



Removal of hexavalent Chromium by Ghassoul Hydrotalcites Membranes (GHTM)

O. Qabaqous^{1*}, M. Naciri Bennani^{1*}, N. Tijani², H. Ziyat¹, S. Arhzaf¹

¹ Laboratory of Chemistry-Biology applied to the environment, Moulay Ismail University, Faculty of Sciences, B.P11201, Zitoun Meknes 50000, Morocco.

² Laboratory of Applied Mineral Chemistry, Moulay Ismail University, Faculty of Sciences, B.P11201, Zitoun, Meknes 50000, Morocco.

Received 23 Sep 2017,

Revised 04 Feb 2018,

Accepted 10 Feb 2018

Keywords

- ✓ Adsorption,
- ✓ Hydrotalcites,
- ✓ Membrane,
- ✓ Microfiltration,
- ✓ Chromium.

mbennani@gmail.com;

Phone: +212660210077;

gomar2010@gmail.com;

Phone: +212676597291;

Abstract

In the present work, the characteristics of low cost Ghassoul Hydrotalcites Membrane (GHTM) for rejection of Cr (VI) was examined. We have prepared the clay ghassoul which is used as a support for membrane (GHTM). The mesoporous support was prepared from a ghassoul clay powders mixed with some organic additives. After sintering the support at 900°C, it showed a porosity of 38%. The GHTM is obtained by forming of the magnesium aluminium hydrotalcite layer HT-MgAlCO₃ with a molar ratio equal to 3 ($Mg^{2+}/Al^{3+}=3$) on the surface of the support. The properties of the ghassoul clay supports, HT-MgAlCO₃ powders and GHTM were characterized by XRD, SEM, BET and water flux permeation. The ability of GHTM to remove the ion chromium from synthesized solution with a concentration of 10⁻³ mol/L was investigated. The microfiltration tests by using the GHTM showed that the rejection reached 98% after 3 hours of filtration at 1bar and room temperature.

1. Introduction

Ceramic membranes have several advantages such as resistance to corrosive environments, high thermal chemical stability, pressure resistance, good resistance to fouling, and mechanical strength [1-5]. The ultrafiltration (UF) and microfiltration (MF) operations are often used to remove particles, microorganisms, and colloidal materials from suspensions [6]. Additionally, the production of industrial membranes provides a limited choice of materials. As a consequence, the price of ceramic membranes is high, and a significant effort has been expended in order to develop new porous ceramic materials by using inexpensive clays and kaolin. These materials are in abundance and require sintering temperature lower than those of metal oxide materials [7,8]. The application of membrane has interest for the researchers, thanks to their potential for treatment of large quantities of drinking water and waste water.

Hexavalent chromium Cr(VI), is present in the waste water, effluents of electroplating, leather tanning and several other industries. It is highly toxic can be detrimental to a variety of species, may be in the form of dichromate Cr₂O₇²⁻ hydrogen chromate HCrO₄⁻ or chromate CrO₄²⁻ in solutions at different pH values [9]. Therefore, the elimination of this metal is important to protect public health. There are various processes to treat Cr(VI) contaminated water such as precipitation, solvent extraction photo-extraction, reverse osmosis, electro-dialysis, and adsorption onto activated carbon. Membrane separation is one of the alternative treatments for removal of heavy metals ions from aqueous solutions [10-14]. Both microfiltration (MF) and ultrafiltration (UF) have been used for concentrated chromium, as they are highly efficient and do not require chemical additives, and are more economical compared to conventional separation techniques[15].

One of the powerful treatment processes for the removal of metal ions from water with a low cost is adsorption. It is reported that the ceramic supports, formed by extrusion of a ceramic paste of kaolin and calcium carbonate mixtures, were used for MF and also used as a support for UF and Nano-Filtration (NF) membranes [16]. Anbri Y. et al. [17] synthesized silicalite membranes on a Moroccan clay support that present an attractive porosity. They reported that the use of these membranes in environment depollution can be an alternative to current technologies by their low price. Saffaj N. et al. [18] developed a low cost membrane support made from Moroccan clay. This clay low cost support is used to support different ultrafiltration or nanofiltration layers, such as TiO₂/ZnAl₂O₄, for economic treatment of waste water containing toxic compounds.

In this research, we have used the hydrotalcite HT-MgAlCO₃ (anionic clay), which has the advantage of being modified by synthesis, in the elaboration of the ghassoul hydrotalcite membrane (GHTM). This membrane was investigated for removal of Cr(VI) ions from aqueous solution which is highly toxic and harmful to living organisms due to its carcinogenic and mutagenic properties.

2. Material and Methods

2.1. Materials

The clay samples used in this study is a commercial ghassoul (ghassoul Chorafa Al Akhdar), it was obtained in powdered form, which is used in their natural state without any chemical treatment. The obtained powder is dried at 100°C to eliminate loosely bound water. The particles sizes, of the natural ghassoul clay powder used to prepare flat-disk are in the range of 250-315µm using sieves standardized according to AFNOR. The clay powder was characterized in elsewhere paper [19] by different methods: X-ray fluorescence, XRD, DTA/GTA, BET and IR analysis.

2.2. Synthesis of GHTM

In the first, the Plane supports (40 mm in diameter, 2mm in thickness) were elaborated by application of uniaxial compaction technique of a powder mixture (Moroccan ghassoul clay and 3% of activated carbon using as organic additive). The obtained plane supports were heat and treated in electrical furnace, according to the following heating program represented in figure 1.

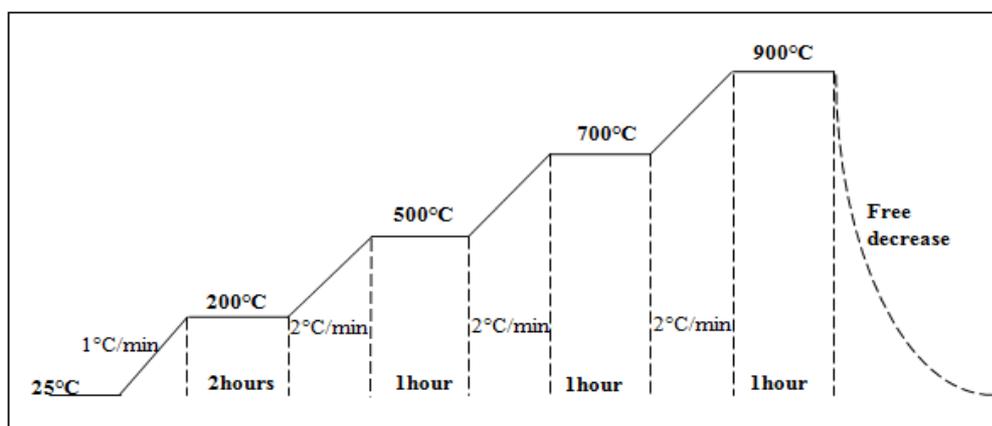


Figure 1 : Heating program of sintered supports

One side of the support was polished with 600 grit-sand papers to obtain a smooth surface. After that, it was washed with deionised water to remove lost particles created during polishing. Next, it was dried at 60°C for 48 hours. Finally, the polished face of the substrate was coated with hydrotalcites (MgAl-CO₃) solution consisting of aluminium magnesium mixed hydroxide.

The deposition of the hydrotalcite phase on the ghassoul clay support was carried out by co-precipitation method. For this purpose, a mixed aqueous solution of AlCl₃.6H₂O and MgCl₂.6H₂O of molar ratio Mg²⁺/Al³⁺ (ratio=3) and an aqueous solution containing NaOH (2.5 M) and Na₂CO₃ (0.05 M) were added slowly on the ghassoul clay support placed horizontally into a beaker containing distilled water under stirring at room temperature. The mixture is then brought to 70°C for 18 h until the solid crystallized completely on the surface of the support. Based on the results reported by [20, 21], the pH being kept constant at 10 in the experimental time. The prepared GHTM was washed several times with deionized water and dried at 100°C for 4 h.

The product precipitate was filtrated and washed at two times in the filter with worm water to remove excess ions (Cl⁻, Na⁺...). The prepared material was dried at 105°C for 18 h, then ground and sieved to obtain the compound HT-MgAlCO₃.

2.3. Characterization techniques

2.3.1. Chemical stability

The chemical resistance (corrosion resistance) of the fabricated support was characterized in a weight loss before and after etching with a concentrated solution of HNO₃ and NaOH. All these quantitative experiments were carried out for the ghassoul clay support prepared for evaluation of their filtration capacity of discharges liquid in acidic and basic environments.

2.3.2. XRD analysis

X-ray diffraction (XRD) patterns of the powders of ghassoul clay support, GHTM and HT were carried out at room temperature on a Philips instrument, using CuKα (λ=1.5406Å) radiation. The diffraction data were recorded in the 2θ range of 5-70° with a step of 0.04° at 40 kV and 20 mA.

2.3.3. Textural characterisation

The textural characterization of the powders ghasoul clay support and GHTM was based on the N₂ adsorption/desorption isotherm, using a Micromeritics Asap2010. In the first, the sample was degassed at 373K for 3h prior to measurement. The specific area was calculated by the BET model. According to the BJH approach, the pore size distribution and the total pore volume were determined at a relative pressure (P/P₀) of 0,99.

2.3.4. SEM analysis

The surface morphologies of the ghasoul clay support and GHTM were monitored by scanning electron microscope (SEM) by using a Zeiss Sigma instrument at 3KeV acceleration voltage.

The membrane sample was analyzed by SEM images of both surfaces of the ghasoul clay support and support with HT-MgAl-CO₃ layer.

2.3.5. Pure water permeation

The permeation experiments of the water through the ghasoul clay support and GHTM were carried out with distilled water using a filtration system consisting of a stainless steel cell sealed by an O-ring facing the feed stream. A porous stainless steel disc was placed under the clay support to prevent cracking under pressure about 1bar. The water flux (L.h⁻¹.m⁻²) was measured at various times by the following equation: $F = \frac{V}{A \cdot t}$

Where V is the volume of the permeated distilled water (L) in time period t (h), A is the effective area of the membrane (m²), which is 8.04x10⁻⁴ m² in this case.

2.3.6. Surface chemistry characterization

The determination of the isoelectric point (IEP) of the GHTM membrane was done by preparing 12 closed flasks which contain 50cm³ of NaCl (0.01M) [22] After, we fixed pH at a value between 2 and 12 by adding HCl (0.1M) or NaOH (0.1M) solutions. Subsequently, 0.15g of GHTM powder sample was added to every flask under agitation at room temperature. After 48hours we measured the final pH. The pH_{IEP} is the point where the pH (initial) =pH (final) which in our case resulted at pH=10.9.

2.3.7. Filtration of heavy metal

The experiments were carried out with synthetic ionic solution of CrO₃, The concentration of the solution was fixed at 100mg/L. The microfiltration of hexavalent chromium which is in the feed solution was processed with the membrane GHTM, and the resulted permeate stream samples were analyzed by molecular absorption spectrometry by using a UV visible Spectrophotometer SHIMADZU UV 2100 from 200 to 800 nm. The retention rates were estimated by the following simple relation:

$$R = \frac{(C_f - C_p)}{C_f} * 100$$

Where C_f and C_p are ions concentrations in the feed and permeate solutions, respectively.

3. Results and discussion

3.1. Test of porosity

Porosity of the ghasoul clay supports sintered at temperature of 900°C is calculated by using the Archimedes principle [23].

At the beginning, the dry mass M_d of the membrane was determined after drying the membrane in the oven at 110 °C for 6 hours. The membrane is then placed in a beaker filled with distilled water. After 24 hours, the membrane is recovered and its wet mass M_w is measured. The porosity (p) of the membrane was calculated using the following relation:

$$p = \frac{M_w - M_d}{M_w} * 100$$

According to equation, we found its porosity reached 39% for the ghasoul clay support, which is important in fabrication of the suitable membranes and to the great mass deposition on the support.

3.2. Chemical resistance

Chemical resistance tests were performed by using 100 mL of HNO₃ and 100 mL of NaOH solutions to check the chemical stability of the ghasoul clay support. The support was placed in the above corrosive environments at room temperature for 24H with stirring at room temperature. Corrosion resistance of the prepared support was analyzed in a terms of weight loss estimated from the value Δm %.

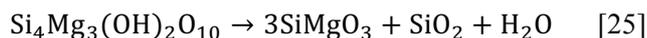
The obtained results revealed that the prepared support shows greater corrosion resistance in both environments acidic and basic. The values of weight loss are 1.3 and 4.3% for acid attack HNO₃ 0.5N and 1N, respectively. For basic attack with NaOH 0.5N and 1N, these values are between 0.5 to 2.3%, respectively. Hence, this support can be utilized for the membrane processes at all pH ranges.

3.3. XRD analysis

The behavior phase transformation of the ceramic support before and after sintering was identified by XRD analysis as displayed in figure 2.

The XRD pattern of raw ghassoul clay showed that the dominant phase is the stevensite with the presence of quartz and dolomite [24].

The phase transformation occurs during the sintering process, resulting in the formation of new phases that were identified by shifting of XRD peaks positions. After sintering of the sample, all the peaks in the patterns due to stevensite disappear; this is due to the transformation of stevensite to enstatite (E). This transformation can be represented by the reaction:



On the contrary, the peaks of quartz and dolomite do not change which confirms the thermal stability of this phase. That means the stevensite phase is only concerned by the thermal treatment. Which confirms the compatibility with the results of DTA/TGA published in elsewhere paper [19].

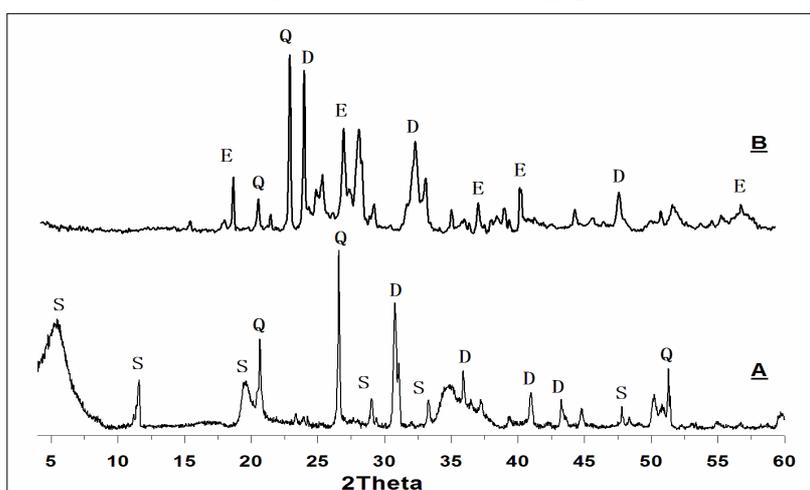


Figure 2: XRD patterns of A) before sintering and B) after sintering at 900°C

3.4. Characterization of the GHTM

3.4.1. XRD analysis

For comparison, we also present in figure 3 the XRD pattern of the Hydrotalcite HT-MgAlCO₃ with Mg²⁺/Al³⁺ ratio = 3 obtained during the elaboration of membrane GHTM.

This diffractogram (a) shows the formation of the well crystallized phase Hydrotalcite [26]. The peaks which correspond to basal planes (003) and (006) are present at low 2θ values 11.40° and 22.72° respectively characteristics of lamellar structure for the synthesized sample.

The XRD patterns of the as-synthesized GHTM (b), shows the predominant clay mineral is as follow: Enstatite (E): d=3.32; 4.025 Å, Quartz (Q): d=3.16; 2.98; 3.48 Å and dolomite (D): d=2.87; 2.49 Å. These results are in good accord with the chemical composition of the sintered ghassoul clay support used. The typical diffraction peaks of HT-MgAlCO₃ powders (003) and (006) characteristic for hydrotalcite-like compounds have been observed at d=8.03Å; d=3.86 Å respectively, suggesting the formation of hydrotalcites layer crystals on the surface of the support ceramic.

3.4.2. Textural characterization by nitrogen adsorption/desorption

The nitrogen adsorption/desorption isotherm of the sintered ghassoul clay support, depicted in figure 4, is attributed to the type IV indicating a capillary condensation steps and characteristic of the mesoporous material to accordance of IUPAC classification [27]. The average pore size is 3,5nm as computed by BJH method from the desorption isotherm. The BET surface area and total pore volume are found to be 4,9 m²/g and 0,0247 cm³/g respectively, which are deducted from the amount of N₂ adsorbed at relative pressure (P/P₀) of 0.99. Figure 5 shows the isotherm of powder mixture for GHTM, which can be identified as type IV. The hysteresis loops is similar to the type H3 associated with the slit-shape pore structure composed by plate-like particles. The specific surface area and a total pore volume are 8,19 m²/g and 0,049 cm³/g respectively. These values are more

important than those obtained for the ghassoul clay support but less than those of pure hydrotalcites [28]. This advantageous modification for the filtration process is vraisemblably due to adjunction of Hydrotalcites on ghassoul support.

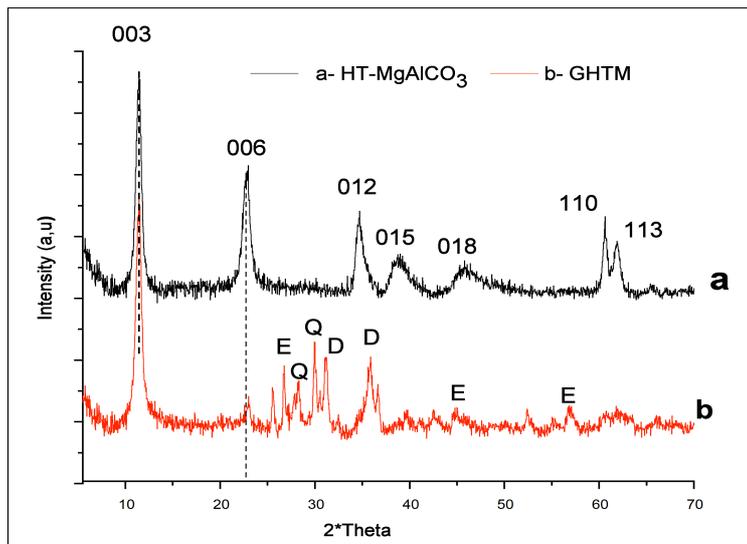


Figure 3: XRD patterns of a) the raw powder mixture for GHTM and b) the obtained hydrotalcites HT-MgAlCO₃.

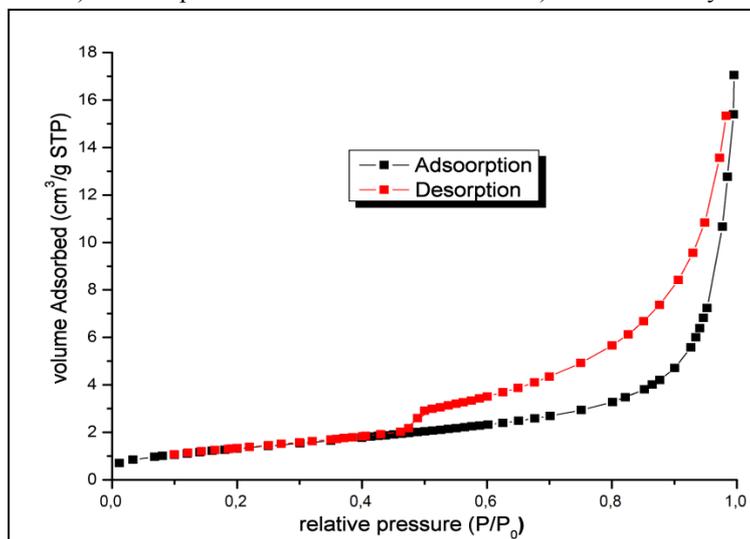


Figure 4: Nitrogen adsorption-desorption isotherm powder of ceramic support

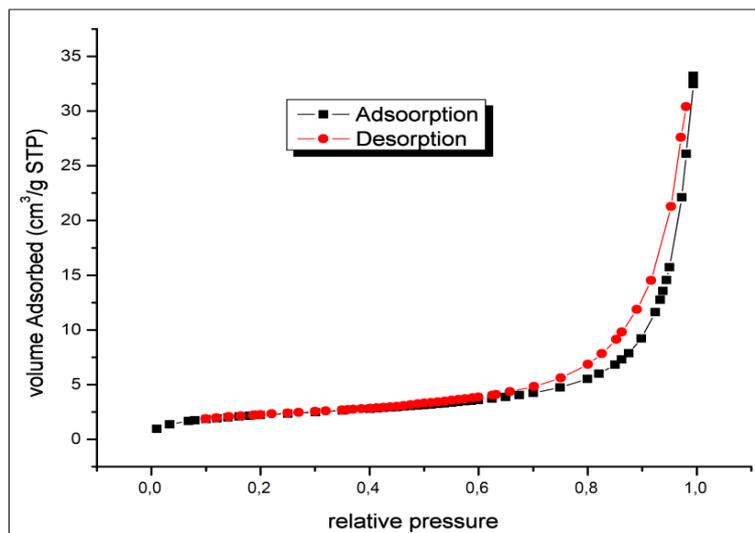


Figure 5: Nitrogen adsorption-desorption isotherm of GHTM

3.4.3. Scanning Electron Microscopy (SEM)

The morphology, surface quality and densification of the sintered ghassoul clay supports and GHTM membrane were followed by Scanning Electron Microscopy (SEM). Figure 6(A) Shows SEM image of the prepared ghassoul clay support. This image gives information on the texture of the surface. We can observe that there are no cracks as well as pinholes on the surface of the supports and that the pores size distribution of the support is uniform and having circularity form, such as selected as substrates for membrane microfiltration [16].

Fig 6(B) shows the surface of the support is covered by a layer of hydrotalcite in the form of laminated sheets, the image demonstrates the crystals are very thin, as some appear semitransparent due to electron beam penetration through the crystal. The crystals appear very flat, which is consistent with the results of XRD analysis of the GHTM [29]. The pores become more closed and the surface more dense. This seems to affect the surface with the possibility of change in the size of pores. The experimental results of water permeation used in flux measurements confirming our observation of SEM photograph.

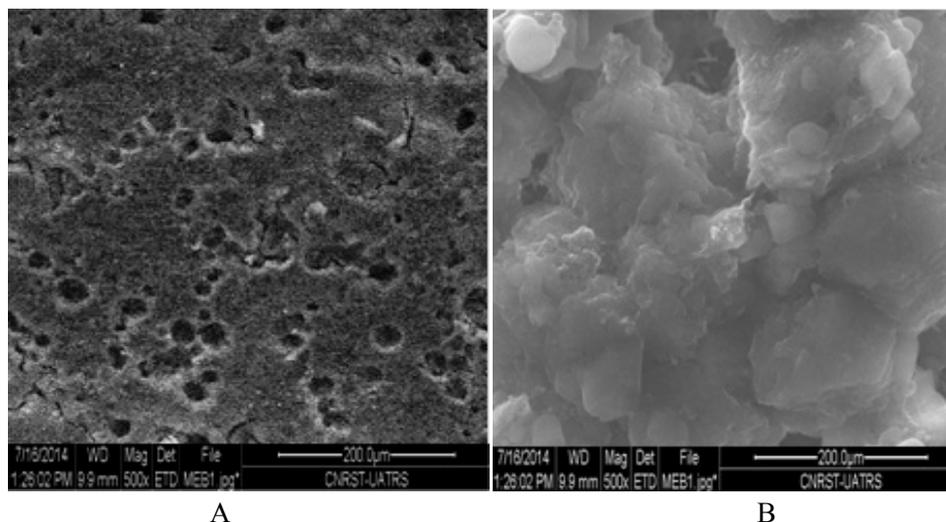


Figure 6: SEM micrographs of the ghassoul clay support (A) and the as-synthesized GHTM (B)

3.4.4. Water permeation measurements

Figure 7 shows the evolution of the permeate flux as a function of the experiment time for the ghassoul clay support and the membrane GHTM under the same conditions of temperature and pressure.

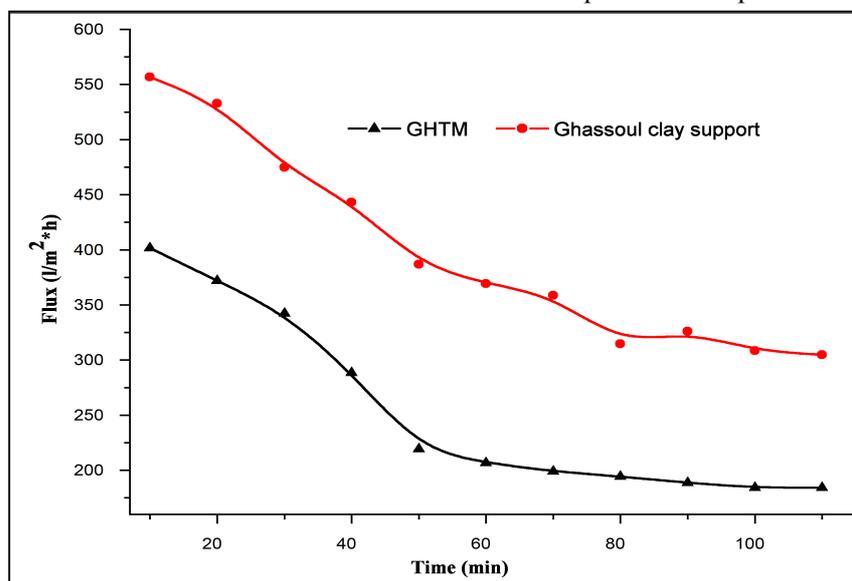


Figure 7: Water flux permeation of the ghassoul clay support and GHTM

When focusing on the permeation flux of the support we can notice a decrease of 65% of the permeate flux during the first 80min of the experiment and stabilize with time around a value of 330L/m².h. In the case of the GHTM, we can observe that the decline of the permeate flux is clearer by the value of 50%, during 50min to stabilize at the value of 221L/m².h. Water flux through the ghassoul clay support is more important than the flux through the GHTM, probably due to the insertion of Hydrotalcite particules in the pores of support, which explains the deposition of hydrotalcite phase on the ghassoul support.

The filtration curves observed with the Ghassoul support and the GHTM membrane (Fig.7) look the same appearance, namely a decrease of the flow at the beginning followed by a stabilization of the latter. This behavior corresponds to a classical dependence of flux with the time characteristic of microfiltration. Daniel et al. [30] and Sybrandus et al. [31] have observed the same decrease of the permeate flux with time for PS-20 UF membrane and polymeric membrane. This was attributed to clogging of the pores.

3.5. Separation of chromium (VI) from aqueous solution

Figure 8 shows the spectra of the permeate stream samples obtained from microfiltration technique operated at pH 5.6 under pressure of 1bar and at room temperature. The figure 8 represents two branches situated at the positions 275nm and 370nm respectively. Both bands gradually drop as a function of time in the range of 30min to 3h. The spectra of the permeate stream samples were obtained in the UV-visible ranges from 240 to 800nm. Wavelengths of 240 to 450 nm were used for analysis and beyond the 450 nm no absorbance was found. Chromium ions show two ranges of resonating wavelengths, viz. 230 to 310 nm where it is independent of the nature of chromium ion, and 340 to 450 nm depending on the nature of the chromium ion [32].

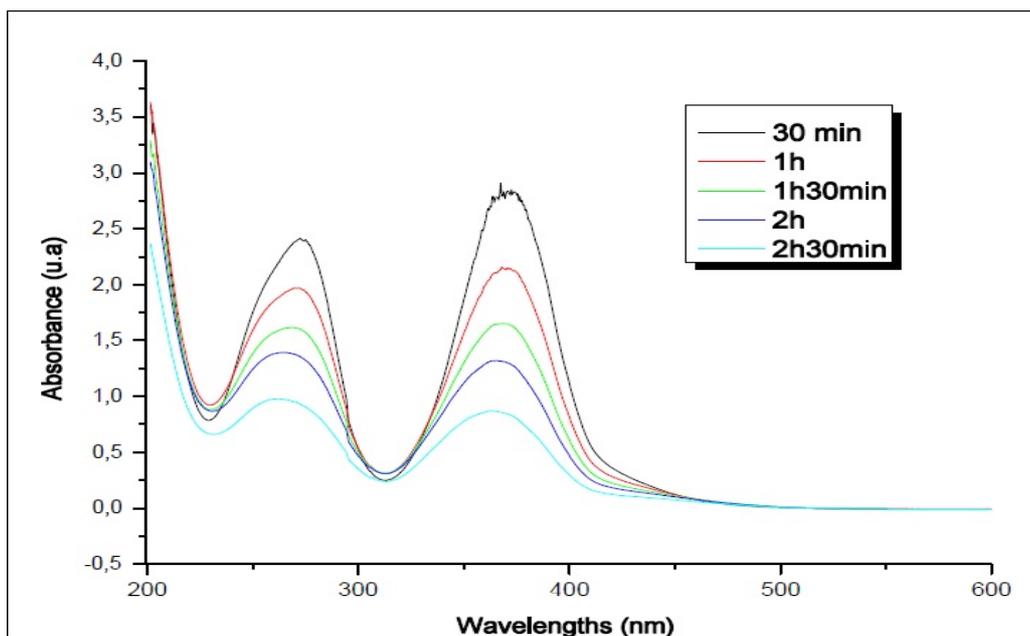
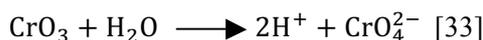


Figure 8: UV-Visible spectra of microfiltration permeate for 100 mg/L concentrated feed solution

For the used chromium oxide in this experiment, it is dissociated in solution according to the following equation:



The pH dependence of metal adsorption is largely related to the metal chemistry in the solution and the properties of the adsorbent. Cr(VI) exists in different ionic forms in solution. The most important Cr(VI) states in a solution are chromate CrO_4^{2-} , dichromate $\text{Cr}_2\text{O}_7^{2-}$ and hydrogen chromate HCrO_4^- , depending on the solution pH and total chromate concentration [34].

Since the distribution of Cr(VI) species is dependent on both pH and total Cr(VI) concentration, according to a predominance diagram is presented using both pH and total Cr(VI) as variables. HCrO_4^- and CrO_4^{2-} are the most predominant species at the experimental total Cr(VI) concentration between 0,05mg/L and 300mg/L, for experimental pH lower than 6.8 HCrO_4^- is the dominant species of hexavalent chromium, and above pH 6.8, only CrO_4^{2-} is stable [35].

The obtained rejection for the filtration of metal chromium Cr(VI) is very important and significant, which proves the interest to use these GHTM membranes for metal pollution control. Since the pH of the treated solution at value of 5.6 and since the isoelectric point of GHTM membrane is 10.9 the surface of membrane should be charged positively, which results to the strong interactions developed between the multivalent species $\text{HCrO}_4^- / \text{CrO}_4^{2-}$ and the positively charged membrane. This efficiency rejection of permeate stream samples as a function of time reaches around 96% after 80min of filtration experiment as plotted in figure 9. Table 1 presents the comparison of results obtained in this work with other membranes for the rejection of hexavalent Chromium from aqueous solution.

The rejection (98%) of Cr (VI) reported in this study at pH between 5 and 6 with an applied pressure of 1bar for the feed concentration of 10^{-3} mol/l is comparable or even better than the value reported in the literature

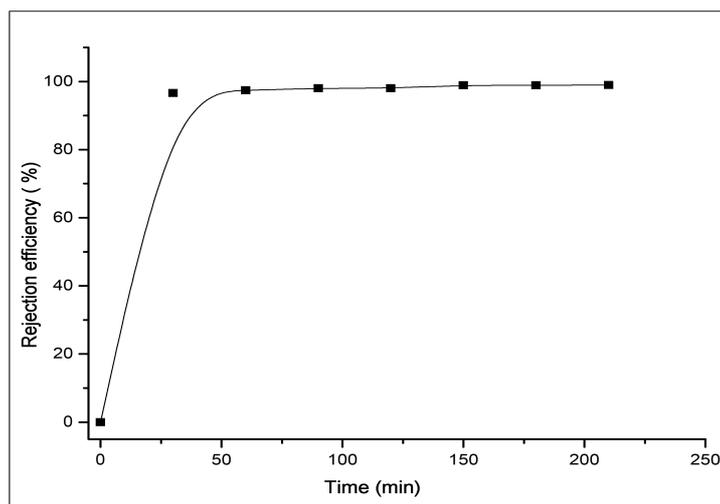


Figure 9: Rejection efficiency of permeate stream samples as a function of time

Table1: Comparison of separation performance of the membrane GHTM with other membranes

Membrane material	Rejection (%)	Reference
Zeolite-clay membrane	66	[36]
MCM-41 ceramic composite Membrane	80	[37]
PMMA-EGDM Membrane	68	[38]
Styrene acrylonitrile membrane	90	[39]
Clay-carbon membrane	96	[40]
Ghassoul Hydrotalcites Membrane (GHTM)	98	Present work

Conclusion

This study allowed developing the GHTM membrane on a ghassoul clay support by co-precipitation method. The support was elaborated by the application of uniaxial compaction technique of a powder mixture of ghassoul clay and activated carbon. The chemical stability of the sintering support at 900 ° C was analyzed in terms of weight loss (2.5% for the acid attack and 2.3% for the basic attack), which also allowed to use it as a support for the membrane GHTM used in all pH ranges.

Separation of chromium from the prepared GHTM membrane is verified by carrying out microfiltration studies of Cr (VI) from an aqueous solution. The obtained results confirm that the highest rejection around 96% after 80 min is obtained at pH 5.6 with an applied pressure of 1 bar and a feed concentration of 100 mg/L. These membranes cited in this work have a potential find an application for the economic treatment of waste water containing toxic compounds in emerging countries in the comparaison other membrane reported in literature for similar purpose.

Acknowledgement: This work was supported by MESRSFC and CNRST – Rabat Morocco, within the framework of the PPR2 project.

References

1. D. Vasanth, G. Pugazhenth, R. Uppaluri, *J. Membr. Sci.* 379 (2011) 154-163.
2. P. Monash, G. Pugazhenth, *Desalin. Water Treat.* 279 (2011) 104-114.
3. J. M. Benito, A. Conesa, F. Rubio, M.A. Rodriguez, *J. Eur. Ceram. Soc.* 25 (2005) 1895-1903.
4. S.H. Lee, K.C. Chung, M.C. Shin, J.I. Dong, H.S. Lee, K.H. Auh, *Mater. Lott.* 52 (2002) 266-271.

5. X. Ding, Y. Fan, N. Xu, *J. Membr. Sci.* 270 (2006) 179-186.
6. C. Gaucher, P. Jaouen, J. Comiti, P. Legentilhomme, *J. Membr. Sci.* 210 (2002) 245-258.
7. S. Masmoudi, R. Ben Amar, A. Larbot, H. El Feki, A. Ben Salah, L. Cot, *J. Membr. Sci.* 247 (2005) 1-9.
8. Ferhat Bouzerara, Souad Boulancer, Abdelhamid Harabi, *Ceram. Int.* 41 (2015) 5159-5163.
9. Ackmez Mudhoo, K. Vinod, Garg, shaobin wang, *Environ. Chem. Lett.* 10 (2012) 109-117.
10. Young-Ok Son, Poyil Pratheeshkumar, Yuting Wang, Donghern Kim, Zhuo Zhang, Xianglin Shi, *Toxicol. Appl. Pharmacol.* 331 (2017) 24-32.
11. D. Pradhan, L. B. Sukla, M. Sawyer, Pattanathu K.S.M.Rahman. *J. Ind. Eng. Chem.* 55, (2017) 1-20.
12. J. S. George, A. Ramos, H. J. Shipley, *J. Environ. Chem. Eng.* 3 (2015) 969-976.
13. P. Biswas, A. K. Karn, P. Balasubramanian, P. G. Kale, *Biosens. Bioelectron.* 94 (2017) 589-604.
14. A. Kumar, H. M. Jena, *Process Saf. Environ.* 109 (2017) 63-71.
15. T. Riaz, A. Ahmed, S. Saleemi, M. Adrees, F. Jamshed, A. Moqheet, T. Jamil, *Carbohydr. Polym.* 153 (2016) 582-591.
16. A. Harabi, A. Guechi, S. Condom, *Procedia Eng.* 33 (2012) 220-224.
17. Y. Anbri, N. Tijani, J. Coronas, E. Mateo, M. Menéndez, J. Bentama, *Desalin. Water Treat.* 221 (2008) 419-424.
18. N. Saffaj, M. Persin, S. A. Younsi, A. Albizane, M. Cretin, A. Larbot, *Appl. Clay Sci.* 31 (2006) 110-119.
19. O. Qabaqous, N. Tijani, M. Naciri Bennani, A. El Krouk, *J. Mater. Environ. Sci.* 5 (2014) 2244-2249.
20. SHIGEO MIYATA, *Clays Clay Miner.* 91 (1984) 64-89.
21. César Jiménez-Sanchidrián, José Rafael Ruiz, *Appl. Catal., B.* 469 (2014) 367-372.
22. P. C. C. Faria, J. J. M. Orfao, M. F. R. Pereira, *Water Res.* 38 (2004) 2043-2052.
23. P. Monash, G. Pugazhenthithi, *J. Appl. Ceram. Technol.* 8 (2011) 227-238.
24. A. Benhammou, "valorisation de la stevensite du jbel rhassoul: application a l'adsorption des metaux lourds" Thesis, Faculty of sciences semlalia, cadi ayyad University Marrakech Morocco (2005).
25. R. Bejjaoui, A. Benhammou, L. Nibou, B. Tanouti, J.P. Bonnet, A. Yaacoubi, A. Ammar, *Appl. Clay Sci.* 49 (2010) 336-340.
26. J. Olszowka, R. Karcz, B. D. Napruszewska, D. Duraczynska, A. Gawel, K. Bahranowsky, E. M. Serwicka, *Catal. Commun.* 100 (2017) 196-201.
27. James B, Condon, *Elseiver* QD547.C65 2006 541'.335-dc22.
28. S. Arhzaf, M. N. Bennani, S. Abouarnadasse, A. Amhoud. *J. Mater. Environ. Sci.* 11 (2016) 4226-4236.
29. Kristy L. Erickson, Thor E. Bostrom, Ray L. Frost, *Mater. Lett.* 59 (2005) 226-229.
30. Daniel J. Miller, Sirirat Kasemset, Donald R. Paul, Benny D. Freeman, *J. Membr. Sci.* 454 (2014) 505-515.
31. Sybrandus, Jacob Metz, *Desalin. Water Treat.* 148 (2003) 303-307.
32. Ashim Kumar Basumatary, R. Vinoth Kumar, Alope Kumar Ghoshal and G. Pugazhenthithi, *J. Membr. Sci.* 475 (2015) 521-532.
33. N. Tijani, H. Ahlafi, M. Smaih, A. El Mansouri. *Med. J. Chem.* 2 (2013) 484-492.
34. M. Muthukrishnan, B.K. Guha. *Desalin. Water Treat.* 219 (2008) 171-178.
35. Yujiang Li, Baoyu Gao, Tao Wu, Dejun Sun, Xia Li, Biao Wang, Fengjuan Lu, *Water Res.* 43 (2009) 3067-3075.
36. A. Shukla, A. Kumar. *Sep. Purif. Technol.* 52 (2007) 423-429.
37. Ashim Kumar Basumatary, R. Vinoth Kumar, Alope Kumar Ghoshal, G. Pugazhenthithi. *J. Membr. Sci.* 475 (2014) 521-532.
38. C. Neelakandan, G. Pugazhenthithi, A. Kumar. *Eur. Polym. J.* 39 (2003) 2383- 2391
39. S. Sachdeva, A. Kumar. *J. Membr. Sci.* 307 (2008) 37- 52.
40. G. Pugazhenthithi, S. Sachan, N. Kishore, A. Kumar. *J. Membr. Sci.* 254 (2005) 229-239.

(2018) ; <http://www.jmaterenviromsci.com>