase in loading of Fe-Ag/f-MWCNTs. This indicated an improvement in antifouling characteristics of PES membranes. Furthermore, high R_r resulted from weak adsorption of materials on the surface of the membranes, which could be removed by simple

Table 3
Leaching studies of Ag and Fe-Ag NPs deposited on f-MWCNTs.

Sonication time (min)	Concentration (ppm)		
	Ag/f-MWCNTs		Fe-Ag/f-MWCNTs
	Ag	Ag	Fe
0	<0.0218	<0.0218	<0.00523
30	<0.0218	<0.0218	<0.00523
60	<0.0218	<0.0218	<0.00523
720	<0.0218	<0.0218	<0.00523
1440	<0.0218	<0.0218	<0.00523

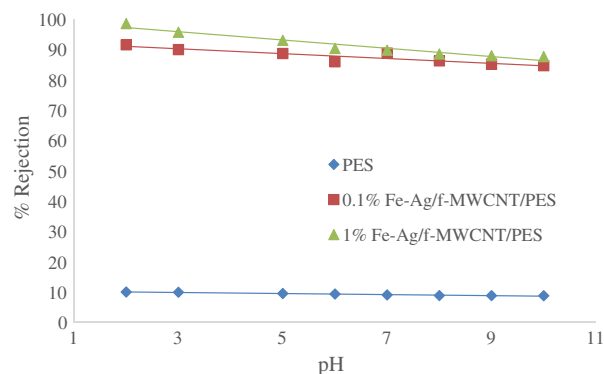


Fig. 9. Rejection of Cr⁶⁺ at different pH values (pH 2–10).

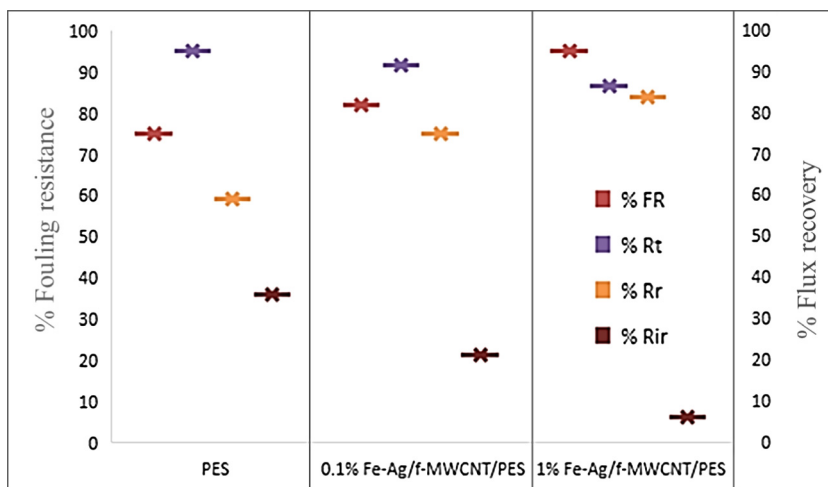


Fig. 10. Fouling resistance of PES and nanostructured hybrid PES membranes.

hydraulic cleaning, while R_{ir} involved strong adsorption on the surface or in the pore of the membranes [38,40,44].

4. Conclusion

Fe-Ag NPs were uniformly dispersed on functionalized MWCNT surfaces without any agglomeration. PES hybrid nanostructured membranes have been fabricated by incorporating Fe-Ag/f-MWCNTs in the PES polymer matrix via a modified phase inversion method, and were found not to leach from the PES polymer. AFM and SEM results showed that the membranes had rougher surfaces and that a dense layer was present on the active site of the membranes. The NPs improved the surface charge density of the membranes. In addition, the NPs significantly enhanced the hydrophilicity of the membranes. Separation studies suggested that the incorporation of Fe-Ag/f-MWCNTs increased the rejection of Cr^{6+} ions and improved the fouling resistance of the PES membranes. The pure water flux of Fe-Ag/f-MWCNT/PES hybrid membranes reached a maximum of $36.9 L/m^2 h$ and Cr^{6+} rejection values reached 94.8%.

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References

- [1] S. Rengaraj, K. Yeon, S. Moon, Removal of chromium from water and wastewater by ion exchange resins, *J. Hazard. Mater.* 87 (2001) 273–287.
- [2] J. Huang, F. Fang, L. Wang, J.-J. Shim, Removal of cobalt ions from aqueous solution by Ag/Fe bimetallic nanoparticles, *Desalin. Water Treat.* 56 (2014) 1–8.
- [3] Y.C. Sharma, V. Srivastava, C.H. Weng, S.N. Upadhyay, Removal of Cr (VI) from wastewater by adsorption on iron nanoparticles, *Can. J. Chem. Eng.* 87 (2009) 921–929.
- [4] G. Bayramoglu, M.Y. Arica, Adsorption of Cr (VI) onto PEI immobilized acrylate-based magnetic beads: isotherms, kinetics and thermodynamics study, *Chem. Eng. J.* 139 (2008) 20–28.
- [5] Z. Wu, S. Li, J. Wan, Y. Wang, Adsorption of Cr (VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent, *J. Mol. Liq.* 170 (2012) 25–29.
- [6] L. Zhang, W. Xia, B. Teng, X. Liu, W. Zhang, Zirconium cross-linked chitosan composite: preparation, characterization and application in adsorption of Cr (VI), *Chem. Eng. J.* 229 (2013) 1–8.

- [7] Y. Wen, Z. Tang, Y. Chen, Y. Gu, Adsorption of Cr(VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent, *Chem. Eng. J.* 175 (2011) 110–116.
- [8] A.A. Attia, S.A. Khedr, S.A. Elkholy, Adsorption of chromium ion (VI) by acid activated carbon, *Braz. J. Chem. Eng.* 27 (1) (2010) 183–193.
- [9] X. Lv, J. Xu, G. Jiang, X. Xu, Chemosphere removal of chromium (VI) from wastewater by nanoscale zero-valent iron particles supported on multiwalled carbon nanotubes, *Chemosphere* 85 (7) (2011) 1204–1209.
- [10] Z. Yue, S.E. Bender, J. Wang, J. Economy, Removal of chromium Cr (VI) by low-cost chemically activated carbon materials from water, *J. Hazard. Mater.* 166 (2009) 74–78.
- [11] C. Jung, J. Heo, J. Han, N. Her, S. Lee, J. Oh, J. Ryu, Y. Yoon, Hexavalent chromium removal by various adsorbents: powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes, *Sep. Purif. Technol.* 106 (2013) 63–71.
- [12] J. Huang, G. Arthanareeswaran, K. Zhang, Effect of silver loaded sodium zirconium phosphate (nanoAgZ) nanoparticles incorporation on PES membrane performance, *Desalination* 285 (2012) 100–107.
- [13] R. Saranya, G. Arthanareeswaran, D.D. Dionysiou, Treatment of paper mill effluent using polyethersulfone/functionalised multiwalled carbon nanotubes based nanocomposite membranes, *Chem. Eng. J.* 236 (2014) 369–377.
- [14] N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura, *Advanced Membrane Technology and Applications*, John Wiley & Sons Inc, Hoboken, New Jersey, USA, 2008.
- [15] N. Maximous, G. Nakhla, W. Wan, K. Wong, Preparation, characterization and performance of Al_2O_3 /PES membrane for wastewater filtration, *J. Membr. Sci.* 341 (2009) 67–75.
- [16] F.S. Shariatmadar, M. Mohsen-nia, Polymeric membranes incorporated with metal/metal oxide nanoparticles: a comprehensive review, *Desalination* 308 (2013) 1–8.
- [17] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li, The influence of nano-sized TiO_2 fillers on the morphologies and properties of PSF UF membrane, *J. Membr. Sci.* 288 (2007) 231–238.
- [18] L. Shen, X. Bian, X. Lu, L. Shi, Z. Liu, L. Chen, Z. Hou, K. Fan, Preparation and characterization of ZnO/polyethersulfone (PES) hybrid membranes, *Desalination* 293 (2012) 21–29.
- [19] W. Liu, T. Qian, H. Jiang, Bimetallic Fe nanoparticles: recent advances in synthesis and application in catalytic elimination of environmental pollutants, *Chem. Eng. J.* 236 (2014) 448–463.
- [20] K. Mphahlele, M.S. Onyango, S.D. Mhlanga, Adsorption of aspirin and paracetamol from aqueous solution using Fe/N-CNT/b-cyclodextrin nanocomposites synthesized via a benign microwave assisted method, *Biochem. Pharmacol.* (2015).
- [21] P. Chairuangkitti, S. Lawanprasert, S. Roytrakul, S. Aueviriyavit, Toxicology in vitro silver nanoparticles induce toxicity in A549 cells via ROS-dependent and ROS-independent pathways, *Toxicol. Vit.* 27 (1) (2013) 330–338.
- [22] M.A. Radzig, V.A. Nadtchenko, O.A. Koksharova, J. Kiwi, V.A. Lipasova, I.A. Khmel, Antibacterial effects of silver nanoparticles on gram-negative bacteria: influence on the growth and biofilms formation, mechanisms of action, *Colloids Surfaces B: Biointerfaces* 102 (2013) 300–306.
- [23] X. Weng, S. Lin, Y. Zhong, Z. Chen, Chitosan stabilized bimetallic Fe/Ni nanoparticles used to remove mixed contaminants-amoxicillin and Cd (II) from aqueous solutions, *Chem. Eng. J.* 229 (2013) 27–34.
- [24] Y. Li, J. Li, Y. Zhang, Mechanism insights into enhanced Cr (VI) removal using nanoscale zerovalent iron supported on the pillared bentonite by macroscopic and spectroscopic studies, *J. Hazard. Mater.* 227–228 (2012) 211–218.
- [25] Y. Zhang, Y. Li, J. Li, G. Sheng, Y. Zhang, X. Zheng, Enhanced Cr (VI) removal by using the mixture of pillared bentonite and zero-valent iron, *Chem. Eng. J.* 185–186 (2012) 243–249.

- [26] S. Luo, P. Qin, J. Shao, L. Peng, Q. Zeng, J. Gu, Synthesis of reactive nanoscale zero valent iron using rectorite supports and its application for Orange II removal, *Chem. Eng. J.* 223 (2013) 1–7.
- [27] J. Wang, G. Liu, C. Zhou, T. Li, J. Liu, Synthesis, characterization and aging study of kaolinite-supported zero-valent iron nanoparticles and its application for Ni (II) adsorption, *Mater. Res. Bull.* 60 (2014) 421–432.
- [28] K. Kardimi, T. Tsoufis, A. Tomou, B.J. Kooi, M.I. Prodromidis, D. Gournis, Synthesis and characterization of carbon nanotubes decorated with Pt and PtRu nanoparticles and assessment of their electrocatalytic performance, *Int. J. Hydrogen Energy* 37 (2) (2011) 1243–1253.
- [29] W. Chen, J. Yang, Z. Liu, Preparation of Pt and PtRu nanoparticles supported on carbon nanotubes by microwave-assisted heating polyol process, *Mater. Lett.* 58 (2004) 3166–3169.
- [30] K. Mphahlele, M.S. Onyango, S.D. Mhlanga, Efficient preparation of greener N-doped carbon nanotube composites for water treatment by the microwave polyol method, *Environ. Chem. Lett.* 11 (4) (2013) 353–358.
- [31] S.D. Mhlanga, K.C. Mondal, R. Carter, M.J. Witcomb, N.J. Coville, The effect of synthesis parameters on the catalytic synthesis of multiwalled carbon nanotubes using Fe-Co/CaCO₃ catalysts, *S. Afr. J. Chem.* 62 (2009) 67–76.
- [32] C.J. Ko, C.Y. Lee, F.H. Ko, H.L. Chen, T.C. Chu, Highly efficient microwave-assisted purification of multiwalled carbon nanotubes, *Microelectron. Eng.* 73–74 (2004) 570–577.
- [33] P.L. Lee, Y.K. Chiu, Y.C. Sun, Y.C. Ling, Synthesis of a hybrid material consisting of magnetic iron-oxide nanoparticles and carbon nanotubes as a gas adsorbent, *Carbon N. Y.* 48 (5) (2010) 1397–1404.
- [34] N. Phao, E.N. Nxumalo, B.B. Mamba, S.D. Mhlanga, A nitrogen-doped carbon nanotube enhanced polyethersulfone membrane system for water treatment, *Phys. Chem. Earth, Parts A/B/C* 66 (2013) 148–156.
- [35] Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, Fabrication and development of interfacial polymerized thin-film composite nanofiltration membrane using different surfactants in organic phase; study of morphology and performance, *J. Membr. Sci.* 343 (2009) 219–228.
- [36] E. Salehi, S.S. Madaeni, L. Rajabi, V. Vatanpour, a.a. Derakhshan, S. Zinadini, S. Ghorabi, H. Ahmadi Monfared, Novel chitosan/poly(vinyl) alcohol thin adsorptive membranes modified with amino functionalized multi-walled carbon nanotubes for Cu(II) removal from water: preparation, characterization, adsorption kinetics and thermodynamics, *Sep. Purif. Technol.* 89 (Mar. 2012) 309–319.
- [37] V. Vatanpour, S. Siavash, A. Reza, E. Salehi, S. Zinadini, H. Ahmadi, TiO₂ embedded mixed matrix PES nanocomposite membranes: influence of different sizes and types of nanoparticles on antifouling and performance, *Desalination* 292 (2012) 19–29.
- [38] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite, *J. Membr. Sci.* 375 (1–2) (2011) 284–294.
- [39] ASTM Standard D4187–82, Zeta Potential of Colloids in Water and Wastewater, 1985.
- [40] V. Vatanpour, S. Siavash, R. Moradian, S. Zinadini, B. Astinchap, Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO₂ coated multiwalled carbon nanotubes, *Sep. Purif. Technol.* 90 (2012) 69–82.
- [41] E. Celik, H. Park, H. Choi, H. Choi, Carbon nanotube blended polyethersulfone membranes for fouling control in water treatment, *Water Res.* 45 (1) (2011) 274–282.
- [42] M. Khayet, M.C. García-Payo, X-Ray diffraction study of polyethersulfone polymer, flat-sheet and hollow fibers prepared from the same under different gas-gaps, *Desalination* 245 (1–3) (2009) 494–500.
- [43] WHO, Guideline for Drinking Water Quality, 2006.
- [44] V. Vatanpour, M. Esmaili, M.H.D.A. Farahani, Fouling reduction and retention increment of polyethersulfone nanofiltration membranes embedded by amine-functionalized multi-walled carbon nanotubes, *J. Membr. Sci.* 466 (2014) 70–81.