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Heavy metals and color retention by a synthesized inorganic membrane

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Abstract   In this study, a new type of a double-layer ceramic membrane was used for the filtration of wastewater. The synthesized membrane consists of a macroporous substrate (with pore size of about 0.1 μm) prepared following the colloid filtration technique and a thin film functional layer (with pore size of about 10 nm) carried out according to the sol–gel preparation method.

The ceramic membranes were tested for the removal of cadmium, zinc, Methylene Blue and Malachite Green from water under a pressure of 5 bar and a treatment time of 2 h. Liquid filtration and flow tests through these membranes resulted in a rejection rate of 100% for Methylene Blue and Malachite Green. This paper also presents the ability of the tubular membrane prepared to separate heavy metals (cadmium and zinc) from their synthetic aqueous solutions. The influence of the applied pressure, feed solute concentration, feed pH on the rejection of cadmium and zinc ions was studied. Retention rates of cadmium and zinc ions of 100% were observed for an initial feed concentration of 10^{-4} mol/L.

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1. Introduction

In recent years, there has been a growing concern about environmental issues and specifically about the presence of dyes and heavy metals in water.

The treatment of industrial wastewater containing heavy metals is a major concern because of their high toxicity (Hestekin et al., 1998; Seiler et al., 1988). The separation of dyes from industrial effluents is one of the most important

environmental concerns (Gonzalez-Mǔnoz et al., 2006; Vieira et al., 2001). Increased awareness on the toxicity of metals prompted the implementation of strict regulations for their disposal. Several physicochemical techniques have been used for the removal of contaminants such as cadmium and zinc including: straining, sedimentation, impaction, interception, adhesion, chemical adsorption, physical adsorption, flocculation, and biological growth (Xu et al., 1999; Zollinger, 1987; Ghezzi et al., 2008; Drew et al., 2006; Polat and Erdogan, 2007; Cioffi et al., 1996). Zinc and cadmium ions are toxic pollutants, which are released into the environment through a variety of industrial operations. They exhibit a long environmental persistence and bioaccumulation in living organisms with the potential to cause kidney and liver damage and blood (Monser and Adhoum, 2002; Van der Bruggen et al., 2001a,b; Ritchie and Bhattacharyya, 2002). Membrane filtration has received considerable attention for the treatment of inorganic effluents,

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since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals as well.

On the other hand, industries such as textile, paper, and plastic industries release colored matter to water bodies often without treatment.

Membrane technology had gained its popularity in dye and metal separation by ultrafiltration, nanofiltration and reverse osmosis (Strano et al., 2002; Song et al., 2006; Tan et al., 2001; Belouatek et al., 2008). Industrial applications of porous ceramic membranes with their various advantages, such as better thermal, chemical and mechanical resistance, controllable micro-structure and little pollution to our environment, have been attracting much attention in the scientific community recently (Belouatek, 1998; Belouatek et al., 2005).

In recent years, mineral-based porous ceramic membranes have been considered for their low costs and additional functions. Tubular ceramic membranes with good performance parameters, such as Permeate flux and filtration efficiency can be obtained by using an asymmetric configuration in which different layers are coated on a porous support that offers sufficient mechanical strength and thermal shock resistance, which is desirable for hot gas filtration application (Belouatek, 1998; Belouatek et al., 2005; Ezziane et al., 2010). Transport properties of the ceramic membranes are significantly influenced by the composition of the treated solution. Cations such as mercury (Hg^{2+}), cadmium (Cd^{2+}), zinc (Zn^{2+}) and lead (Pb^{2+}), and anions such as nitrate (NO_3^-) and chromate ($Cr_2O_7^-$) can be easily removed via facilitated transport (Elmaleh and Naceur, 1992; Mulder, 1996).

In this work, the feasibility of a new ceramic membrane synthesized for ultrafiltration application was investigated. The main objective of this study was to evaluate the ability of the prepared membrane to separate polluting substances (dyes and heavy metals) from wastewater.

2. Materials and methods

The tubular support was synthesized from high purity kaolin. Tubular supports were prepared in the laboratory by the extrusion method. A powder of oxide was mixed with kaolin powder (particle size 0.1–0.2 μm) and then with water in the proportion of 30–35% of the powder weight. The kaolin barbotine had a 65–75 centipoise final viscosity as measured by a torsion Gallenkamp viscometer.

After mixing, the obtained kaolin barbotine was put in plaster molds. The plaster was then extruded to obtain a tubular support of 4 mm internal diameter and 30 cm length. After drying, the support was sintered at 1373 K for consolidation (Belouatek et al., 2005, 2008; Belouatek, 1998; Ezziane et al., 2010).

A microfiltration layer consisting of an intermediate mixture of 50% kaolin and 50% ZrO_2 was then coated on the ceramic support before depositing the final sol–gel layer. This intermediate layer allows the membrane to be maintained without infiltration into the support and serves to bridge the gap between the macroporous support and the ultrafiltration layer. After firing the assembly at 1373 K for 2 h, a double layer support named (DLS) with a mixture layer of 0.1 μm pore diameter and a thickness of 10 μm was obtained.

To improve the membrane performance, a thin layer of alkoxide (98% tetraethylorthosilicate) was added onto the DLS

support to obtain a ceramic membrane named activated double layer support (ADLS). The third layer was prepared via a dip coating technique from colloidal boehmite nanoparticle suspensions synthesized with the alkoxide prepared. Hydrolysis was followed by peptization under acidic conditions. The slip-casting procedure was followed by drying and calcination at a temperature of 753 K.

Filtration was of tangential type under an applied pressure of 5 bar (Belouatek et al., 2005, 2008; Belouatek, 1998; Ezziane et al., 2010). The feed colored solutions were prepared from Malachite Green (MG) and Methylene Blue (MB) of analytical grades. The rate of retention (R (%)) = $1 - C_P/C_o$ where C_o is the initial solution concentration and C_P the concentration in the filtrate) of the colored solution was measured by visible spectrophotometry (Optizen 120 UV). The maximum wavelength at λ_{max} = 615 nm and λ_{max} = 665 nm for MG and MB, respectively (Khattri and Singh, 2009; Mukerjee and Gosh, 1970).

The structure and morphology of the ADLS membrane were characterized by scanning electron microscopy (Philips SEM5050 microscope 3000F). The porosity of the samples was calculated by using an AutoporeII 9220 V3.01 mercury porosimeter (down to 3 nm pore diameter). The thermal stability of the membranes was determined by thermogravimetric analysis (TGA) using a (Setaram–setaram) thermogravimeter. Phases present in the mixture of 50% kaolin and 50% ZrO_2 (raw powder and heated to 1373 K) were analyzed using an X-ray diffractometer (Siemens, Germany) with $CuK\alpha1$ radiation (λ = 1.54056 Å).

3. Results and discussion

3.1. Thermal analysis

Thermal analysis was used to determine the weight changes within the membrane as a function of temperature. Calcination has great influences on the structure and permselectivity of the DLS and ADLS membranes. In order to establish an efficient heat treatment procedure, the modified membrane support powders were examined by thermogravimetric analysis as shown in Fig. 1.

The measurement was carried out under air in the temperature range of 293–1273 K with a heating rate of 283 K/min. The thermogravimetric analysis curve of membrane powders showed that the total weight loss was about 2.5% and
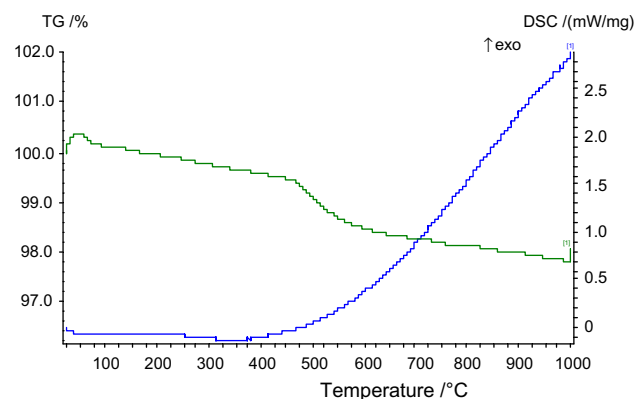

Figure 1 Thermogravimetric analysis of DLS membrane.

occurred in three steps, (1) 0.5% weight loss at 323–423 K arising from water desorption, (2) 0.5% weight loss at 423–673 K arising from combustion and decomposition of the material and (3) 1% weight loss at temperatures above 753–853 K arising from the allotropic transformation of silica quartz from an alpha to beta phase.

3.2. Phase identification

X-ray diffraction was used to identify the formed phases. For kaolin mixed with 50 wt.% ZrO_2, raw powder, the main observed phases are: kaolinite (K), muscovite (M) and quartz (Q) as shown in Fig. 2(a). However, for samples sintered at 1373 K, the kaolinite phase disappeared Fig. 2(b). It shows that the mullite phase (M) is the main crystalline mineral present in this powder, and zirconia (monoclinic system) was detected as a minor phase. Moreover, this means that the porosity is independent of the formed phases. These identified phases are of great importance because of their promising physical and mechanical properties.

3.3. Microstructures

Fig. 3 shows the scanning electron micrographs for the surface and cross-section of the synthesized DLS, calcined twice. The SEMs recorded at the 10 kV voltage and amplification × 20000 show a rough surface, with an average pore size of about 10 nm (Fig. 4).

The pore size distribution of the ADLS layers versus pore diameter is represented in Fig. 5.

3.4. Filtration tests

The performances of the DLS and ADLS membranes were mainly evaluated by water flux (F) and rejection rate (R) of solutions, using a pilot filtration unit described elsewhere (Belouatek et al., 2005, 2008; Belouatek, 1998; Ezziane et al., 2010).

3.5. Study of distilled water permeability

The permeability characterizes the quantity of water per time and unit area which crosses the membrane at a given pressure and temperature. Membrane permeability was determined using distilled water.

Fig. 6 shows the variation of flux values of distilled water for DLS and ADLS membranes as a function of pressure. It can be observed that permeate flux increased proportionally with pressure.

The results revealed that ADLS membrane fluxes were lower than those obtained using the DLS membrane.

The water flux varies linearly with the pressure drop in accordance with Darcy's law. The water permeability as computed from the slope of the curve at a pressure of 6 bar is 820 L/h m^2 for the DLS membrane whereas for the ADLS membrane it is 260 L/h m^2.
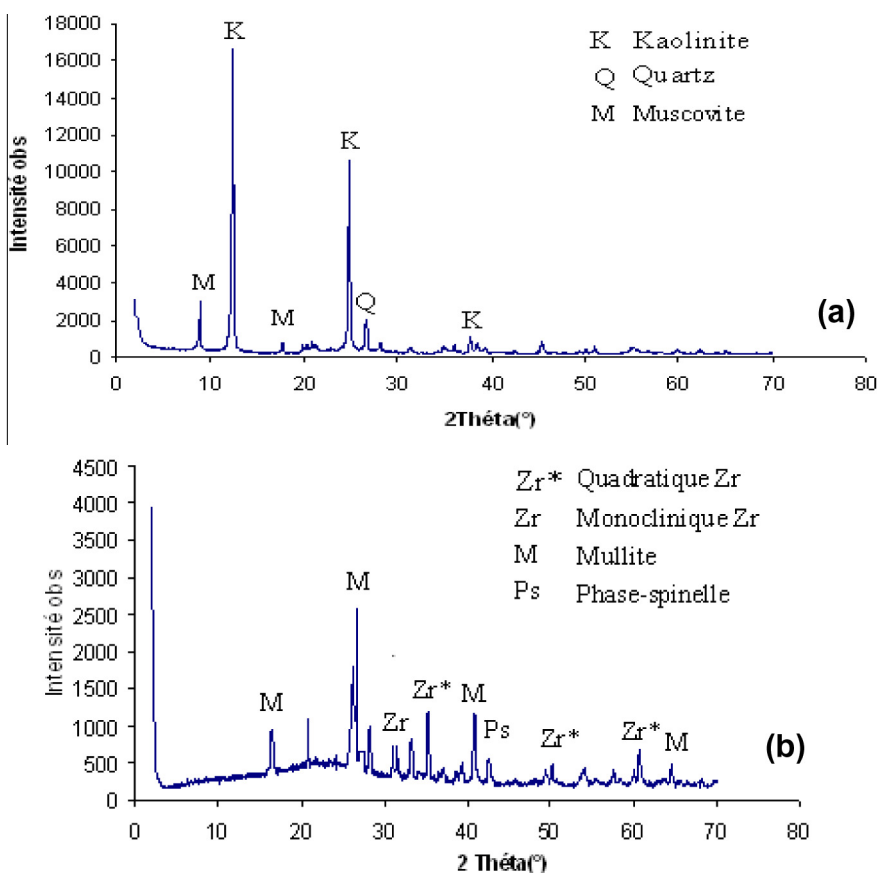

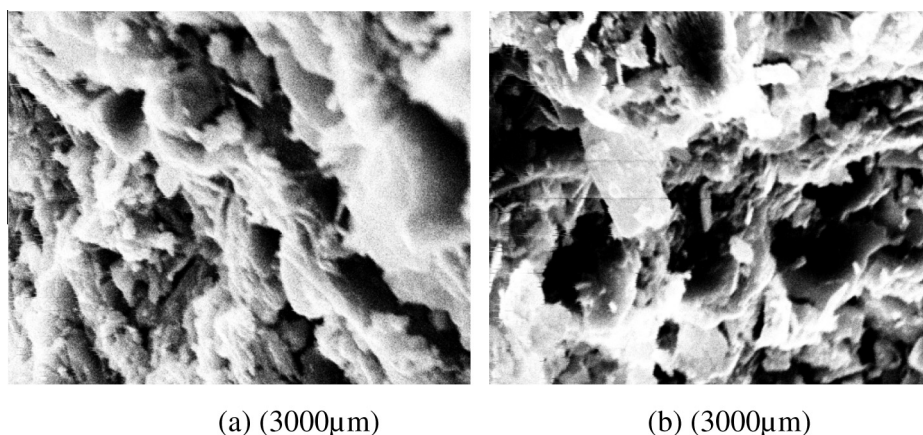**Figure 2** X-ray diffractogram of the mixture of kaolin and 50% ZrO_2 (a) raw powder; (b) heated to 1373 K.

(a) (3000µm)   (b) (3000µm)

Figure 3   SEM images of DLS layer formed on kaolin with: (a) surface section; (b) cross-section.

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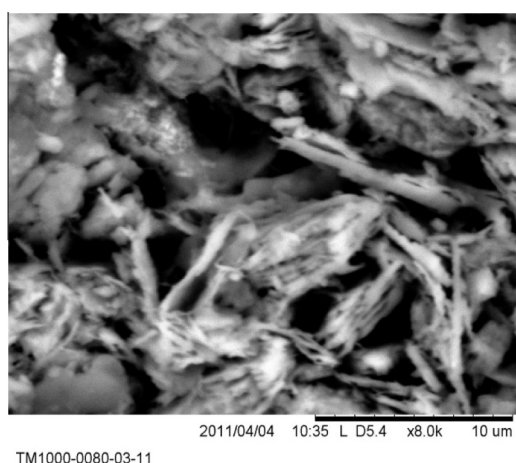
Figure 4   SEM images of ADLS layer surface section.

Figure 6   Flux of water permeates versus the pressures of ADLS and DLS.

g/mol) and Methylene Blue ($C_{16}H_{18}ClN_3S$; MW = 319.86 g/mol)).

The removal of cationic dyes Methylene Blue (MB) and Malachite Green (MG) from their aqueous solutions is depicted in Figs. 7 and 8.

The retention of organic molecules by membranes depends not only on the molecular size, but also on the charge interactions between membrane and solution. Depending on the nature of the membrane (charge), a higher or lower retention rate can be obtained than expected on the basis of molecular weight or any other size parameter. Significant differences between membranes exist due to the influence of charge, which is small for membranes with small pores but can be important when the pore sizes are larger. When the pores are very large, charge effects can be the decisive factor in determining the retention of highly charged membranes. These effects are important for applications such as the removal of dyes from wastewater.

The present results showed that the ADLS membrane has a high rejection for dyes and the rejection rate depends on membrane pore diameter, interaction between solute ions and material charges, and solute molecular weight. For the DLS membrane the retention for Malachite Green attained 100% in 30 min of treatment and began to decrease gradually afterward.

For the ADLS membrane, the maximum retention of 100% for Methylene Blue was observed while for the solution of
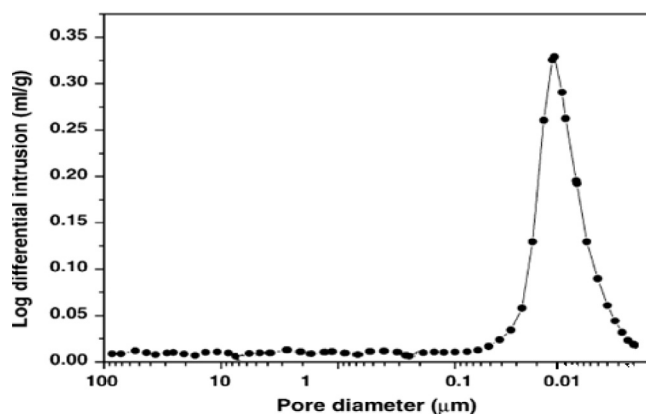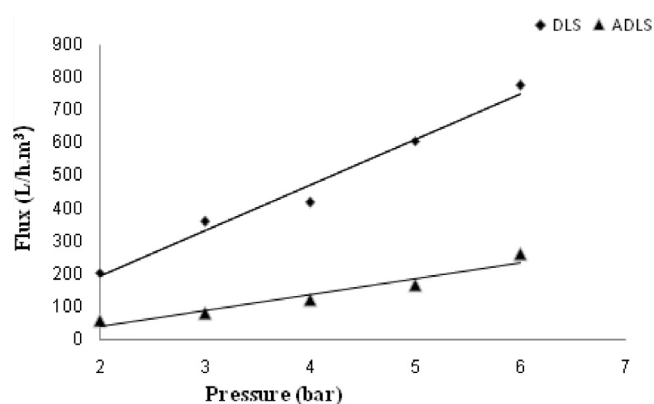

Figure 5   The pore size distribution of ADLS layer.

4. Retention rate of dyes

The synthesized dye solutions (5 L) of concentration 10^{-4} mol/L were filtered tangentially for 2 h under a pressure of 5 bar.

The ADLS membrane was evaluated by analyzing the rejection rate of the 10^{-4} M colored solutions of varying dye molecular weight (Malachite Green ($C_{23}H_{25}ClN_2$; MW = 364.91
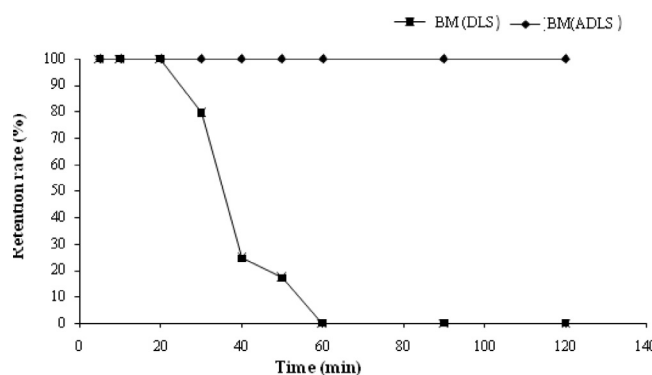
Figure 7 Retention rate of Methylene Blue solutions (10^{-4} M) versus time of the DLS and ADLS membranes.

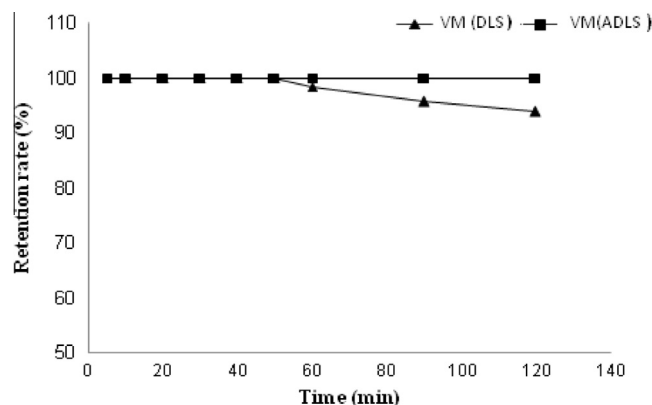**Figure 8** Retention rate of Malachite Green solutions (10^{-4} M) versus time of the DLS and ADLS membranes.

Figure 9 Retention rate of cadmium by DLS and ADLS membranes.
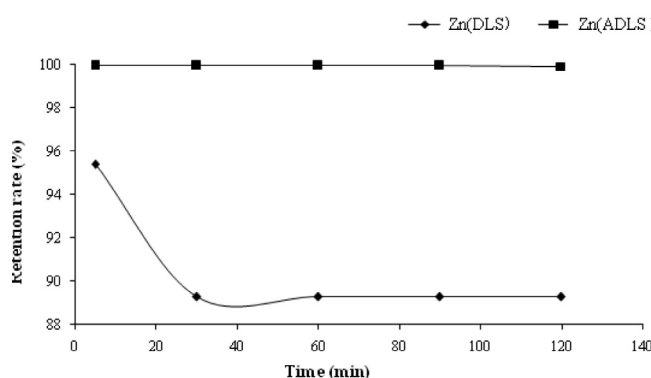
Figure 10 Retention rate of zinc by DLS and ADLS membranes.

Malachite Green a retention rate of 100% was reached after one hour, the rate decreased to a value of 98% afterward.

The results indicate that dye rejection is mainly determined by charge interactions. Therefore higher rejection of cationic dyes is due to higher charge repulsion of Cl^- with the charge present on the membrane surface. In multi-component solutions, interactions between different components may cause a bias in the results. Due to the positive charges in Methylene Blue and Malachite Green a high retention was obtained for these molecules. This is due to Donnan exclusion of the negatively charged molecules of Cl^- from the membrane, which is also negatively charged at this pH value. Similar observations were reported by different authors (Saffaj et al., 2004a,b; Broussous et al., 2001; Van der Bruggen et al., 1999; Akbari et al., 2002).

On the other hand, these phenomena are attributed to the fact that the dye accumulation on membrane surface increased with operating time. The layer formed by the rejected dyes on the membrane surface may operate as an additional resistance to the Permeate of dyes (Koyuncu, 2002). Therefore, the permeate flux decreased and rejections increased as the operating time elapsed.

5. Heavy metals removal

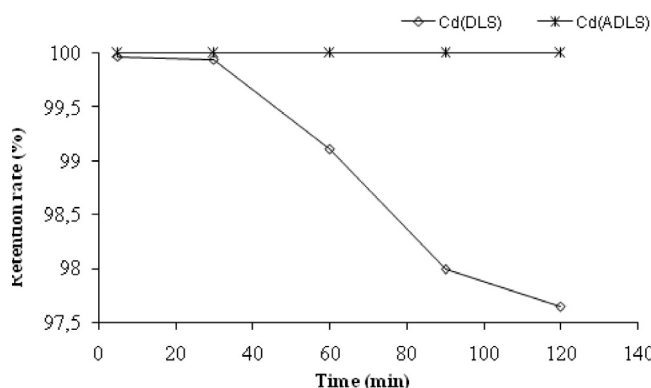The performance of the DSL and ADLS membranes, prepared in our laboratory for the retention of Cd^{2+} and Zn^{2+}, under a pressure of 5 bar, from a 10^{-4} M solution concentration (at a pH of 5.8) is illustrated in Figs. 9 and 10.

Cadmium and zinc amounts in permeate; feed, and retentate water were determined using atomic emission spectrometry (Perkin Elmer 2000).

The retention or rejection rate of cadmium and zinc were very high using ADLS. Retention rate of 100% was attained after few minutes of treatment. The removal of cadmium and zinc is mainly due to the strong interactions developed between Cd^{+2}, Zn^{2+} and the surface of the support. By controlling these electrostatic effects, the effective pore size of ultrafiltration ADLS membrane can, to some degree, be regulated and therefore the separation efficiency of the modified membrane support can be enhanced due to electrostatic exclusion. Adsorption of the Cd^{2+} and Zn^{2+} cations is not expected to occur on the Si–OH groups of the surface at the specific pH conditions, thus the retention efficiency of Si–OH can be mainly attributed to the strong electrostatic repulsion between the positively charged surface and the heavy metal (Zn^{2+} and Cd^{2+}) hydrated cations. The same results in the retention rates ($> 93\%$) were obtained for the separation of heavy metals such as zinc and cadmium elsewhere (Wang et al., 1995, 1997).

In general, it can be concluded that the charge effect is important when the molecules are much smaller than the pore diameters. The membrane charge can increase or decrease the retention because of electrostatic interactions. For multi-component solutions, the interactions become more difficult.

When the molecules have approximately the same size as the pores, charge effects have only a minor importance, as the molecules are mainly retained by a sieve effect (Wang et al., 1995).

6. Conclusion

A new membrane support containing a barrier layer was prepared in this study. The ADLS membranes can be successfully applied for wastewater cleaning applications as they exhibit significant dye and metal retention efficiency by combining, size and charge exclusion and adsorption capacity of membranes.

The prepared membrane exhibited both high flux and retention rates which are suitable for ultrafiltration applications such as separation of dyes and heavy metals from water. The results obtained with the ADLS membrane prepared can be applied to the treatment of liquid effluents.

The flux of the ADLS membrane for dyes was observed to increase greatly with operating pressure and constant rejection rates. Experiments show that the real rejection rate of Methylene Blue, Malachite Green, cadmium and zinc is in the range of 99–100% depending on the membrane used, electrostatic interactions, pressure and concentration of the feed. The ADLS membranes showed the best performance in terms of dye and heavy metal removal efficiency and permeate flux values.

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