

The International Ozone Association  
is pleased to present the

## 22<sup>nd</sup> World Congress & Exhibition

28 June – 3 July 2015, Barcelona, Spain

# Ozone and Advanced Oxidation Leading-edge science and technologies

## PROCEEDINGS

No. ISBN: 979-10-92607-02-4

Water Treatment  
Science and Technology  
Research Development Events Members  
Knowledge Advances  
Standards Awards  
Fundamentals Industry News  
Field application Engineering  
Food Processing Worldwide  
Ozone Therapy Publications  
Agriculture



## Removal of Acid Red 1 by TiO<sub>2</sub> nanoparticles coated polyethersulfone membrane under UV irradiation

Ildikó Kovács<sup>1</sup>, Szabolcs Kertész<sup>1</sup>, Sándor Beszédes<sup>1</sup>, Cecilia Hodúr<sup>1</sup>, Ibolya Zita Papp<sup>2</sup>, Ákos Kukovecz<sup>2,3</sup>, Zsuzsanna László<sup>1</sup>

1. University of Szeged, Department of Process Engineering, Moszkvai str.9, H-6725 Szeged, Hungary

2. Department of Applied and Environmental Chemistry, University of Szeged, H-6720 Szeged, Rerrich Béla tér 1., Hungary

3. MTA-SZTE "Lendület" Porous Nanocomposites Research Group, H-6720 Szeged, Rerrich Béla tér 1., Hungary

### Abstract

Polyethersulfone (PES) membranes are used in a wide range for water and wastewater treatment due to their physical and chemical properties, but despite their improved properties membrane fouling remains a problem. In order to overcome this problem a great deal of interest has been focused on modifying membranes with TiO<sub>2</sub> as a photocatalyst to reduce fouling and to make the organic component removal more efficient.

In this study polyethersulfone membranes with different pore sizes (0.05 and 0.2 μm) were coated with commercial TiO<sub>2</sub> P25 and synthesized TiO<sub>2</sub> nanoparticles (NP) by filtering the TiO<sub>2</sub> solution through the membrane. In order to test the photocatalytic activity of Acid Red 1 dye solutions were filtered with commercial PES membranes with and without TiO<sub>2</sub> coating. Coated membranes had significantly lower fluxes compared to the neat membranes. Contact angle measurements showed that TiO<sub>2</sub> P25 formed a very hydrophilic coat on the membranes on the contrary TiO<sub>2</sub> NP increased the hydrophobicity of the surface. UV irradiation had an effect on both the neat and coated membranes flux values. Relative dye fluxes were calculated against the equivalent water fluxes and were compared. UV irradiation increased the dye elimination efficiency of the coated membranes, which proves the TiO<sub>2</sub> coatings photocatalytic activity.

**Key-words:** Membrane filtration, Polyethersulfone (PES) membrane, TiO<sub>2</sub> nanoparticles, Acid red 1

### Introduction

Colored effluents from textile industries represent one of the major problems concerning textile wastewaters. Dyes are intensely colored and represent a special problem by their discharge into waste streams without treatment by the textile industry worldwide. Most of the dyes are difficult to decolorize due to their complex structure and synthetic origin [1]. Acid Red 1 (AR1, Azophloxine) dye was used as a model pollutant to determine the photocatalytic activity of the membranes TiO<sub>2</sub> coating. AR1 is a reactive azo dye belonging to the largest class of dyes commonly employed in textile industry [2].

Advanced oxidation processes (AOPs) are extensively investigated and used in water, air and wastewater treatment. AOPs are very effective and useful for the degradation of substances that are resistant to conventional treatment technologies [3]. AOPs generate hydroxyl radicals (<sup>•</sup>OH) that are very effective in degrading organic pollutants due to their non-selectivity and strong oxidant power ( $E^0 = 2.80$  V) [1]. Semiconductor photocatalysis with a primary focus on TiO<sub>2</sub> as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification. It has been shown to be useful amongst many others for the destruction of microorganisms such as bacteria and viruses, for odor control and for the cleanup of oil spills [3].

In membrane preparation nanoparticles have been used to produce membranes with a desirable structure or to control the membrane fouling [4]. PES membranes are used in a wide range for water and wastewater treatment due to their physical and chemical properties. Despite

their great properties like high temperature and good chemical resistance, wide pH tolerances, broader range of pore sizes, membrane fouling remains a problem [5].

Chemical membrane modifications, by assembling additional compounds in membrane composition, have been proposed to realize high membrane permeability over a prolonged period of time [6]. Over the last decades, a great deal of interest has been focused on modifying membranes with  $\text{TiO}_2$  as a photocatalyst, among others to reduce fouling and to make the organic component removal more efficient.  $\text{TiO}_2$  is favored over other semiconductors due to its good physical and chemical properties, availability, photocatalytic activity, desirable hydrophilic and potential antifouling properties [4] and [7].

The mechanism of the heterogenous photocatalysis is as follows (Fig. 1): when a semiconductor is irradiated by a ray equal or greater than the band gap energy in ordinary conditions, an electron is transferred from valence band to conduction band of the semiconductor. Therefore a pairs of holes and electrons are created on the surface of the semiconductor. Since  $\text{TiO}_2$  is a semiconductor, the UV ray leads to the appearance of the electrons and holes. The photo-generated electrons can reduce the dissolved oxygen and produce super-oxide ( $\text{O}_2^{\bullet-}$ ) radical anions. The photo-generated holes have a very high oxidation potential and can react with water which is adsorbed on the catalyst surface and generate ( $\text{OH}^{\bullet}$ ) radicals. These two types of created groups are among strong oxidant reagents that lead to the decomposition and removal of the impurities especially organic compounds [8] and [3].

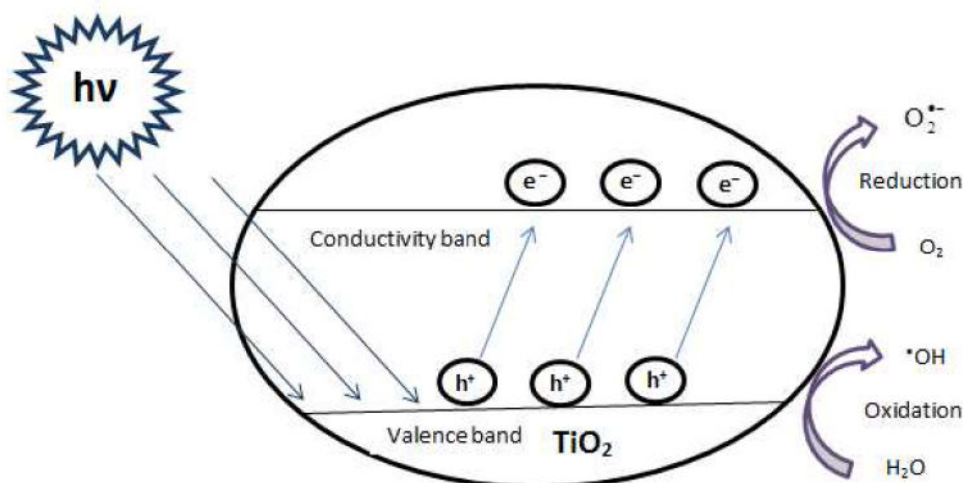


Figure 1. Mechanism of photocatalysis

Nanocomposite  $\text{TiO}_2$  PES membranes have been manufactured by two ways: coating the nanoparticles on the surface of the porous membranes or blending them with polymeric casting solution [4] and [7]. Most of the proposed processes apply the phase inversion technique to produce hybrid polymeric membrane adding a known amount of  $\text{TiO}_2$  in the main solution. This mixture is then precipitated in a solvent solution. An alternative procedure is to dip the neat polymeric membrane into a  $\text{TiO}_2$  solution [6]. Rahimpour et al. showed that coating  $\text{TiO}_2$  onto membrane surface is a superior method compared to entrapping  $\text{TiO}_2$  particles in the membrane matrix. The former option enables higher permeate fluxes and smaller membrane resistances[6].

In this study the membrane performance and azo dye (Aid red1) removal of PES membrane coated with commercial  $\text{TiO}_2$  P25 and synthesized  $\text{TiO}_2$  NP under UV irradiation was investigated. Contact angle measurements were carried out to determine the coatings effect on the membrane surfaces wettability.

## Material and methods

### Materials

TiO<sub>2</sub> (anatase) (BA01-01), TiO<sub>2</sub> P25 (80% anatase, 20% rutile) and Acid red1 were supplied by UNIVAR, EVONIC Industries and Synthesia respectively. The concentration of AR1 solution used in membrane filtration measurements was 15 mg L<sup>-1</sup>.

### Preparation of TiO<sub>2</sub> nanoparticles

In 1L 10M NaOH solution 250g TiO<sub>2</sub> (anatase) was suspended, then for 24 hours the suspension was stirred in a rotating autoclave at 3 rpm and 155°C. Then the resulting product was washed and protonated with 0.1M HCl, after maintaining a pH value between 3 and 4 for 30 minutes the product was washed with 0.01M HCl for 3 days than with distilled water to remove the remaining chloride ions. The resulting TiO<sub>2</sub> nanotubes were dried at 80°C for a day. The TiO<sub>2</sub> nanotubes (NT) were then heat treated at 600°C for 6 hours. As a resulting product TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub> NP) arose (Fig. 2).

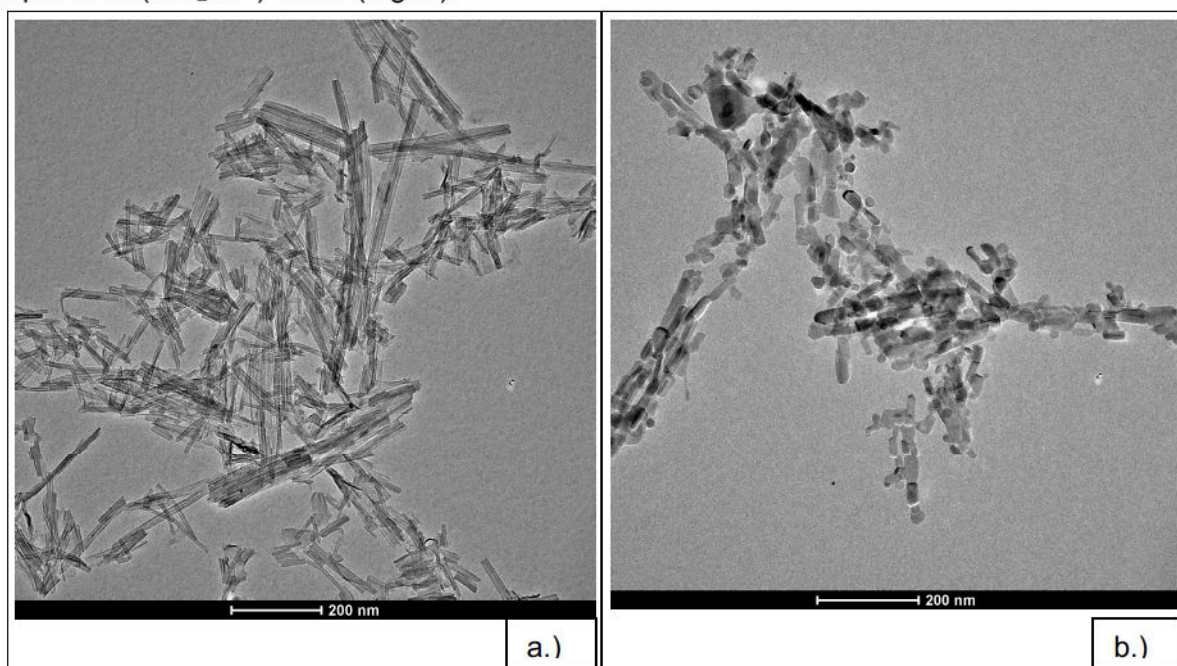


Figure 2. TEM images of a) TiO<sub>2</sub> NT and b) TiO<sub>2</sub> NP

### Membrane modification

Polyethersulfone membranes (PES-MF and MP005 (NEW LOGIC Research INC, USA) with a 0.2 µm and 0.05 µm pore size respectively were coated with commercial TiO<sub>2</sub> P25 and TiO<sub>2</sub> NP. Membranes were prepared by filtering 50 mL, 0.4 g/L TiO<sub>2</sub> suspension through the membranes using a dead end cell. The applied transmembrane pressure (TMP) of 0.1 MPa was constant and achieved by inert nitrogen gas. Neat membranes were pretreated in distilled water for 24 hours before use.

### Membrane filtration

Water flux was measured using a dead end cell (Millipore, N°96) coupled with a low pressure mercury UV lamp (Lightech, Hungary). The flux measurements of distilled water and the azo dye were done at 1 bar and room temperature with the effective membrane area of 0.00342 m<sup>2</sup>. UV irradiation of certain samples was done in the dead end cells before the filtration as a pretreatment for 60 minutes.

### Analytical methods

Transmission electron microscopy (TEM; Philips CM 10) images were recorded to determine the morphology and size of the TiO<sub>2</sub> NT and TiO<sub>2</sub> NP.

The concentration of the dye was measured by spectrophotometer (Nanocolor® UV/Vis, Macherey-Nagel GmbH, Germany) at  $\lambda=532$  nm.

Membrane hydrophobicity was quantified by measuring the contact angle that was formed between the (neat and coated) membrane surface and distilled water. 10 $\mu$ L water was carefully dropped on the top of the membrane surface. Contact angles were measured using the sessile drop method (Datapysics Contact Angle System OCA15Pro, Germany).

## Results and discussion

### The effect of modification with TiO<sub>2</sub> P25 and TiO<sub>2</sub> NP on the membrane performance

Water fluxes for unmodified and modified PES-MF and MP005 membranes with TiO<sub>2</sub> P25 and TiO<sub>2</sub> NP were measured. The coated membranes showed a lower flux compared to the neat membranes, which suggests that TiO<sub>2</sub> nanoparticles narrow and plug the membrane pores (Fig. 3). The primary particle size of commercial TiO<sub>2</sub> nanoparticles such as P25 is about 20 nm, its particle size as powder or in dispersions is in a range of hundreds of nanometers due to agglomeration [7]. A similar behavior was observed on the TEM pictures of the TiO<sub>2</sub> NP with a singular nanoparticle sizes about 60nm. TiO<sub>2</sub> NP coated membranes had a higher flux compared to the TiO<sub>2</sub> P25 coated ones and that this growth was more expressed in case of the MP005 membrane which has the smaller 0.05  $\mu$ m pore size. This could suggest that the TiO<sub>2</sub> P25 particles cause a more pronounced membrane fouling.

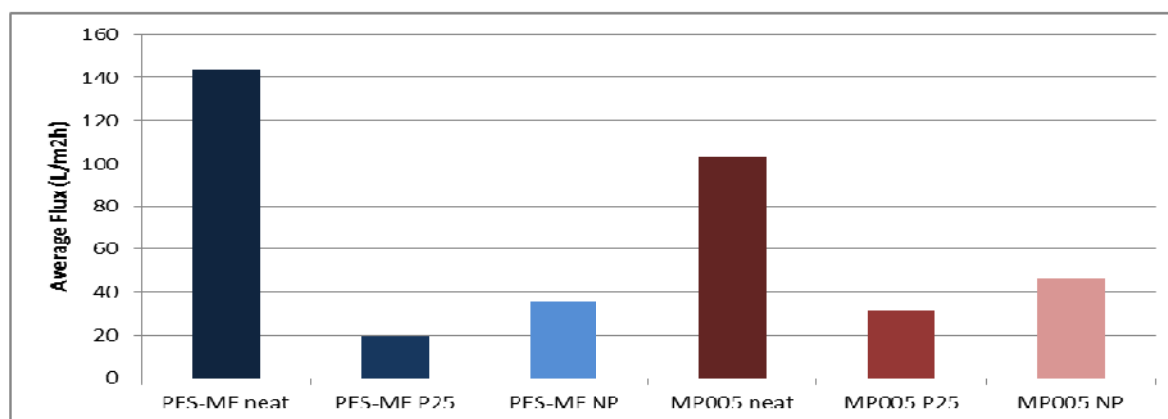


Figure 3. Influence of different coatings on the average water fluxes

Contact angle measurements showed that the wettability of TiO<sub>2</sub> NP coated membranes decreased compared to the neat membranes (Fig. 4). In case of TiO<sub>2</sub> P25 coated membranes contact angle was unmeasurably low due to the catalysts extent hydrophilic character. It has been recognized that the reactivity of TiO<sub>2</sub> surface, and in particular its affinity toward water is dependent on TiO<sub>2</sub> crystal phase. The hydrophilicity of the mixture of the two polymorphs (anatase and rutile) is close to that of the main component, i.e. anatase [9].

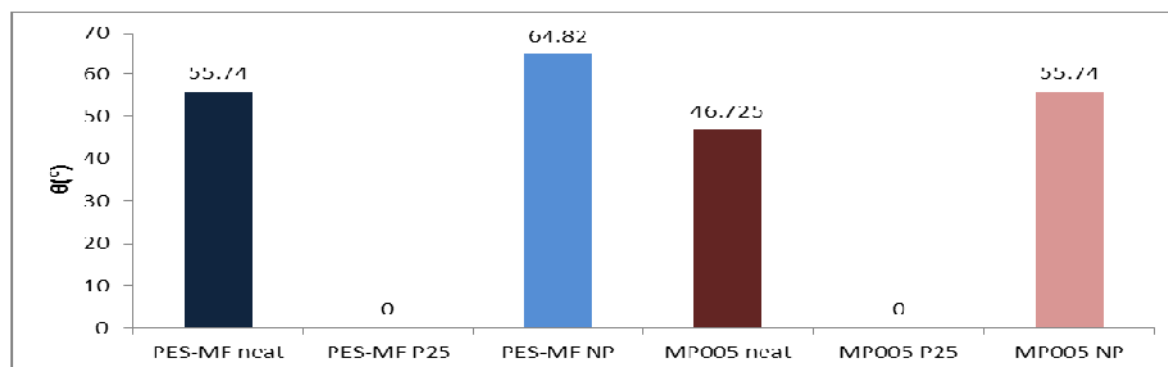


Figure 4. Neat, TiO<sub>2</sub> NP and P25 coated PES membranes wettability

### Microfiltration of AR 1 solution

Microfiltration of AR 1 was carried out with coated membranes and with the coated membranes coupled with UV irradiation. In case of UV irradiation the water fluxes without an exception were about 50% higher than without the irradiation (Fig. 5). This can be explained by that the irradiation of PES membranes by UV light causes crosslinking and chain scission, two parallel competitive processes, shaping the transport properties of the modified membrane [11]. Similar behavior was observed in the case of dye solution fluxes; the UV irradiation resulted in higher fluxes in both membranes.

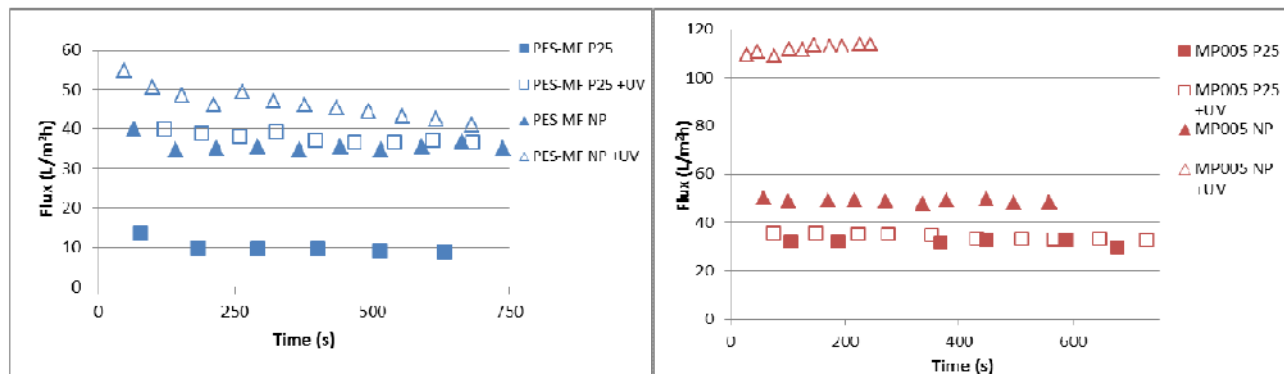


Figure 5. TiO<sub>2</sub> NP and P25 coated PES membranes relative dye flux

### Photocatalytic and elimination efficiency of TiO<sub>2</sub> P25 and TiO<sub>2</sub> NP coated membranes during MF of AR 1

Elimination and photocatalytic efficiencies of TiO<sub>2</sub> P25 and TiO<sub>2</sub> NP coated membranes in the presence of UV irradiation during MF of AR 1 were compared (Figure 6). The membranes with smaller pore size (0.05 μm) showed higher dye retention. The dye retention of the irradiated membrane decreased due to the degradation of dye molecules, but the overall dye elimination increased by combining heterogeneous photocatalysis and microfiltration. In case of 0.2 μm pore size PES membranes TiO<sub>2</sub> P25 coated membrane showed lower elimination and photocatalytic efficiency compared to the TiO<sub>2</sub> NP coated PES-MF membrane. It was found that the highest dye elimination and photocatalytic efficiency was achieved by TiO<sub>2</sub>NP coated MP005 membranes. Membrane pares which only differ in the aspect of irradiation show that the decrease of relative flux is in correlation with the elimination efficiency. Higher elimination efficiency caused lower relative fluxes due to the concentration polarization on the surface of the membrane.

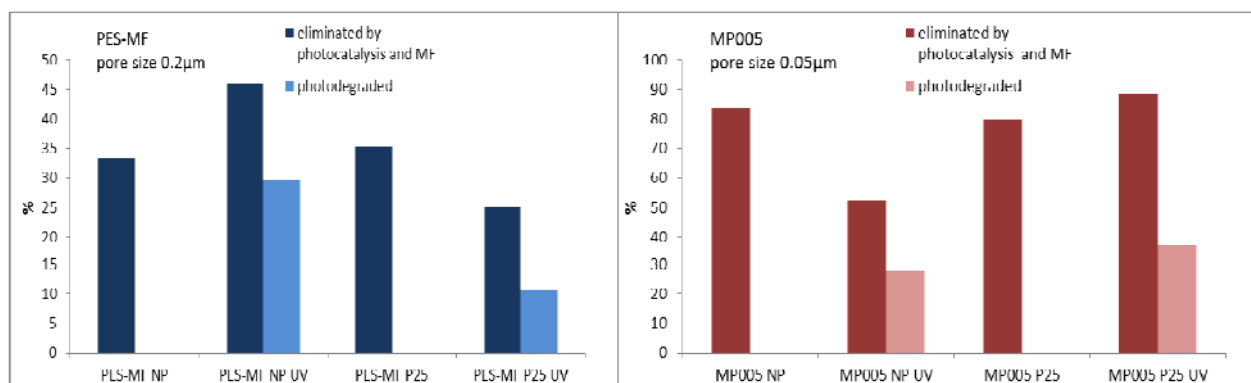


Figure 6. Elimination and photocatalytic efficiencies

## Conclusions

Removal of AR 1 by MF using MP005 and PES-MF membranes coated with TiO<sub>2</sub> P25 and TiO<sub>2</sub> NP was an indicator whether these membranes gain any positive qualities as a result of coating. It was found that coated membranes had significantly lower fluxes compared to the neat membranes due to the fouling of the pores by nanoparticles. Contact angle measurements showed that TiO<sub>2</sub> P25 formed a very hydrophilic coat on the membranes on the contrary TiO<sub>2</sub> NP increased the hydrophobicity of the surface. UV irradiation had an effect on both the neat and coated membranes flux values; UV light may cause crosslinking and chain scission shaping the transport properties of the modified membrane. The retention and photocatalytic qualities of the coated membranes were significant which makes them candidates for further investigations to determine whether they can be used in water and wastewater treatment.

## References

1. Daud K., Hameed B., Decolorization of Acid Red 1 by Fenton-like process using rice husk ash-based catalyst, *Journal of Hazardous Materials*, 176 (1-3), 938-944 (2010).
2. Földváry Cs., Wojnárovits L., The effect of high-energy radiation on aqueous solution of Acid Red 1 textile dye, *Radiation Physics and Chemistry*, 76, 1485-1488 (2007).
3. Hoffmann M., Martin S., Choi W., Bahnemann D., Environmental Applications of Semiconductor Photocatalysis, *Chemical Reviews*, 95, 69-96 (1995).
4. Vatanpour V., Maadaeni S. S., Khataee R. A., Salehi E., Zinadini S., Monfared A. H., TiO<sub>2</sub> embedded mixed matrix PES nanocomposite membranes: Influence of different sizes and types of nanoparticles on antifouling and performance, *Desalination*, 292, 19-29 (2012).
5. Li J. F., Xu Z. L., Yang H., Yu L. Y., Liu M., Effect of TiO<sub>2</sub> nanoparticles on the surface morphology and performance of microporous PES membrane, *Applied Surface Science*, 255 (9), 4725-4732 (2009).
6. Bergamasco R., Silva F. V., Arakawa F. S., Yamaguchi N. U., Reis M. H. M., Tavares C. J., Amorim M. T. P. S., Tavares C. R. G., Drinking water treatment in a gravimetric flow system with TiO<sub>2</sub> coated membranes, 174 (1), 102-109 (2011).
7. Razmjoua A., Mansouri J., Chen V., The effects of mechanical and chemical modification of TiO<sub>2</sub> nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes, *Journal of Membrane Science*, 378 (1-2), 73-84 (2011).
8. Rahimpour A., Madaeni S. S., Taheri A. H., Mansourpanah Y., Coupling TiO<sub>2</sub> nanoparticles with UV irradiation for modification of polyethersulfone ultrafiltration membranes, *Journal of Membrane Science*, 313 (2008) 158-169.
9. Bolis V., Buscoa C., Ciarletta M., Distasi C., Erriquez J., Fenoglio I., Livraghi S., Morel S., Hydrophilic/hydrophobic features of TiO<sub>2</sub> nanoparticles as a function of crystal phase, surface area and coating, in relation to their potential toxicity in peripheral nervous system, *Journal of Colloid and Interface Science*, 369 (1), 28-39 (2012).
10. Diebold U., Ruzycki N., Herman G.S., Selloni A., One step towards bridging the materials gap: surface studies of TiO<sub>2</sub> anatase, *Catalysis Today*, 85, 93-100 (2003).
11. Kaeselev B., Kingshottb P., Jonsson G., Influence of the surface structure on the filtration performance of UV-modified PES membranes, *Desalination*, 146 (1-3), 265-271 (2002).