ABSTRACT

of the thesis for the degree of philosophy doctor (PhD)

by the specialty 6D074000 - Nanomaterials and Nanotechnology

Seitzhanova Makpal Azizovna

Synthesis and application of membrane technologies for desalination of seawater

General characteristics of the research

Graphene-based membranes are a great and promising field of nanotechnology for desalination. This important area of nanotechnology is constantly evolving and is gaining more and more practical value every year.

The dissertation is devoted to the development of a technique for the synthesis of graphene membranes from rice husks and its application for desalination of seawater.

The first chapter is devoted to a literature review of the main and alternative methods of desalination of seawater. The modern achievements in the desalination industry, world experience and trends in the development of membrane technologies are considered. A review of the literature on the cost of desalination, environmental risks, the health effects and development of the desalination process is presented.

The second chapter of the dissertation presents the used synthesis methods and analytical techniques. The methods used in the work were: pre-carbonization of rice husk, desilication of carbonized rice husk with NaOH, activation of carbonized rice husk with KOH and exfoliation. Modern methods of analysis were used: scanning and transmission electron microscopy in combination with an energy dispersive X-ray analysis (EDAX) detector, mass spectroscopy, elemental analysis, Raman spectroscopy on samples, thermogravimetric analysis and infrared spectroscopy.

The third chapter presents the results of the synthesis of graphene layers from rice husks and the study of the physicochemical characteristics of the obtained materials.

The fourth chapter presents the results of the production of graphene membranes by vacuum filtration and immersion precipitation. In addition, desalination efficiencies of the obtained graphene membranes are presented.

The research results are presented in the form of one article in a journal that has an impact factor according to the Scopus information database, three articles in journals recommended by Committee of the Control in Field of Education and Science, 11 abstracts at International conferences and symposia, also one innovative patent of the Republic of Kazakhstan for a utility model.

Actuality of the research theme

Membranes and membrane technologies are used for the production of drinking water from the sea, for the treatment of industrial effluents and the extraction of valuable components, for the concentration, purification or fractionation of macromolecular mixtures in the food and pharmaceutical industries, as well as for the separation of gases and vapors. They are also key components in energy conversion systems, as well as in artificial organs and drug delivery devices. The membranes used in various fields of application vary greatly in their structure and functions, as well as in the method of their operation, therefore it is difficult to obtain a sufficiently complete and complete overview of the entire area of membranes and membrane-based processes.

In recent years, the concept of nanotechnology has also entered the field of membrane production. Indeed, by adding nanofunctional materials to conventional membrane materials, it has become possible to modify and optimize membrane performance. In particular, in recent years various attempts have been proposed to use the properties of graphene also in membrane technology.

According to the estimates of the Asian Development Bank, the average volume of drinking water supplied to the population is decreasing at a rate of 3-5% per year due to the continuing deterioration of the existing infrastructure. One of the most promising approaches to solving the problem of water scarcity is the desalination method, which can provide high-quality water without harming natural freshwater ecosystems. Seawater makes up 97.5% of all water on the planet. To date, desalination of seawater has been carried out mainly with the help of multi-stage distillation and reverse osmosis. These types of desalination plants consume large amounts of heat and electricity, resulting in a significant amount of greenhouse gases. Desalination of seawater on a large scale, more than 50% of the total volume, is provided by reverse osmosis systems, due to technical efficiency. However, this technology requires high capital costs, which complicates its widespread use.

In this regard, the relevance of the research topic of the doctoral dissertation on the development of a method for producing new graphene membranes from rice husks and the study of their physicochemical and desalination properties is undoubtedly relevant.

Objects of study

Rice husk, carbonized rice husk, graphene layers, graphene-based membranes.

Subject of scientific research: Obtaining graphene materials by pre-carbonization followed by chemical activation of rice husk, for use in the desalination of seawater.

The purpose of the thesis

The aim of this work is to obtain graphene materials from rice husks by thermochemical activation followed by the production of nanoporous membranes for desalination of seawater.

To achieve this goal, the following tasks:

1) Obtaining graphene materials from rice husk. Development of optimal conditions for carbonization and activation, selection of the composition for obtaining nanoporous graphenes from rice husk;

2) Study of the physicochemical properties of obtained graphene materials;

3) Production of desalination membranes from graphene materials;

4) Determination of the effectiveness of graphene membranes in the sorption of various salts from water.

Scientific novelty

For the first time, the following results were obtained:

- A new simpler and more environmentally friendly method is proposed for producing graphene materials from rice husks by carbonization and chemical activation. Graphene materials were obtained and investigated.

- The maximum specific surface area of graphene materials determined by the BET method was 2818 m^2/g. The study of the surface and sorption properties of materials obtained under various conditions using modern methods made it possible to identify patterns of synthesis of graphene materials depending on temperature (850°C) and time (2 h) of carbonization and chemical activation with KOH (1/4 and 1/5).

- Physico-chemical studies of synthesized graphene membranes based on rice husks showed the possibility of obtaining new nanoporous membranes for desalination of seawater.

Scientific and practical relevance of the research

The results presented in this paper develop the representation about membranes based on nanomaterials - graphenes. Graphene materials obtained from rice husks can be used as sorbents and filters of treatment facilities, for the manufacture of electrodes of supercapacitor.

The production of graphene materials for membranes is very advantageous for solving desalination problems. Vacuum filtration graphene membranes can desalinate seawater up to 99% and can adsorb heavy ions in water.

The main provisions for the defense:

1. Carbonization of rice husk and activating agent at a ratio of 1: 5 (g/g) results in a 4-5-layer graphene structure. It was found that such an activation ratio of 1: 5 is optimal and provides a higher graphene content than other ratios of rice husk and activating agent.

2. Graphene materials synthesized from rice husk are highly porous with an average pore size <100 nm, contains 80-90% carbon and has a specific surface area of 2500-3000 m^2/g.

3. FTIR results showed that the functionalization of graphene with sulfuric acid for 24 hours leads to the introduction of sulfonic groups in the membrane.

4. Graphene membranes obtained from rice husk by vacuum filtration desalinate seawater to 99%.

Research methods

In carrying out research on the topic of the dissertation, the following synthesis and research methods were used: methods of preliminary carbonization and activation, desilication, exfoliation, X-ray diffraction method, scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, IR spectroscopy, thermogravimetric analysis, atomic absorption flame emission spectrophotometry.

The source study base and research materials are 112 sources of literature on nanotechnology and membrane synthesis based on graphenes, methods for the synthesis of nanoporous carbon materials, possible activation and carbonization mechanisms.

The theoretical significance of the study. The main regularities of the synthesis of membranes based on graphene by vacuum filtration and immersion deposition are established.

The main results of the dissertation research are published in 16 scientific papers, including:

- in 1 article published in an international scientific journal included in the Scopus database;
- in 3 articles published in magazines recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- in 11 abstracts of reports at foreign and republican international conferences, and symposia;
- in 1 innovative patent of the Republic of Kazakhstan for a utility model.

The structure and scope of the thesis.

The dissertation consists of an introduction, four chapters, a conclusion, as well as a list of sources used from 112 items. The work is presented on 85 pages, contains 49 figures, 14 tables and 5 formulas.

According of the results of the dissertation research, the following conclusions are made**:**

1. Received graphene materials from rice husks. It was found that carbonization/activation of rice husk leads to the formation of a mixture of graphene layers and amorphous carbon. With the optimal ratio of rice husk and activating reagent

(1:5), the relative amount of graphene component increases. The results of Raman spectroscopy indicate that in the samples Gr(1/5) and Gr(1/4) the ratio I_G/I_{2D} is close to 1.56 ± 0.10, which corresponds to the 4-5 layer state of the graphene film.

2. It was found that the obtained graphene material is highly porous with an average pore size <100 nm, contains 80-90% carbon and has a specific surface area of 2500-3000 m^2/g.

3. Graphene membranes deposited on a cellulose acetate membrane were obtained by vacuum filtration and immersion deposition. It was found that the membranes obtained by vacuum filtration have a more microporous and nanoporous structure with a dense upper layer and water permeability of 4, 5 and 30 ml/min compared with membranes obtained by immersion deposition.

4. Desalination properties of graphene membranes were tested for salts of NaCl, KCl, $MgCl_2$, $CaSO_4$ and $MgSO_4$. It was revealed that after filtration of salt solutions through graphene membranes, their concentration decreases till 99.5% (NaCl), 99.8% (KCl), 99.5% ($MgCl_2$), 77.6% ($CaSO_4$) and 99.3% ($MgSO_4$).

Assessment of the completeness of the solutions to the tasks

The tasks set in the work are completely solved. Graphene materials are obtained from rice husks and used as membranes for desalination of seawater. The results are reliable and reasonable, since all measurements were carried out on calibrated instruments using standard methods.

Part of the study was conducted at the Federico II University of Naples in Naples (Italy) in the group of prof. Marco Triffuogy and under the foreign scientific supervisor, PhD, Professor Roberto Di Capua: performing scanning electron microscopy (SEM) coupled with energy dispersive x-ray Analysis (EDAX) detector, ICP Mass Spectroscopy, elemental analysis, Raman Spectroscopy on samples. The second part of study was performed in laboratories of Institute of research for combustion, under the continuous supervision of Dr. Michela Alfe and Dr. Valentina Gargiulo: purification and functionalization (to add sulfonic groups) processes of the sample, and then in the preparation and first characterizations of prototypes membranes for desalination purposes by using instrumental analytical techniques such as EDAX-SEM, ICP-MS, elemental analysis, thermogravimetric analysis (TGA) and infrared spectroscopy (FTIR).

Assessment of technical and economic efficiency proposed in the dissertation

The results obtained in the framework of this dissertation can be proposed for producing graphene membranes synthesized based on rice husks. An advantage of the proposed method for the synthesis of graphenes is the relative availability of the initial reagent - rice husk. Rice husk-based graphene materials can also be used as sorbents and filters of treatment facilities, for the manufacture of supercapacitor electrodes.

Assessment of the scientific level of the work performed in comparison with the best achievements in this field

Currently, most researchers use commercial graphene for desalination of seawater, which is one of the most expensive materials from a commercial point of view (1 g of graphene oxide costs $ 160). This work may open up prospects for the production of domestic materials based on graphene from rice husks as affordable, cheap and effective sorbents for wastewater treatment. The results obtained are of practical interest for obtaining new improved nanomaterials for the purification and desalination of water.

In addition, the scientific level of the presented dissertation complies with international standards for research conducted in the selected field. This is evidenced by a good level of publications, the presentation and discussion of the results of work at international symposia and conferences.