U.P.B. Sci. Bull., Series B, Vol. 75, Iss. 3, 2013 ISSN 1454-2331

COMPOZITE ZEOLITE-POLYANILINE MEMBRANE MATERIAL FOR WATER TREATEMENT

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This paper presents the synthesis of a new PANI-MOL SIEVE composite material, designed for recovery or removal of cobalt ions from wastewater by ultrafiltration The membrane material was obtained by oxidative polymerization of aniline in synthetic zeolite matrix, molecular sieve 5A. The structure and morphology of the synthesized materials were studied by FT-IR spectroscopy and scanning electron microscopy SEM, and to determine the efficiency of cobalt removal from wastewater, ultrafiltration was used. Dynamic membranes made from composite material have high separation efficiency both to the dynamic membranes, obtained from synthetic zeolite, as well as those based on polyaniline.

New composite membrane material allows removal of cobalt ions from synthetic aqueous solutions, 10^{-4}- 10^{-6}M, in a single step ultrafiltration using dynamic membranes, reaching an average retention exceeding 98%, with an average flow of over 115 l/m^2 h

Keywords: composite membrane materials, zeolite-polyaniline materials, cobalt removing, ultrafiltration, dynamic membranes

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1. Introduction

Continual synthesis of new composite materials is justified by the need to obtain higher performance process [1-3]. One of the current areas in which new composite materials are applied, is membranes and membrane processes because they constitute the development of green and ecological technologies [4-7].

Between membrane materials zeolites [8-10], and polyanilines [11-13], are increasingly widely used in water treatment processes or to remove organic substances, either for separation and concentration of metal cations [14 - 16]. However, composites based on these two materials were relatively less studied [15].

This paper shows the synthesis of zeolite-polyaniline composite material, PANI- Zeolite, which is destined for recovery or removal of cobalt ions from wastewater by ultrafiltration.

2. Experimental

2.1 Materials

Zeolite **MOLECULAR SIEVE 5A** (SUPELCO Analytical), Polyaniline, emeraldine base, Mw approx. 65,000 (Aldrich), quartz filters (Frisenette ApS, QF.047) hydrochloric acid (Sigma Aldrich), cobalt nitrate (Merck), potassium hiroxid, acetic acid and sodium acetate (Riedel-deHaen), aniline (Merck), $(NH_{4)2}S_2O_8$ (Merck) and pure water obtained by Milipore module.

2.2. Methods

Synthesis of composite material

In the 500 ml autoclave of colloidal mill Retsch PM 100, place 50 g of quartz grinding machinery of 1 mm diameter, 40 g of zeolite **MOLECULAR SIEVE 5A** and 50 ml of aniline. After 2 hours of homogenous mixing at 250 rpm, open the autoclave and add 150 ml of hydrochloric acid solution 37%, then add 100 ml of 1 M potassium persulphate solution. After 4 hours, a brown material is obtained and is filtered in portions of 100 ml suspension on quartz filters, 47 mm in diameter, in a Sartorius funnel, is washed with distilled water four times and dried for 48 hours at 105°C in the vacuum oven. In parallel are obtained dynamic membranes by filtering a zeolite suspension on quartz filters (MZ) and, respectively, dynamic membranes by filtering a suspension of polyaniline on quartz filters (MP).

Morphological characterization of materials

Scanning electron microscopy (SEM) and EDAX analysis was performed with a FEI instrument (Hitachi S4500 FESEM). The FT-IR spectroscopy was performed using a Bruker Tensor 27 instrument with diamond ATR.

Membrane materials testing

Quartz filters with polyaniline, zeolite or PANI-Zeolite composite material (MPZ) were placed in the ultrafiltration module (Fig. 1).

Membrane flux was calculated based on the volume of permeate measured in a period of time, using following formula:

$$J = \frac{1}{A} \cdot \frac{\left(\Delta V_{permeat}\right)}{\left(\Delta t\right)}, \quad \left(\frac{L}{m^2 \cdot h}\right) \tag{1}$$

Where:

A= effective area of the membrane (12 cm^2)

ΔV= volume of permeate collected in time Δt

Retention of divalent ions M^{2+}, in this case, cations (Co^{2+}), 10^{-4}-10^{-6}M ($R_M{}^{2+}$%) is determined using equation (2):

$$R_M{}^{2+} (\%) = [1-(C_{Mf}-Ca_e)/C_{Mf})x100 \tag{2}$$

Where: C_{Mf}- feeder ion concentration

C_{Me}- effluent ion concentration

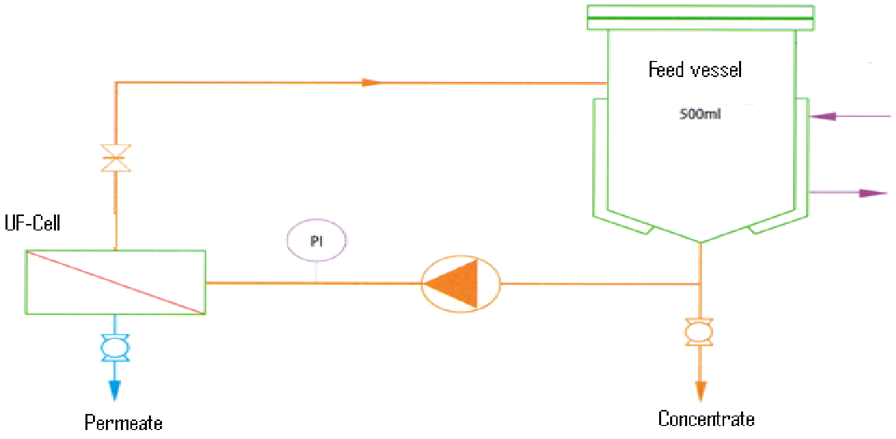


Fig. 1. KOCH ultrafiltration installation LABCELL-CF1, general view.

Metal ions determination is done by atomic absorption [16], using a Perkin Elmer AAS spectrometer.

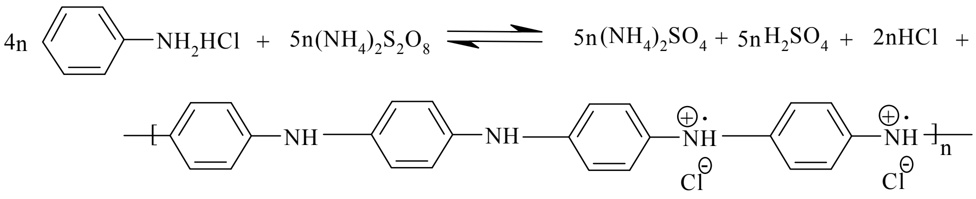
3. Results and discussion

3.1. Material synthesis

Chemical oxidation of aniline (3) was often performed in aqueous solution, but also in polymer matrices [17-20].

For chemical synthesis of polyaniline sulfuric or hydrochloric acid is used, and ammonium peroxidisulphate as oxidizing agent [18,19].

In this paper polyaniline was prepared by chemical oxidation of aniline with ammonium peroxodisulphate (Scheme I), in chosen inorganic matrix.



Scheme I

In our case the matrix is made of a commercial synthetic zeolite **MOL SIEVE 5A** (Fig. 2 a, c) and aniline polymerization occurs after its adsorption by colloidal mill homogenization. Zeolite soaked in aniline is oxidized in acidic solution of ammonium persulphate, obtaining a composite PANI-Zeoltite (Fig. 2 b, d).

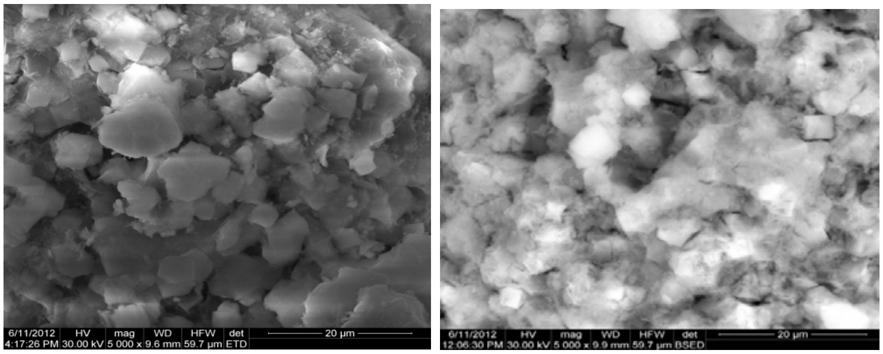


Fig. 2 (a) (b)

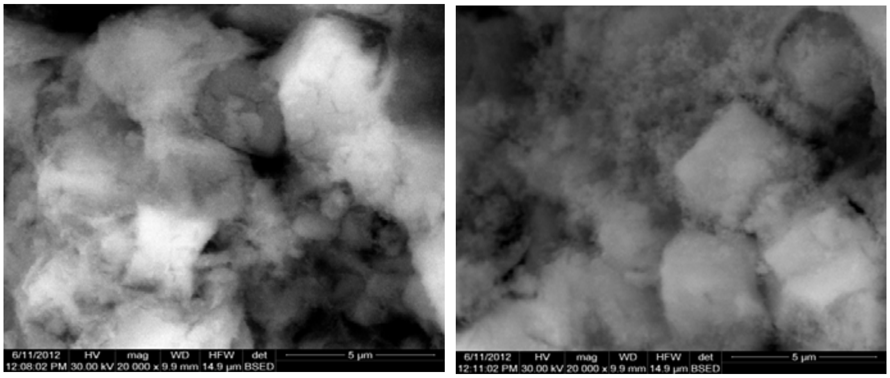


Fig. 2 (c) (d)

Fig. 2. Zeolite morphology (a and c) and zeolite-polyaniline composite material (b and d)

3.2. Scanning electron microscopy analysis

SEM analysis, performed with an FEI instrument (Hitachi S4500 FESEM) reveals a morphology dominated by the crystalline zeolite (Fig. 2 a, c), and by the appearance of fibers and threads of PANI (Fig. 2 b, d). Microcrystalline zeolite does not undergo any major changes in the process of ultrafiltration of aqueous solutions, while polyaniline threads changes insignificant their size and shape after the process, Figure 3 a and c compared with Figure 3 b and d.

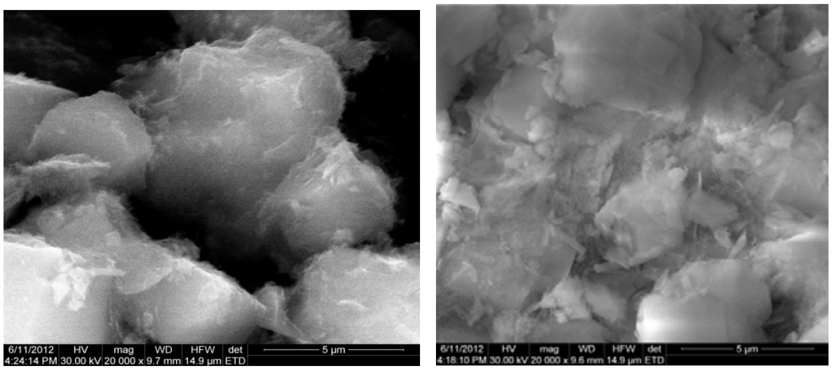


Fig. 3 (a) (b)

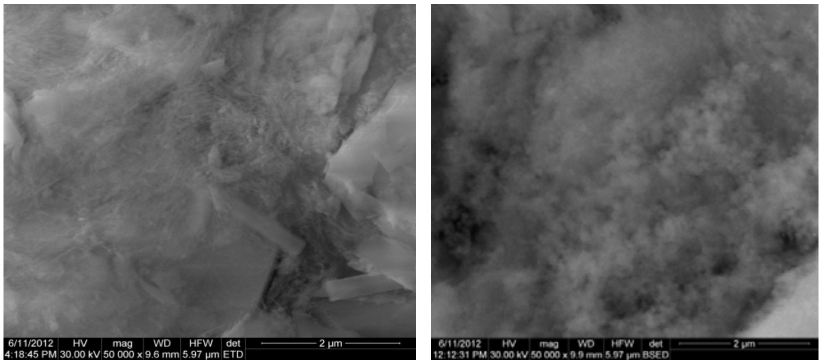


Fig. 3 (c) (d)

Fig. 3. The morphology of zeolite and of micro-composite material PANI Zeolite before (a, c) and after adsorption of cobalt (b, d) in two resolutions x8,000 (a, b) and x16,000 (c, d).

3.3. Energy dispersive X-ray spectroscopy analysis

Map and EDAX spectrum (Fig. 4) shows the elemental distribution of the micro-composite material, ***PANI-Zeolite***, after the ultrafiltration of synthetic aqueous solutions.

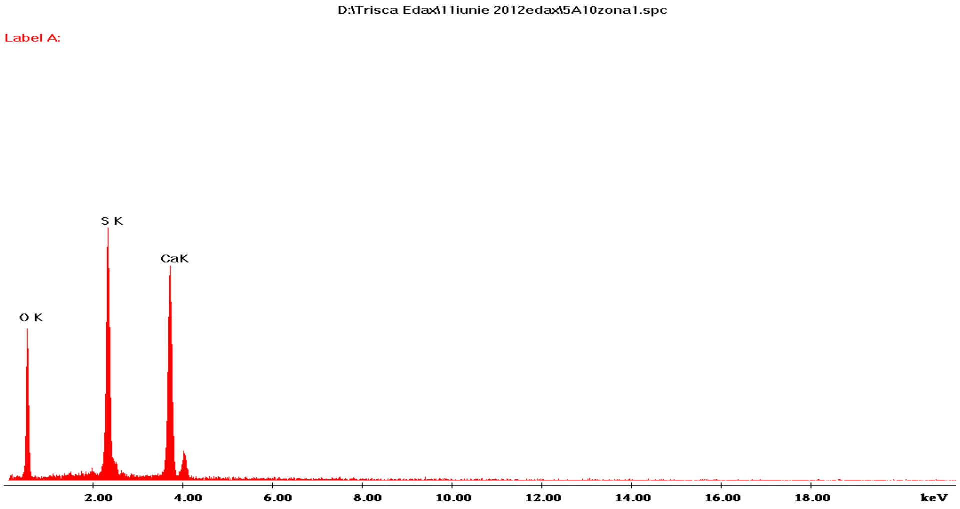


Fig. 4 (a)

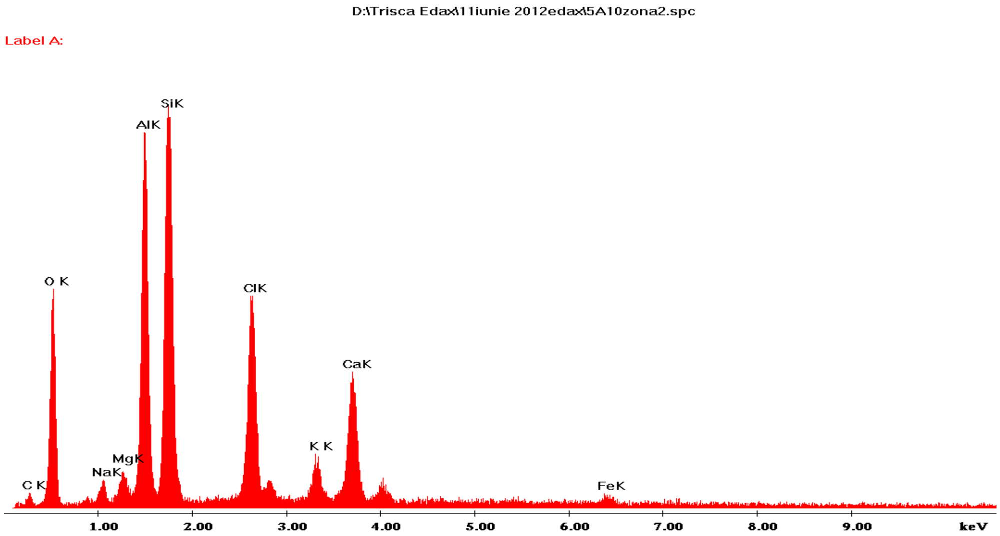


Fig. 4 (b)

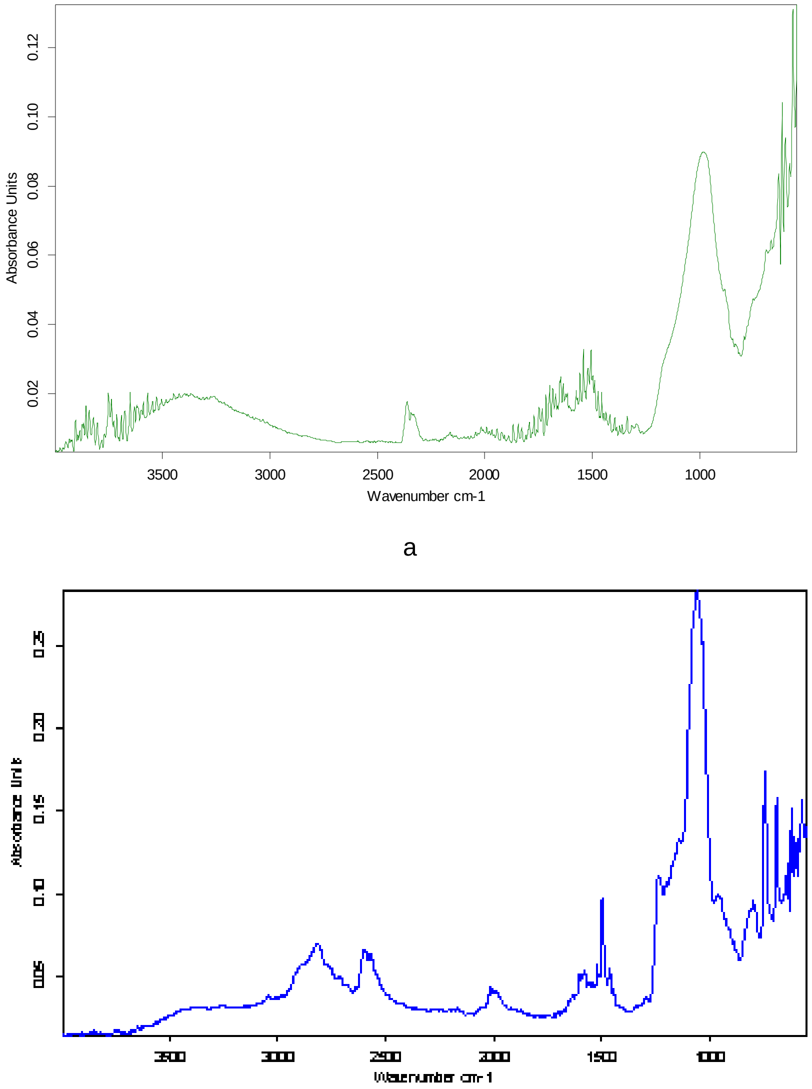
Fig. 4. EDAX image of zeolite material before (a) and after ultrafiltration (b).

The elemental distribution shows that the micro-structured material, retains common ions from aqueous solution on the zeolite surface even after washing and preparation for analysis (fig. 4 b).

3.4. Infrared spectroscopy

FT-IR spectra were obtained with Bruker Tensor 27 instrument with diamond ATR (Fig. 5).

In order to characterize the obtained materials, the following have been analyzed by infrared spectroscopy: polyaniline, emeraldine base, zeolite-polyaniline composite material obtained by chemical oxidation of aniline on the chosen zeolite. There are interesting variances that appear between polyaniline spectrum (Fig. 5a) and composite material zeolite-polyaniline spectrum (Fig. 5b). They suggest that polyaniline obtained in situ interacts chemically with the zeolite.



a

b

Fig. 5. FTIR spectra of PANI (a) and PANI-Zeolite composite (b).

Spectrum region between 3000-3600 cm^{-1}, shows the formation of hydrogen bonds and electrostatic interactions probably between imine groups of polyaniline and hydroxyl groups of the zeolite. Also, polyaniline obtained by polymerization in the presence of zeolite has shifted specific adsorption bands, thereby confirming the physical-chemical interaction polyaniline-zeolite.

Imine nitrogen atom from polyaniline (emeraldine-based Bronsted) is protonated by the hydroxyl groups of the dopant (acidic solution for oxidation), and this process is actually an acid-base equilibrium.

Polyaniline doping with the oxidation acid is confirmed by the presence in the FTIR spectrum of one absorption due to the presence of non ionized OH groups in the remaining molecular architecture of inorganic material (3000-3600 cm^{-1}).

3.5. Retention tests

Retention of divalent metal cations, especially, cobalt cation from wastewater is an important aspect of labor toxicology and environmental protection both in electrical and hydrometallurgical industry, as well as coating metals and nuclear.

Even though adsorption systems using polymeric and inorganic materials present satisfactory results, the use of organic-inorganic composite materials, as zeolite-polyaniline (PANI-Zeolite), present the advantage of physical retention on the inorganic material, and of physico-chemical retention on the organic polymeric material.

This observation is confirmed by results in retention of cobalt ions from synthetic aqueous solutions, 10^{-4}-10^{-6} M (Table 1).

Table 1

The medium flux and retention of the dynamic membranes

Membranes	**Flux (L/m^2 h)**	**Retention (%)**
Zeolite	151.42	67.58
PANI	126.36	77.43
Zeolite-PANI	118.87	98.20

The data show that dynamic membranes obtained by depositing zeolite, polyaniline, and respectively zeolite-polyaniline composite material have permeate average flows specific for ultrafiltration, composite retention is definitely higher for cobalt ions, in composite case, reaching specific values for reverse osmosis; although, on working pressure, 6 bar, characteristic for ultrafiltration.

It can be said that the new composite membrane allows removal of cobalt ions from synthetic aqueous solutions, 10^{-4}-10^{-6} M, in a single-step of ultrafiltration, using dynamic membranes. Average flow for organic-inorganic composite decreases by approx. 10%, compared to individual constituent materials, which is not a practical impediment to operate the process.

4. Conclusions

This paper presents the synthesis of zeolite composite polyaniline, obtained by oxidative polymerization of aniline in synthetic zeolite matrix, **MOLECULAR SIEVE 5A**. The material can be easily used for recovery or removal of cobalt ions from wastewater by ultrafiltration.

The structure and morphology of the obtained materials were studied by FT-IR spectroscopy and scanning electron microscopy SEM, then ultrafiltration was used to determine the efficiency of cobalt removal from wastewater.

Dynamic membranes made from composite material have high separation efficiency compared with dynamic membrane obtained from synthetic zeolite, as well as those based on polyaniline. The new composite membrane allows removal of cobalt ions from synthetic aqueous solutions, 10^{-4}-10^{-6} M, in a single step ultrafiltration using dynamic membranes, reaching an average retention exceeding 98%, with an average flow of over 115 l/m^2 h.

Acknowledgment

The work has been funded by the Sectoral Operational Program Human Resources Development 2007-2013 of the Romanian Ministry of Labor, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/60203.

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