Adsorption of Chromium (VI) from Water Solution onto Polymeric Membrane Systems

SOFIA TEODORESCU[1], RODICA MARIANA ION[2,3]*, GHEORGHE NECHIFOR[4], IOAN ALIN BUCURICA[1], IOANA DANIELA DULAMA[1], RALUCA MARIA STIRBESCU[1], NICOLAE MIHAIL STIRBESCU[1]

[1] Valahia University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, 13 Sinaia Alley, 130004, Targoviste, Romania

[2] Valahia University of Targoviste, Faculty of Materials Engineering and Mechanics, 13 Sinaia Alley, 130004, Targoviste, Romania

[3] National Institute of Research and Development for Chemistry and Petrochemistry – ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania

[4] University Politehnica Bucharest, Faculty of Applied Chemistry and Materials Science, Department Analytical Chemistry and Environmental Engineering, 1-7 Polizu, 011061, Bucharest, Romania

The toxic metals have shown a significant concentration increases in the superficial waters as a result of inappropriate residuals discharge by the municipality and industry. For chromium species can be clearly distinguished two oxidation states: Cr(VI) and Cr(III). Also, chromium's hexavalent form, can be included in A group of human carcinogen for its mutagenic and carcinogenic characteristics. For Cr(VI) separation and recovering, different systems have been used, the chemical membranes being a valuable solution. In order to increase their efficacy, magnetite has been added, creating a complex system. The morphology and surface characteristics of the new systems (polysulfone (PSf) membrane in N-methyl-pyrrolidone (NMP) with magnetite) have been proved with the following types of analysis: FT-IR, Raman, SEM, OM and colorimetric determination of chromium. Magnetite incorporated in the polysulfone/NMP/Fe_3O_4 membrane is one new solutions used with success in retention of Cr (VI) from wastewater (85%).

Keywords: polysulfone, membrane, NMP, magnetite, Cr(VI)

In the past, the toxic metals have shown a significant concentration increase in superficial waters as a result of inappropriate residuals discharge by the municipality and industry [1, 2].

The presence of Chromium in different states was observed in the river effluents and were described as the effect of textile dyeing, electroplating, steel works, wood preservation and artificial fertilizer and metal finishing industries, fact that cause a major environmental and public health concerns. In this study, it can be clearly distinguish two oxidation states of Chromium species: Cr(VI) and Cr(III). Also, chromium's hexavalent form, is assimilated as an *A* group of human carcinogen for its mutagenic and carcinogenic characteristics [3]. If chromium ions penetrates the cells, DNA replication process [4] is affected, as they are reduced in the first stage to a pentavalent compound Cr(V) by adding electrons and, in the second stage, to trivalent chromium Cr(III) . The inland discharging of Cr(VI) into water is tolerated if the limits does not exceed 0.1 mg/L in surface water and 0.05 mg/L in potable water [5]. In order to remove Cr(VI) from aqueous solution it is required some chemical and physical process such as: electro-chemical precipitation, ultra-filtration, ion exchange, adsorption. Although, these processes required some high financial costs, they do not guarantee the complete removability of chromium.

The widespread field of nanotechnology, show in our days a real concerning about the importance of studding the inside disciplines as it is polymer sciences, mostly based on nanoparticles and nanocomposites [6].

For a better understanding of the process, the information is divided in two segments as it follows: syntheses and preparation methods of some membrane structures and the efficacy and the performances of the new membrane in the separation process of hexavalent chromium.

For membranes manufacturing process, it can be used different types of materials with distinct properties and characteristics as: mechanical strength, fouling resistance, hydrophobicity, hydrophillicity and chemical tolerances [7]. The main advantage of nanocomposite membranes it combines the adsorption capacity for heavy metals of magnetite and their flexibility of polymers.

For a better dispersion of the inorganic material in the polymer membrane, it was introduced an organic functional group into an inorganic filter surface. This aspect, help also to a better absorption and transportation of penetrants, contributing to a favorable selectivity and permeability [8]. One of the most used polymers in the manufacturing of microfiltration and ultrafiltration membranes is Polysulfone (PSF) for its mechanical, chemical and high thermal resistance properties [9].

This paper discusses the obtaining proccess of nanocomposite membranes from polysulfone/ magnetite non-solvent system for wastewater remediation with Cr^{6+} ions content and also it's utility. The role of the membrane is very important for separation processes and behaves as a selective barrier, regulating the transport of substances [10]. The morphology and surface characteristics of the new system (polysulfone (PSf) membrane in N-methyl-pyrrolidone (NMP) with magnetite) together with the efficiency have been proved with the following types of analysis: FT-IR, Raman, SEM, OM and colorimetric determination of chromium. Magnetite incorporated in the polysulfone/NMP/Fe_3O_4 membrane is one new solutions used with success in retention of Cr (VI) from wastewater (85%).

The processes of separation through membrane prove to be very efficient, also, as time and energy aspects, are

* email: rodica_ion2000@yahoo.co.uk.

economic and truly important for the further development of environmental technologies [11]. Many applications such as drug delivery, hyperthermia supplying or magnetic resonance imaging have successfully used magnetite particles [12].

Experimental part

In this paper were obtained polysulfone magnetite nanocomposite membranes with phase inversion method.

Procedure

To obtain the polysulfone magnetite nanocomposite membranes were used: Polysulfone (Psf) (pellets, with nominal M. W. 75000, density: 1.24 g/cm^3), 1-methyl-2-pyrrolidone (N-methylpyrrolidone) (NMP) (Merck, 99%, MW: 99.13 g/mol, density at 20 °C: 1.03 g/mL, solubility in water: 1000 g/L at 25°C, boiling point: 202°C) and magnetite (Aldrich provenience). So, 2 g of magnetite, 200 mL of NMP and 10% dissolved polysulfone have been mixed with 50 glass beads of 2 mm diameter. All these, have been placed in a planetary mill of the type Retsch in order to homogenize the composition. This composition was mixed for 7 h, at 300 rpm. Also, 5 mL of polymer solution and magnetite was afterwards uniformly distributed on a glass substrate. The standard thickness of the deposition layer was approximately 250μm. In the next stage, the distributed polymer layer over the glass was immersed in the coagulation bath (distilled water and isopropanol, 50%) for 15 min [13].

Analytical equipment

The morphology and surface characteristics of the new systems together with the efficiency have been proved with the following types of analysis: ATR-FTIR, Raman, SEM, OM and colorimetric determination of chromium.

For molecular identification of chemical functional groups of organic compounds were used attenuated total reflection - Fourier transform infrared spectrometry using Vertex 80v spectrometer (Bruker), which absorbs infrared radiation in 350-8000 cm^{-1} range and is equipped with diamond attenuated total reflection accessory [14- 18]. This equipment present high spectral resolution (0.2 cm^{-1}) and accuracy 0.1 %T. Raman investigation was performed using Xantus-2 (Rigaku). This portable dual wavelength Raman analyzer equipped with options of 785 and 1064 nm stabilized laser, providing high sensitivity [17].

The morphology and surface characterization were performed using Scanning Electron Microscope (SEM) SU-70 (Hitachi). Main characteristics of this equipment are: ZrO/W Schottky electron source, accelerating voltage from 0.1 kV to 30 kV, SEM magnification range 30x – 800000x and resolution 1 nm (at 15 kV) [19, 20]. For optical microscopy was used Primo Star microscope (Zeiss), which offers the possibility to investigate the samples in transmitted light at a magnification between 4X – 100X, coupled with a digital video camera Axiocam 105.

Results and discussions

FTIR spectra show the presence of magnetite (877, 962, 1082, 1450 ºi 3686 cm^{-1}), and specific bands of the polysulfone membrane (1044 cm^{-1} (SO_3H), 1106 cm^{-1} (C-O), 1150 cm^{-1}, (R(SO_2)-R), 1241cm^{-1} (C-O), 1488 cm^{-1} (aromatic bonds), 2966 cm^{-1} (CH aliphatic), 2879 cm^{-1} (CH aromatic) ºi 3362 cm^{-1} (OH). By adding Cr over the membrane alone, no changes in the absorption spectrum are observed (fig. 1).

The magnetite incorporated into the polysulfone membrane is one of the solutions successfully used in retention Cr (VI) from wastewater. The FTIR spectra are significantly changed after magnetite presence on the membrane, as FTIR spectra could show, (figs. 2 and 3).

The wide FTIR bands from 3000-4000 cm^{-1} disappear after Cr(VI) solution through the membrane, as a possible interaction via hydrogen bonds (via OH groups) and electrostatic interactions between individual components of the system. Also, the bands from 1700 - 1800 cm^{-1} disappear, too, as a proof of the encapsulation of chromium into membrane pores.

The FTIR analyzes was confirmed by Raman spectroscopy (through the fourth bands from 800 -1400 cm^{-1}) (fig. 4) and by dissapearing of the band around 1700 cm^{-1}.

With optical microscopy were obtained data on the pore distribution (pores with a diameter > 5 μm and pores with diameter <1μm) (fig. 5). Optical microscopy

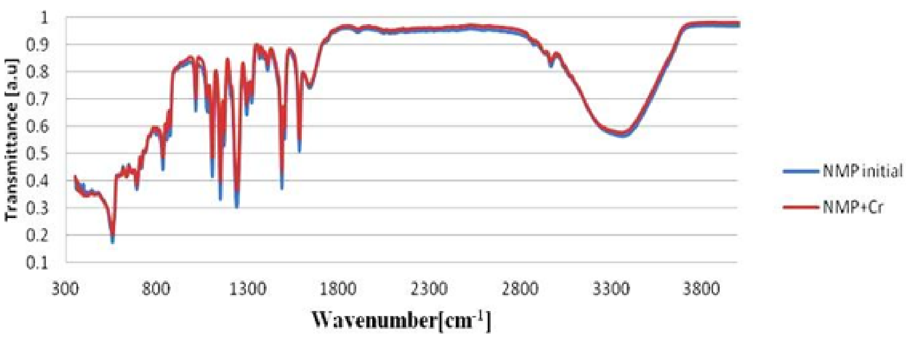

Fig. 1. The FTIR spectra of NMP membrane alone and with chromium.

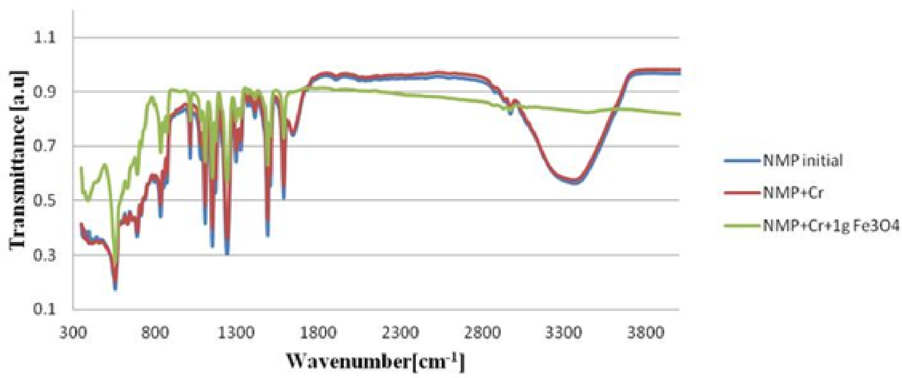

Fig. 2. FTIR spectrum for NMP membrane +1g Fe_3O_4.

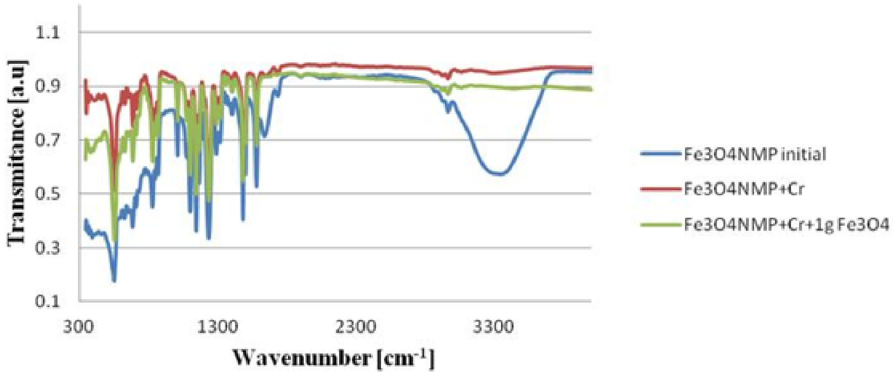

Fig. 3. FTIR spectrum for NMP/magnetite membrane +1g Fe_3O_4

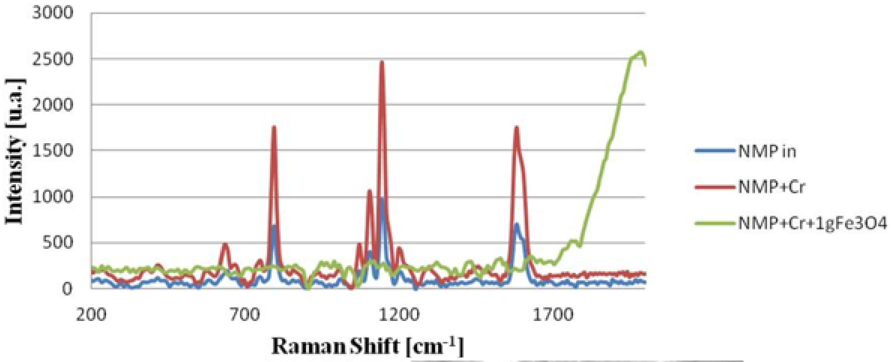

Fig. 4. Raman spectrum for NMP/ magnetite membrane +1g Fe_3O_4.

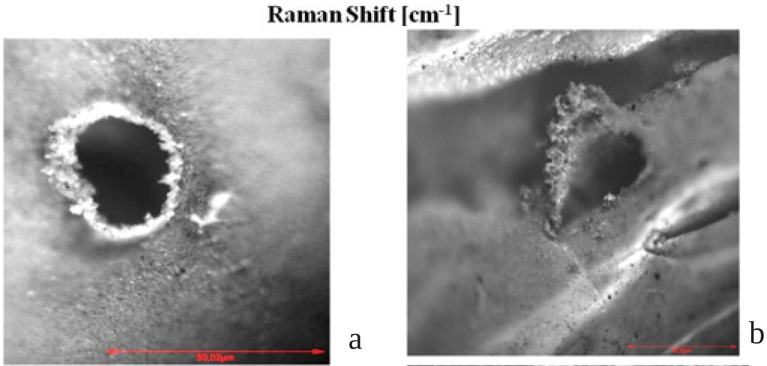

Fig. 5. Optical microscopy image for NMP /magnetite membrane before (a) and after (b) adsorption of chromium particles

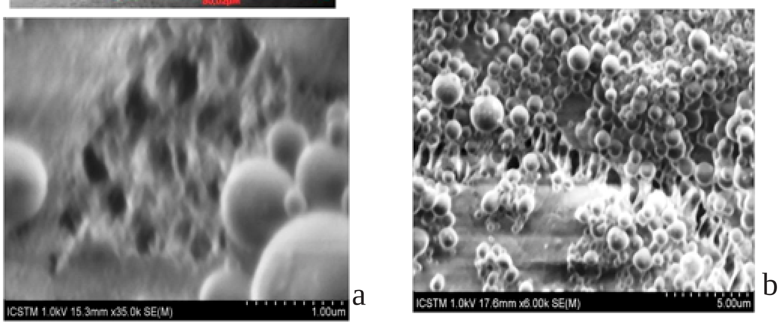

Fig. 6. SEM image for NMP membrane before (a) and after (b) adsorption of chromium particles

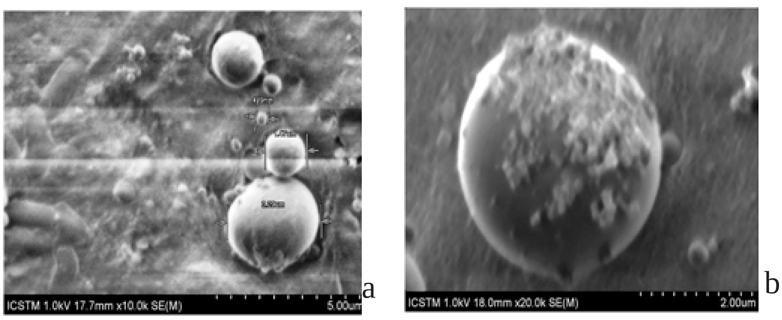

Fig. 7. SEM image for NMP /magnetite membrane before (a) and after (b) adsorption of chromium particles

demonstrated that the pores with a diameter of 5 μm was formed due the presence of magnetite, while the others pores are formed due to the particles of magnetite < 1 μm. In the presence of Cr(VI), large pores are covered by this pollutant, while small pores are broken after the implosion generated during the precoagulation of the bubbles from membrane, Cr(III) being incorporated in these pores and even in the magnetite particles < 30 nm present in pores.

Scanning electron microscopy (SEM) was used for understanding the topology and morphology of polysulfone membranes, before and after retention of Cr(VI), as figures 6 and 7.

The concentration of Cr (VI) in the solution was determined by the colorimetric method with diphenyl-carbazide at 540 nm.

The magnetite is very efficiently with size <30 mm, because is prevented from agglomerating (fig. 8).

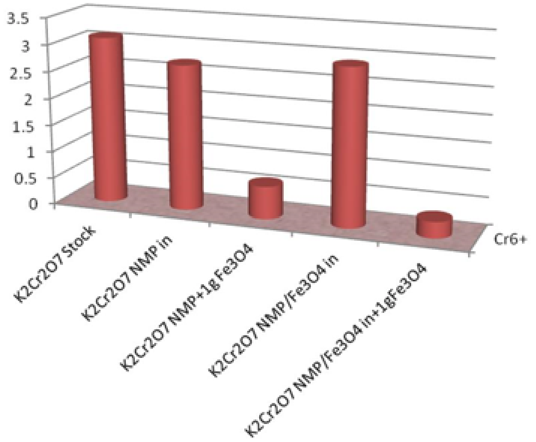

Fig. 8. The adsorption kinetics of Chromium on PSf membrane with magnetite incorporated

Absorption of Cr (VI) on magnetite involves the transformation of Cr (VI) to Cr (III) and probably could replace Fe (III) from magnetite network. Future experiments and publications will show detailed aspects about the interaction between all the components present in this system.

Conclusions

The application of magnetite for the first time in the literature as nanostructured encapsulated polymeric membrane. It acts as selective barrier that participate actively or passively at mass transfer from phases which they separate. The use of magnetite was found to be very effective in recovering of hexavalent chromium in a short time and low costs. In conclusion, magnetite incorporated in the polysulfone/NMP/Fe_3O_4 membrane is one new solutions used with success in retention of Cr (VI) from wastewater (85%).

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