



## Research paper

# Developing of titania-smectite nanocomposites UF membrane over zeolite based ceramic support



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## ABSTRACT

In the present work, UF ceramic membrane from smectite (Sm) nanoparticle as active layer and zeolite as a support was prepared. The nanoparticle clay powder was obtained by using a colloidal route method. Thus, titanium (IV) isopropoxide was incorporated within the organophilic layer and developed on the surface of the aluminosilicate-grains. Firstly, the nanoparticle powders were characterized by using various methods (XRD, IR, SEM-EDX and BET).

Hence, the morphology and properties of the resulting membrane sintered at 900 °C were then determined by SEM, FTIR and BET, whereas its performance was investigated by conducting pure water permeation and application for treatment of four types of different industrial waste water. The microstructure observed from SEM showed that the separation layer has a homogenous structure with no cracks resulting in an average pore diameter of 18 nm. Furthermore, water permeability was found to vary from 1218 Lh<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup> for the support before layer deposition to 80 Lh<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-1</sup> after coating. This value confirms that the Sm/Z membrane is suitable for operating in ultrafiltration domain. Finally, the application to the treatment of industrial wastewaters revealed an important decrease in turbidity, color and chemical oxygen demand (COD) while the permeate flux was maintained at acceptable value. The overall data suggest that the elaborated titania-smectite nanocomposite membrane may be an effective remediation means aimed at industrial effluents treatment.

## 1. Introduction

Membrane technology has received a great interest in a wide range of fields and particularly, the development of ceramic membranes, which is due to their several advantages, such as high chemical, mechanical, thermal stabilities in addition to their separation efficiency and long life (Cham and Brownstein, 1991; DeFriend and Barron, 2003; Elyassi et al., 2008; Sarkar et al., 2012).

Furthermore, ceramic membranes, as compared to polymeric composite membranes, provide also high permeate flux as resulting from their better antifouling property (Weir et al., 2001; Liu et al., 2013).

Generally, the commercialized ceramic membranes are prepared from metal oxides such as alumina, silica, zirconia and titania (Defriend

et al., 2003<sub>b</sub>). However, these membranes are expensive due to their high fabrication costs, which limit their use in the industrial scale in comparison to polymeric membranes (Weir et al., 2001; Liu et al., 2013).

Thus, in order to promote the use of ceramic membrane in a wide range of applications, a great number of research works have been devoted to the development of new type of inorganic membranes (Khemakhem et al., 2015), mainly made from low-cost, natural materials, such as apatite (Masmoudi et al., 2005), clay (Khemakhem et al., 2006), fly ash (Jedidi et al., 2009), carbon (Tahri et al., 2013) and graphite (Ayadi et al., 2013). It is worthwhile observing that ceramic membranes have asymmetric and composite structure formed by deposition of a layer on previously fabricated support, such a layer

Abbreviations: Sm/Z, Mesoporous UF membrane; MF, Microfiltration membrane; UF, Ultrafiltration membrane; NF, Nanofiltration membrane; CTAB-Sm, CTAB – smectite; CTAB-Ti-Sm, TiO<sub>2</sub> - CTAB – smectite nanoparticle; -, Smectite (Sm) nanoparticle; PVA, Polyvinyl alcohol; CTAB, Hexadecyltrimethylammonium bromide; FTIR, Fourier Transform Infrared; SEM, Scanning Electron Microscopy; EDX, Energy Dispersive X-ray; XRD, X-ray diffraction; BET, Méthode: Brunauer, Emmett et Teller; TMP, Transmembrane Pressure; COD, Chemical Organic Demand; EF1, Textile industry wastewater; EF2, Inkpots washing water; EF3, Heavy metals contaminated effluents from electroplating industry; EF4, Agro-food industry wastewater

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deposition can be achieved by slip-casting (Khemakhem et al., 2009), dip coating (Sahoo et al., 2016) and sol-gel (Larbot et al., 2004; Das et al., 2014). Ceramic membranes pore size ranges include: macropores, with pore size ranging from 1 to 10  $\mu\text{m}$  for microfiltration (MF) membranes, mesopores, with pore size ranging from 2 to 50 nm for ultrafiltration (UF) membranes, and micropores, having a pore size range (below 1 nm) for nanofiltration (NF) membrane (Almandoz et al., 2004; Almandoz et al., 2015). NF membranes are generally used for color removal from wastewater, although they require more energy than UF membranes since higher values of trans-membrane pressure are actually needed. UF ceramic membranes exhibit either mesoporous or microporous ceramic structures (Cot et al., 2000). Preparation of UF ceramic membrane needs the use of powder having a size range commonly below the interval of membrane pore size (Rastgar et al., 2017). Nevertheless, membrane pore size can be reduced by the application of various polymers or nanoparticles on the active layer (Kasemset et al., 2017; Wan et al., 2017).

It is well known also that dispersion of nanoparticles either in submicroscopic or nanoscopic size is an important precursor used in membrane preparation for having tailor made pore size distribution in UF and NF membrane. The use of dispersion of ceramic particles such as alumina, titania or zirconia has been demonstrated also for various applications (Bandyopadhyay et al., 2006; Raichur, 2007; Aranda et al., 2008; Biswas and Raichur, 2008). For example, the dispersion of zirconia in organic media using bio surfactants has been studied taking into account the pH and the concentration range (Biswas and Raichur, 2008). The synthesis of nanoparticles supported clay mineral can be efficiently used as ceramic material for mesoporous membrane preparation. Among the clay mineral family, the layered silicates belonging to the smectite group characterized by their hydrophilic character are the most common class of materials used to prepare clay nanoparticles. Several authors have investigated the preparation and the use of inorganic-inorganic nanocomposite from clay microfibers (Aranda et al., 2008). Organically modified smectite can be obtained by the exchange of their inorganic cations with organic cations from a cationic surfactant, which is definitely the most common chemical used in this process (Su et al., 2011; Mirmohamadsadeghi et al., 2012). The cationic exchange occurring between the inorganic nanoparticles such as titania and the organically modified clay leads to the development of titania-clay nanostructured porous materials (Manova et al., 2010).

Other layered silicate groups were also extensively used such as palygorskite, sepiolite and smectite. Thus, Bouna et al. (2011) found that the synthesized  $\text{TiO}_2$  supported natural palygorskite microfibers leads to the formation of a stable anatase crystalline  $\text{TiO}_2$  structure at 600 °C. This clay- $\text{TiO}_2$  nanocomposite exhibits a high photocatalytic activity against the degradation of Orange G dye in aqueous solution. Aranda et al. (2008) have reported the preparation of  $\text{TiO}_2$ -sepiolite nanocomposites using a colloidal route method in presence of CTAB surfactant. The test on the photocatalytic activity shows high efficiency reaching 90% of conversion in case of phenol degradation (Aranda et al., 2008). Manova et al. (2010) have shown the possibility of the formation of stable active  $\text{TiO}_2$  anatase onto smectite clay, thus achieving high efficiency in the degradation of 2, 4-dichlorophenol. The success of the colloidal procedure for nanocomposite preparation using clay as ceramic material depends generally on the nature of clay minerals (Letaief et al., 2006).

Among the clay mineral family, the smectite group was the most common support used usually to perform  $\text{TiO}_2$  nanocomposite preparation, owing to their lamellar structure, their high specific surface area and microporous volume, as well as, their adsorption properties (Bouberka et al., 2009). The literature study in this research area has shown that the photocatalytic and green adsorbent activities were the most explored (Chen et al., 2012; Hamza et al., 2014; Pettinato et al., 2015).

In the field of membrane preparation, several works have been performed to enhance the porous membrane structure following

different ways such as the addition of a separating layer on the membrane surface by means of various coating process using dispersion of nanocomposite. For example, Saffaj et al. (2005) coated the cordierite support with  $\text{TiO}_2$ - $\text{ZnAl}_2\text{O}_4$  in order to reduce the pore diameter up to 4 nm for UF membrane preparation.

The aim of the present study is the preparation of a nanostructured ceramic membrane based on clay nanocomposite. The delaminated  $\text{TiO}_2$  clay was prepared by sol-gel reaction of titanium alkoxides taking place on the smectite in the presence of hexadecyltrimethylammonium bromide CTAB. The resulting nanoparticles powders were used as a basic material to prepare UF membrane.

Thus, a previously-prepared mesoporous zeolite tube was coated by the clay- $\text{TiO}_2$  nanoparticles using the layer-by-layer method, followed by the sintering process. Thereafter, the resulting membrane was successfully applied for the treatment of various industrial contaminated effluents coming from different activities.

## 2. Materials and methods

### 2.1. Materials

The smectite was sampled from jebel Stah located at about 20 km to the west of Gafsa city in the west-central Tunisia. This clay comprise about 50% of smectite, 30% of kaolinite and 10% of illite with variable amount of carbonate and gypsum (d-spacing is 14 Å).

Hexadecyltrimethylammonium bromide (CTAB) with a purity of 98% (purum by Sigma, Aldrich), was used in the preparation of the cetyltrimethylammonium (CTA) smectite organoclay derivat. Distilled water and isopropanol (Fluka,  $\geq 99.8$ ) were used as solvents or reactants. Titanium (IV) isopropoxide (TIPOTI, purum, Fluka) was used as a titania source.

### 2.2. Sample preparation

#### 2.2.1. Clay purification

The clay material was dispersed in distilled water (3–4 h). After sedimentation, fractions with particle size smaller than 2  $\mu\text{m}$  were recovered. 20 g of the purified smectite was refluxed in 100 mL of 1 M NaCl solution and malaxed for 24 h. This step was repeated 3 times. The dispersion was then filtered and washed thoroughly with distilled water till the absence of chloride ions was confirmed (AgNO<sub>3</sub> test), then, dried at 80 °C under reduced pressure. This obtained material is denoted Na<sup>+</sup>-smectite (Fernández et al., 2013).

#### 2.2.2. CTAB-smectite preparation

The smectite was organically modified by cation exchange reaction between Na-smectite and CTAB. 3 g of Na<sup>+</sup>-smectite was dispersed in 300 mL of distilled water at 80 °C and was maintained under stirring for 30 min. The surfactant (1 M solution) was slowly added and was then kept for 2 h at 80 °C under stirring followed by ultrasonication for 15 min. A contact time with the CTAB solution longer than one day is required for completing the ion-exchange reaction. The surfactant excess was eliminated by repeated washings with distilled water and the resulting organo clay was air-dried at room temperature in the ambient atmosphere (Manova et al., 2010). This obtained material was denoted CTAB-Sm.

#### 2.2.3. Modification of clay by colloidal route method

$\text{TiO}_2$ -smectite nanocomposite was prepared by adding 1 g of CTAB-Sm, 7 cm<sup>3</sup> of isopropanol and 5 cm<sup>3</sup> of titanium (IV) isopropoxide suspensions. After 1 h of stirring, water was added drop wise under stirring until the spontaneous formation of a gel at room temperature (25 °C). Prior to calcination, the gel was dried at 60 °C in atmospheric air for 24 h and finally, the dried samples was calcined at 600 °C for 1 h (Fig. 1) (Bouna et al., 2011). The preparation of  $\text{TiO}_2$ -smectite nanoparticles materials consists of slow addition to the CTAB-Sm, of water

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