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SYNTHESIS OF A NEW ION EXCHANGE MEMBRANE AND ITS SURFACE MORPHOLOGY

Dinitrocellulose (DNS) with a nitrogen content of 10.7 % – 12.2 % was synthesized by nitration cotton cellulose in this research work. After that, an ion exchange membrane was obtained by modifying the resulting DNS with aniline (AN). The resulting dinitrocellulose polyaniline (DNSPA) copolymer was dissolved in various solvents and converted into a porous ion exchange membrane by a special molding method. The produced substances were synthesized based on different applications of mole ratios of starting materials, reaction temperature, and reaction time, and the optimal conditions of the process were determined. Based on the physicochemical results of DNSPA, its application as new ion exchange membranes was studied. In addition, the composition of the synthesized DNSPA was determined based on the infrared spectrum (IR-spectrum), and the element composition and surface morphology were determined based on scanning electron microscopy (SEM) and their data were presented. Nano- and microporous membranes were also obtained using various solvents and porogens.

Keywords: ion exchange membrane, dinitrocellulosepolyaniline, cellulose, aniline, dinitrocellulose.

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Жаңа ион алмасу мембранасының синтезі және оның беткі морфологиясы

Бұл ұсынылған зерттеу жұмысында мақта целлюлозасын нитрлеу арқылы азоты 10,7 % – 12,2 % болатын динитроцеллюлоза (DNS) синтезделді. Осыдан кейін алынған DNS-ті анилинмен (AN) өзгерту арқылы ион алмасу мембранасы дайындалды. Алынған заттар бастапқы заттардың әртүрлі молярлық қатынасын, температура мен реакция уақытын пайдаланып синтезделді және процестің оңтайлы шарттары анықталды. Алынған заттар бастапқы заттардың молярлық қатынасын, температура мен реакция уақытын әртүрлі қолдануды ескере отырып синтезделді және процестің оңтайлы шарттары анықталды. DNSPA физика-химиялық нәтижелеріне сүйене отырып, оның жаңа ион алмасу мембранасы ретінде қолданылуы зерттелді. Сонымен қатар, инфрақызыл спектр (IR спектрі) негізінде синтезделген DNSPA құрамы анықталды және сканерлеуші электрондық микроскопия (SEM) негізінде элементтік құрамы мен беткі морфологиясы анықталды және олардың деректері ұсынылды. Сканерлеуші электрондық микроскопия арқылы алынған суреттері нано- және микрокеуектері бар синтезделген мембрананың беткі морфологиясы ион алмасу процесінде қолдануға жарамды екенін көрсетеді. Сондай-ақ, әртүрлі еріткіштер мен кеуекті түзгіштер көмегімен нано- және микрокеуекті мембраналар дайындалды.

Түйін сөздер: ион алмасу мембранасы, динитроцеллюлозаполианилин, целлюлоза, анилин, динитроцеллюлоза.

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Синтез новой ионообменной мембраны и морфология её поверхности

В данной исследовательской работе методом нитрования хлопковой целлюлозы была синтезирована динитроцеллюлоза (DNS) с содержанием азота 10,7 % – 12,2 %. После этого получена ионообменная мембрана путём модификации полученного DNS анилином (AN). Полученный сополимер динитроцеллюлозы и полианилина (DNSPA) был растворен в различных растворителях и специальным методом формования был превращён в пористую ионообменную мембрану. Таким образом, полученные вещества синтезированы с использованием различных мольных соотношений исходных веществ, температуры и времени реакции и определены оптимальные условия проведения процесса. На основании физико-химических результатов DNSPA изучено их применение в качестве новых ионообменных мембран. Кроме того, на основе инфракрасного спектра (ИК-спектра) определен состав синтезированных в работе DNSPA, а на основе сканирующей электронной микроскопии (CЭM) определён элементный состав и морфология поверхности и представлены их данные. Представленные изображения, полученные с помощью CЭM, показывают, что морфология поверхности синтезированной мембраны с нано- и микропорами пригодна для использования в процессе ионного обмена. Также были получены нано- и микропористые мембраны с использованием различных различных растворителей.

Ключевые слова: ионообменная мембрана, динитроцеллюлозаполианилин, целлюлоза, анилин, динитроцеллюлоза.

Introduction

Membrane treatment is a crucial technique for maintaining and wisely using water resources, improving water quality, and enabling the reuse of water in technological processes using physicochemical wastewater detoxification methods [1-2]. Because it is simple to use and quite inexpensive, membrane technology is one of the many methods for extracting different cations and anions from solutions [3]. Ion exchange membranes are the most popular and very effective kind of membranes. Ion exchange membranes (IEM) offer a lot of promise, particularly in the industrial sector where they are employed for high-efficiency material purification, synthesis of novel materials, energy production, and mixture separation [4-5].

Ion exchange membranes are also frequently made using cellulose and its esters as a starting point for fabrication. Cellulose acetate, ethyl cellulose, and cellulose nitrate have all been used to generate a variety of nano and microporous membranes [6]. Nitrocellulose, for instance, is a crucial substrate in the manufacturing of anion exchange membranes, which are used to detect and separate proteins from solutions with low concentrations [7]. Porous thin films with a kerosene size are formed from ethyl cellulose, and materials that serve as separators and conductors are produced by adding the required ingredients to it [8-9].

Furthermore, an ion-exchange nanocomposite was created by using an in situ chemical oxidation polymerization technique to join microcrystalline cellulose and polyaniline. When it came to the operations of removing heavy metals and different dyes from wastewater, this nanocomposite performed well [10]. Recycled polyaniline-based high ion exchange membranes with improved electrical conductivity and ion exchange are used [11-12]. We modified dinitrocellulose with polyaniline to create a novel nanoand microporous ion exchange membrane, taking into consideration the characteristics of the aforementioned materials.

Experimental part

Materials and Methods

The following materials and equipment are needed to prepare the ion exchange membrane and its raw materials. Cotton cellulose (CS), nitric acid 68%, sulfuric acid 98%, aniline (AN) 99%, ethyl ether (EET) 99%, diethyl ether (DET) 98%, acetone (AT) 96%, ammonium persulfate (AP) 96%, Glycerin(GL) 96%, N-methyl-2-pyrrolidone (NMP) 98%, Isobutyl alcohol (IBA) 99%, Ethylene glycol (ETG) 98%, Hydrochloric acid 24%, and distilled water. Refractory flasks, a thermometer and a magnetic stirrer were used to carry out the reaction processes. DNS synthesis based on cellulose and nitric acid

Dinitrocellulose was initially synthesized by attaching nitric acid to cotton cellulose under the catalysis of sulfuric acid [13]. According to this method, nitrocellulose belonging to the colloxylin family with a nitrogen content of 10.7-12.2% was produced. First, a 2 L flask was placed in an ice bath, and then 400 g of 62% HNO₃ was slowly added. In the next step, 34 ml of concentrated H₂SO₄ was added to the flask dropwise over 30 minutes with continuous stirring. The temperature was raised to 20-23 °C under ice water until the solutions were mixed and kept in this state. After mixing all the ingredients, the substance turned light yellow and the container was closed and kept at room temperature for a day,

periodically shaking every 6 hours. At the next stage, 45 grams of cotton cellulose, washed three times in distilled water and dried, was placed in a raw material container cooled by bringing the solution temperature to 15-20 °C and mixed for another 30 minutes. The obtained raw material was washed in distilled water until it became neutral. After that, the resulting DNA was placed in a 5-7% nitric acid solution and heated at 100 °C for 1.5 hours at a pressure of 4 atmospheres in an autoclave, and the ready-to-use dinitrocellulose fiber was obtained by washing it again in distilled water until it became neutral. The synthesis of dinitrocellulose was carried out under several conditions and excipients. Its synthesis reaction equation is shown in Figure 1.



Figure 1 – Reaction equation of DNS synthesis based on nitration of cotton cellulose.

Synthesis of dinitrocellulose polyaniline (DNSPA) based on the binding of dinitrocellulose and aniline

DNPA was copolymerized by in situ chemical oxidation polymerization of dinitrocellulose and aniline in the presence of ammonium persulfate and hydrochloric acid as catalysts. First, 5 g of dinitracellulose was taken and dried at 40-45 °C for 12 hours and placed in a refractory flask. Then 5 g of aniline was added to the reactor and mixed with dinitrocellulose at low temperature. At first, a solution of hydrochloric acid and ammonium persulfate was slowly added dropwise as a catalyst.

During the reaction, the substances were continuously stirred. After the catalysts were completely incorporated, they were stirred for another 4 hours, and blue-colored DNSPA was obtained and neutralized by washing with distilled water. Then the product was dried in an oven at a temperature of 45-50 °C for 12 hours. During the experiment, reactions were carried out by introducing aniline and dinitracellulose raw materials in different proportions. The synthesis reaction scheme of the synthesized DNSPA copolymer is shown in Figure 2. In the reaction of dinitracellulose and aniline with a mass ratio of 1:1 the yield of the process was 84% (Fig. 3).



Figure 2 – The reaction equation for the synthesis of dinitrocellulosepolyaniline (DNSPA) based on dinarcellulose and aniline.



Figure 3 – Effect of the mass ratio of the initial DNS and AN substances on the reaction product during the synthesis of DNSPA raw materials.

Membrane preparation

The following procedures were used in the fabrication of the DNSPA membrane. After setting





the reaction flask on a magnetic stirrer, 30 g of NMP and 6 g of DF were added, and the mixture was agitated for 35 minutes at 20-24 °C. The following

stage involved adding 3 g of IBS and 2.5 g of PANS to the mixture and mixing it for an hour at 35-37 °C to dissolve it evenly. The bulk solution's color transitioned from white-yellow to light brown at this point. Next, 0.2 g of the GLT solution was constantly stirred at this temperature. Next, 10g of AT was added to the entire mixture. The product was next agitated for two hours at 40 to 45 degrees Celsius. A polyvinyl chloride mold created using a casting solution was filled with the resultant DNSPA membrane solution. The amount of solution that is injected into the mold can be adjusted to control the thickness of the membrane. The resultant sample was then dried in a special oven at 45 °C and 30-55% air humidity in order to evaporate the solvent. When the DNSPA membrane had lost 45-55% of its weight, it was cleaned by submerging it in DI water. It was then dried once more for six hours at 45 to 50 °C in the oven. Additionally, DNSPA membrane production was carried out using various complements and circumstances.

Characterization

Infrared spectrum (IR) of synthesized DNSPA membrane and raw materials

Based on the relevant literature, the study of a substance's infrared spectrum was first investigated. The SHIMADZU IR-Fure spectrophotometer, made in Japan, was used to investigate the infrared spectra of the synthesized DNSPA membrane as well as the raw materials DNS and PA at 400 and 4500 cm⁻¹. The analysis based on the IR spectrum is presented in Figures 5-6.

Scanning Electron Microscope (SEM)

A TouchScope electron microscopy (SEM) campaign from China JEOL Ltd. used JSM scanning to examine the morphological structure of the membrane. Using SEM, the porosity and elemental analysis of thin membranes were ascertained The analysis of results obtained based on SEM is presented in Figures 7-8.

Results and Discussion

IR spectroscopic analysis of substances

DNSPA membrane and IR spectrometer of dinitracelluloses were obtained. The results obtained are analyzed and illustrated in Figures 5-6.

Valence vibrations of the O-NO2 bonds in the area interval of 1647.21 cm-1, the C-O-C-bonds in the area interval of 1271.09 cm-1, and 1116.78 cm-1 are found in the values in Figure 5. Valence vibrations of the -C-OH bond in the cm-1 region, the >CH-bond in the 1101.35 cm-1 region, and the >CH2 bond in the 731.02 cm-1 region are all clearly visible. This suggests that the dinitrocellulose polymer is responsible for all valence fluctuations in the data.



Figure 5 – The IR spectrum of synthesized DNS.

In Figure 6's values, the valence vibrations of the -CH= bonds are located in the area of 2929.87 cm-1, the valence vibrations of the -O-NO2 bonds are located in the area of 1722.43 cm-1, the valence vibrations of the Ar-NH-bonds are located in the range of 1247.94 cm-1, the valence vibrations of the -C–O–C–bonds are located in the range of 1247.94 cm-1, and the >CH-bond is located in the range of 1205.51 cm-1. Valence vibrations of >CH2 bonds are visible in the region of 731.02 cm-1. It is evident that the valence vibrations listed below match the compounds' chemical formulas.



Figure 6 – IR-spectrum of DNSPA synthesized on the basis of modification of dinitrocellulose with aniline.

Scanning electron microscopic (SEM) analysis of DNSPA ion exchange membranes

The surface morphology, pore structure, and elemental analysis of the ion exchange membrane were studied on the basis of the scanning electron microscope (SEM) device - showed porous structures on the surface and cross-sections of the membrane synthesized on the basis of DNSPA. If we look at the results, we can notice that small irregular pores of different sizes were formed in the membrane with the help of pore formers during the synthesis of this membrane.





Figure 7 – In the SEM photo of the prepared DNSPA membrane: a) a photo taken from the upper part of the membrane, b) a photo taken from the cross-sectional part of the membrane.



Figure 8 – Energy dispersive spectrum and compositional element ratios of the ion exchange membrane synthesized on the basis of polyanilinenitracellulose.

The SEM images show that the surface morphology of the synthesized membrane with nano- and

micropores is suitable for use in the ion exchange process.

Conclusion

DNSPA membrane was synthesized based on dinitrocellulose and polyaniline in different mass ratios and conditions. The bonding nature of its atoms was studied by Infrared Spectroscopy (IR) and its pores characteristic of ion exchange membranes were determined by Scanning Electron Microscope (SEM). Using various solvents and pore formers, nano and microporous membranes were obtained.

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