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Research paper

Removal of dyes by a new nano–TiO_2 ultrafiltration membrane deposited on low-cost support prepared from natural Moroccan bentonite

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ABSTRACT

This paper reports the preparation and characterization of a low-cost nano-TiO_2 ultrafiltration membrane deposited on a bentonite support. The ultrafiltration layer was obtained by dip-coating process using nano-TiO_2, followed by sintering at 750 °C. Environmental Scanning Electron Microscope (ESEM) analysis of prepared ultrafiltration membrane showed that the deposited layer is homogeneous and shows a good adhesion on the support presenting a mean thickness of 4 ± 0.2 μm. The average pore diameter and water permeability of the obtained membrane are respectively 10 ± 0.5 nm and 16.08 L/h m^2 bar. The membrane performance was evaluated by filtration of three different dyes: two anionic (Direct red 80 and Acid orange 74) and a cationic one (Methylene blue). Effect of feed pH and dyes concentration on membrane rejection was investigated at a pressure of 4 bar. The experimental filtration results showed that rejection of Direct Red 80, Acid Orange 74 and Methylene Blue achieved maximum values of 98%, 85% and 94% respectively, depending on filtration conditions and each dye characteristics.

1. Introduction

Safe water supply and environmental protection of water reserves have become two major preoccupations for many countries. Currently, many regions in Morocco, rest of Maghreb and most of Mediterranean countries are experiencing a problem of water shortage (Barrouk et al., 2015). This lack of water has been aggravated by the irrational use of natural resources and the rapid industrialization of the exposed areas. Given the gravity of the problem, it is necessary to consider adequate solutions to solve it.

Textile, paper and plastic industries have often rejected colored wastewater without previous treatment. On the other hand, most of the dyes used in the textile industries are stable and resistible to ultraviolet light (they are not degraded due to sun rays attack) as well they are not biodegradable (Saffaj et al., 2004). They are also impervious to aerobic digestion, making these dyes long term water pollutants. To minimize the risk of environmental pollution, it becomes necessary to treat dye effluents before discharging them into water streams (Baraka et al., 2014).

Several physicochemical techniques have been used to treat these dye effluents eliminating their contaminants, including solicitation, sedimentation, impaction, interception, adhesion, chemical adsorption, physical adsorption, flocculation and biological growth (Chinoune et al., 2016; Luo and Nguyen, 2017; Shi et al., 2006).

Membrane technology has shown potentiality in the separation of dyes by microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) (Jana et al., 2010; Aouni et al., 2012; Liu et al., 2017) and it is increasingly used in industrial processes such as water treatment. Therefore, the use of membrane technology could replace or at least minimize in a short future the conventional separation and purification techniques in many industrial processes, thus reducing the whole amount of energy being consumed (Seffaj et al., 2005).

In recent years, industrial applications of porous ceramic membranes have attracted more and more the attention of scientific community. This interest is due to their numerous benefits such as better thermal, chemical and mechanical resistance and controllable microstructure (Ezziane et al., 2010). However, the use of composite ceramic membranes for wastewater treatment is still limited due to the high price of ceramic membranes.

Looking for the economic feasibility of the use of membranes in many wastewater recovery applications, the development of low-cost ceramic membranes based on natural materials and some other waste

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materials was investigated by several authors (Medjemem et al., 2016; Bouazizi et al., 2017; Achiou et al., 2016, 2017; Fatimah et al., 2015; Liu et al., 2016). Barrouk et al. (2015) and Khemakhem et al. (2015) elaborated and characterized ceramic membranes made from a mixture of natural and synthetic phosphates. Saffaj et al. (2006) described the elaboration of an UF membrane deposited on a support prepared from natural Moroccan clay. In other work (Saffaj et al., 2005), they used a macroporous substrate made of Moroccan clay as support for an intermediate ZrO_2 layer and then a $TiO_2/ZnAl_2O_4$ UF layer; and tested it for the separation of mineral salts. Kumar et al. (2015) fabricated a composite membrane of zirconia by in-situ hydrothermal technique whish was applied for separation of methyl orange.

In order to ameliorate the flux through the membrane, the use of nano-scale additives as TiO_2, ZrO_2, Al_2O_3 and SiO_2, serves to enhance the hydrophilic character of the membrane, (Kocherginsky et al., 2003; Chang et al., 2014; Xu et al., 2016). There exist many methods for preparation of ceramic UF membranes. The sol-gel method is widely described in the literature. Especially, the colloidal sol–gel route is preferred due to its advantages of low volatilization and easy operation. However, few works have been reported regarding the preparation of UF membranes using the colloidal sol route (Zhang et al., 2017).

A variety of nanoparticles such as ZrO_2 (Zhai et al., 2006), Al_2O_3 (Widjojo et al., 2008), and TiO_2 (Li et al., 2016) are directly blended with dope solutions, which are known a simple and useful route to prepare a hybrid membrane.

Titanium oxide is commonly used as additive for making mineral membranes because it has a very good resistance to acids (HCl, HNO_3, H_3PO_4 …) and bases (NaOH, KOH …). On the other hand, the role of TiO_2 is to adjust permeability and increase the hydrophobicity of the membrane. (Leong et al., 2014).

According to this point of view, we have focused on the development of low-cost inorganic membranes presenting as interesting feature their low-cost. In a previous work (Bouazizi et al., 2017), obtained a UF membrane by depositing a TiO_2 layer by spin-coating on a ceramic support made from bentonite and micronized phosphate. The resulting membrane was successfully tested to filtrate Direct Red 80 solutions.

Another approach is reported in this paper. To this aim, a bentonite MF support was used to develop an UF layer made of nano-TiO_2 particles in aqueous media by using the colloidal solution destabilization technique. The thin-layer of nano-TiO_2 was deposited by dip-coating method. Then, the separation performance of resulting membrane was investigated by soluble dyes removal (Direct Red 80, Acid Orange and Methylene Blue). In addition, various operating conditions such as pressure and feed concentration were studied.

2. Experimental

2.1. Membrane preparation

2.1.1. Raw materials

Bentonite was collected from Nador (Morocco). The raw material was dried in the stove at 100 °C for 24 h, grinded in a ball mill and sieved through a sieve of 45 μm. The chemical analysis of the raw bentonite showed that siliceous (SiO_2) and aluminous (Al_2O_3) material are the most significant components of bentonite. The montmorillonite is the major mineral compound of the bentonite. The characteristics of raw bentonite powder were detailed in our previous paper (Bouazizi et al., 2016).

Anatase Titanium (IV) oxide nanoparticles (TiO_2, ≥ 99.5% purity), with a nominal average diameter of 21 nm and 65 m^2/g of surface area and cetytrimethylammonium bromide ($C_{16}H_{33}N$ $(CH_3)_3$ Br) (CTAB), were used as acquired from Sigma–Aldrich without further purification. Poly-vinyl alcohol (PVA), 99% was acquired from Prolabo.

The soluble dyes used for filtration test were Direct Red 80 (DR 80), Acid Orange 74 (AO 74) and Methylene Blue (MB); and they were acquired from Sigma-Aldrich. Fig. 1 shows the chemical structures of these tested dyes.

2.1.2. Bentonite support

The ceramic support used in this work, as a basis to deposit an UF layer, is made from natural bentonite by pressing method followed by sintering at 950 °C (Bouazizi et al., 2016). The characteristics of bentonite support are described in Table 1.

2.1.3. Preparation of the nano-TiO_2 membrane

The UF layer was prepared from nano-TiO_2 powder by a dip-coating process at room temperature. The colloidal solution was prepared by dispersing of 3.00 g of nano-TiO_2 in 66.00 g of deionized water. Then, 0.05 g of CTAB added as surfactant. The mixture was stirred for 2 h using magnetic agitation and followed by 30 min of ultrasonic treatment. 1 g of nitric acid (2 M) and 30 g of PVA solution (12 wt% aqueous solution) were added under strong stirring to the mixture as peptizing agent and binder respectively. Finally, the resulting dispersion was exposed again to ultrasonic radiation during 15 min followed by 30 min of rigorous stir before use.

One face of flat bentonite support was polished by abrasive paper in order to obtain a smooth surface and then cleaned by distilled water. The other face of the support was covered by Teflon paper. And then support was vertically dipped into the colloidal solution for coating during 30 min. After retracting back, the resulting membrane was finally dried for 24 h at 80 °C and thermally treated. The thermal program applied was essentially composed by the plateau of 2 h at 300 °C to eliminate completely PVA, and sintering step at 750 °C during 3 h. A 0.5 °C/min heating rate was used between plateaus to prevent the formation of cracks.

2.2. Membrane characterization

Several characterization techniques were used to determine the characteristics of prepared nano-TiO_2 UF membrane.

A microscopic analysis was performed using a Quanta 200 FEG Environmental-SEM (FEI Company, USA) for imaging the surfaces of resulting nano-TiO_2 membrane.

The surface roughness is one of the most important characteristics of ceramic membranes. It influences the adsorption/desorption of species on the membrane surface and therefore affects its clogging. For the case of hydrophilic membranes, there is a close relationship between membrane surface characteristics and fouling (Bouazizi et al., 2017; Madaeni et al., 2013). On the other hand, pure water flux increases when roughness increases, due to a corresponding increase of surface area of the asymmetric membrane (Vatanpour et al., 2012; Peng et al., 2004). For this reason determining the surface roughness becomes necessary. Atomic Force Microscopy (AFM) was employed to study the surface roughness of the elaborated UF membrane. A Mobile AFM microscope from Nanosurf (Switzerland) was used, with 133 kHz resonant frequency. Small squares of the membrane (approximately 1 cm^2) were cut and glued on a glass substrate.

The pore size distribution of the membrane was obtained by N_2 adsorption-desorption experiments at a temperature of 77 K (TristarII 3020, Micromeritics, USA). To validate these results, they were compared with image analysis of the ESEM membrane surface pictures performed by using ImageJ software.

Hydrophilicity is one of the most important properties of the nano-TiO_2 membrane which influences its flux, its resistance to become fouled. A membrane with lower water contact angle deliberately manifests better hydrophilic properties (Shokri et al., 2016; Wang et al., 2016) and presents lower fouling degrees for similar experimental conditions. This hydrophilicity of membrane is generally expressed in terms of the contact angle for a water drop on the membrane surface. Therefore, the hydrophilicity of our membrane was investigated by contact angle measurement (PGX, Thwing-Albert Instrument Co.) by using the image analyzer software provided with the device. After three