Commercial Gooseberry Buds Extract Containing Membrane for Removal of Methylene Blue Dye from Synthetic Wastewaters

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In this work, a synthetic effluent containing Methylene blue dye has been treated by novel membrane enriched with commercial gooseberry buds extract using a mini-laboratory electrodialysis cell. The electrodialysis system was operated at various time and constant voltage applied at electrodes. Methylene blue removal percentage (CR %) and energy consumption (E.C.) were calculated. The obtained results showed that pH increase in solution and lead to an increase of deprotonated methylene groups, which may favor methylene dichloride complex formation. The values of CR % and E.C. increased with time. The high value of CR % was obtained at 60 min(CR > 89 %). The membranes were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Environmental Scanning Electron Microscopy (ESEM).

Keywords: Methylene blue, wastewater, plant extract, membrane

Synthetic dyes containing effluents resulting from different industries such as textile, paper, rubber, leather, cosmetic, food and drug have been extensively discharged into the environment or reused. The majority of dye containing waste waters results from activities which use dyes to color their products. The presence of dyes in effluents is a major concern due to their high occurrence, persistence and toxic impact on the environment and human health [1-3].

Several methods, such as precipitation, membrane filtration (reverse osmosis, ultrafiltration, nanofiltration and electrodialysis) coagulation, coagulation-flocculation, electrochemistry, ion exchange, chemical oxidation, and adsorption, were developed to remove dissolved dyes from wastewater [1, 2, 4-7].

Reverse osmosis, ultrafiltration and nanofiltration are more suitable for treatment of textile dyes contaminated waste waters, but the major drawback is the flux, that decline in permeate flux due to the polarization concentration and fouling processes [6-8].

Coagulation–flocculation process has been paid a great deal of attention due to its very high pollutant removal efficiency. Unfortunately, the major drawback of the flocculation treatment is that it yields a large amount of sludge, which creates disposal problems, thus increasing the operation costs [7, 8].

Adsorption is an effective process in dyes removal, but adsorbent with large specific surface area, high adsorption capacity, and special surface reactivity must be carefully chosen and the regeneration of adsorbent must be done [8].

Electrochemical methods were used for the treatment of textile dyes waste waters because of several advantages such as: environmental compatibility, versatility, low energy consumption, low investment, easy replacement of membranes and electrodes and variables which can be easily controlled [7].

Electrodialysis used to transport salt ions from one solution through polymer membranes is an important membrane separation process. This process was used in many fields such as: seawater and brackish water desalination [9], metal ions recovery [10, 11], removed alkali and alkaline earth metal halides from aqueous dye solutions [12], treatment of organic dye [13, 14] etc.

Natural products, such as plants extract, either as pure compounds or as standardized extracted, were used for traditional medicine contain a wide range of substances that can be used to treat chronic as well as infectious diseases [15, 16].

The gooseberry (scientific name *Ribes nigrum*) is a woody shrub grown for its berries. Gooseberry fruits (9.5 to 10% fruits) contain sugars, organic acids: citric and mail, protein 2.1 mg%, calcium 3.8 mg%, iron 2.1 mg%, phosphorus 3.5 mg%, potassium 316 mg%, sodium 28 mg%, zinc 3.5 mg%, copper 1.5 mg% chlorine 3.4 mg%, flor 0.01 mg%, carotenoids, vitamin B1, B2, B6, 150 mg% vitamin C, flavonoids, etc. and are not only valuable as food but also as medicine. These fruits have tonic effects, increased resistance body at infectious processes, stimulates the formation of red blood cells, and influences the growth and formation of bones at children. The currant fruits increase diuresis and elimination of uric acid and urinary calculi [17].

Methylene blue is a cationic dye that at room temperature appears as a solid, odourless, dark green powder, when dissolved in water yield a blue solution [18].

Methylene blue is used in textile dying especially for cotton and silk fibers, in aquaculture and tropical fish hobbyists as a treatment for fungal infections, as redox indicator in analytical chemistry, by biologists as a dye that assists in the identification of bacteria and in some medical treatments (Alzheimer's dementia; cancer photodynamic treatment, as a treatment for methemoglobinemia, as a

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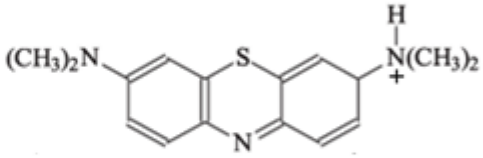
Characteristics	Indication
Other names	Desmoid piller, Desmoidpillen, Panatone, Urolene Blue, and Vitableu
IUPAC name	3,7-bis(Dimethylamino)-phenothiazin-5-ium cloride
Chemical formula	$C_{16}H_{18}ClN_3S$
Molecular structure	
Molecular weight	319.85 g/mol
Absorption maximum (water)	670 nm
Color	Dark green crystals or powder from chloroform-ethyl ether
Melting temperature	180^0

Table 1
CHARACTERISTICS OF METHYLENE BLUE DYE

drug for the treatment of manic-depressive psychosis - schizophrenia) [19-23]. Some characteristics of Methylene blue dye are given in Table 1 [8, 23, 24].

This study was aimed to determine the removal percentage of Methylene blue dye from synthetically prepared solutions with a mini-laboratory electrodialysis cell using novel polymer membranes containing commercial gooseberry buds extract. The prepared membranes were characterized by Fourier Transforms Infrared (FTIR-ATR) and Environmental Scanning Electron Microscopy (ESEM) techniques.

Experimental part

Materials and methods

Methylene blue was purchased from Fluka. Acrylonitrile (AN) and vinyl acetate (AcV) were supplied by Merck and distilled out to remove the inhibitor. Polyvinyl alcohol was prepared in laboratory by vinyl acetate solution polymerization in methanol, followed by methanolysis conducted using sodium hydroxide as catalyst. Dimethyl sulfoxide (DMSO) and isopropyl alcohol (IsOH) were supplied by Fluka. Sodium chloride (NaCl) was supplied by Sigma-Aldrich. The commercial plant extract (gooseberry extract) was purchased from Hofigal, Romania. Distilled water was used for solution preparation. All chemicals used in the current study were of analytical grade.

The experiments were carried out in a mini-laboratory electrodialysis cell (fig. 1) consisting of three polypropylene compartments (anodic, central and cathodic) in configuration with two parallel pure lead electrodes and two polymer membranes. In this electrodialysis process the dye degradation occurred in cathodic compartment, indicated by the low values of dye concentration registered here.

The membrane and electrode surface area were for each one of approximately 14.09 cm^2. Each compartment has an inside diameter, external diameter and thickness of approximately 42.3 mm, 89.2 mm and respectively 10.7 mm. All the compartments (approximately total volume of 45.22 cm^3) were filled with Methylene blue $5 \cdot 10^{-5}$ M synthetic solutions. The experiment was carried out at a constant voltage of 10 V. The operation time was of 30 and 60 min for each experiment.

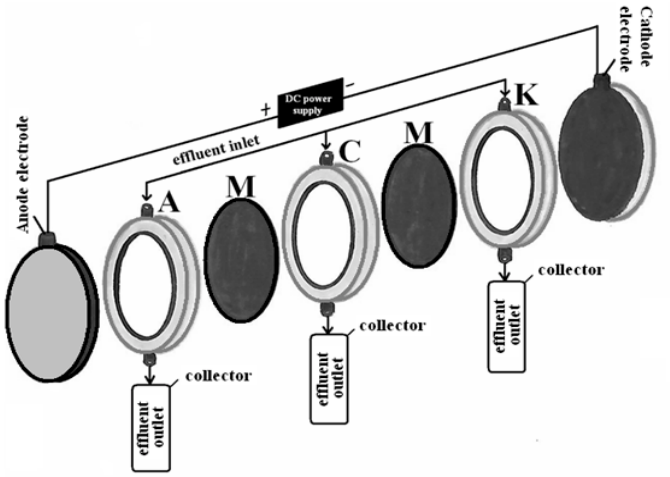


Fig. 1. Scheme of mini-laboratory electrodialysis cell with three compartments and membrane A - anodic compartment, C - central compartment, K - cathodic compartment, M - membrane

Methylene blue solution with an initial concentration of $5 \cdot 10^{-5}$ M was used in electrodialysis cell. In order to adjust the solution conductivity, 1 g/L sodium chloride (NaCl) was dissolved into dye synthetic solution. Sodium chloride was used to increase the electrical conductivity of the wastewater.

A laboratory model DC power supply apparatus (Protek, Germany) was used to maintain a constant voltage. The membrane thickness and dimensions of electrodialysis cell was performed with a stainless steel digital calliper with Metric/SAE/Inch-Fractions (China).

The *p*H value measurements were performed with a Hanna Instruments pH meter.

Preparation of membranes

A mixture composed of 85% acrylic copolymer (80% AN – 20% AcV ratio) and 15% polyvinyl alcohol was dissolved in 42 mL of DMSO with constant stirring at 100°C for 2 h. To this homogenous solution, 2 mL of commercial gooseberry buds extract (Ribes nigrum, containing 45 %vol. ethyl alcohol) (Hofigal, Romania) were added with regular stirring at 100 °C for another 3 h. A viscous and clear solution was obtained. The casting solution was allowed to cool down to room temperature and was kept for 24 h in a

Membrane sample	Notation	Thickness of sample, mm
Membrane with commercial extract, blank	A1	0.35
Membrane with commercial extract, tested at 30 min	A2	0.38
Membrane with commercial extract, tested at 60 min	A3	0.36
Membrane without commercial extract, blank	B1	0.33
Membrane without commercial extract, tested at 30 min	B2	0.34
Membrane without commercial extract, tested at 60 min	B3	0.34

Table 2
MEMBRANES NOTATION

sealed flask to remove micro bubbles formed in the solution.

Polymer solution, homogenized and without aer bubbles, was cast at room temperature on a glass plate and a draw-down technique was used to produce films. The films were drawn with special knifes, each one having different slits (200, 250 or 360 μm), leading to three wet films thicknesses. These films were quickly immersed in the coagulation bath containing a 10% water– 90% IsOH mixture and kept for 30 min in order to stabilize their structure. The polymer membranes with gooseberry buds extract were obtained by wet-phase inversion method. The phase inversion occurred at room temperature. Membranes (table 2) were examined before and after exposure to electrodialysis process.

Characterization of membranes

FTIR spectra for prepared membranes were recorded using a FT-IR spectrophotometer (Tensor 37, Bruker) and the attenuated total reflectance (ATR, Golden Gate unites) technique. The wavelength range was from 4000 to 400 cm^{-1} at 64 scans per spectrum, with a resolution of 4 cm^{-1}. The morphological analysis of investigated membranes was carried out using an Environmental Scanning Electron Microscope (FEIQuanta 200).

Result and discussions

Electrochemical experiments

Electrolysis of Methylene blue dye in the presence of sodium chloride generates active species of chlorine, in order to catalyze their degradation reaction [24]:

$$2Cl^- - 2e^- \rightarrow Cl_2 \quad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2)$$

The studies conducted by other researcher [25] showed that the electrolysis of Methylene blue with NaCl, formed a novel compound (leuco dye 4,6-dichloro-7-dimethylamino-3*H*-phenothiazin-3-one) by the combined effects of chlorination at C_4 and C_6 and the replacement of dimethylamino group with an oxygen atom at C_3 (fig. 2).

Measurement of pH value

The *p*H values for samples taken from anodic compartment (A), central compartment (C) and cathodic compartment (K), after 1 h of electrochemical process, are presented in table 3.

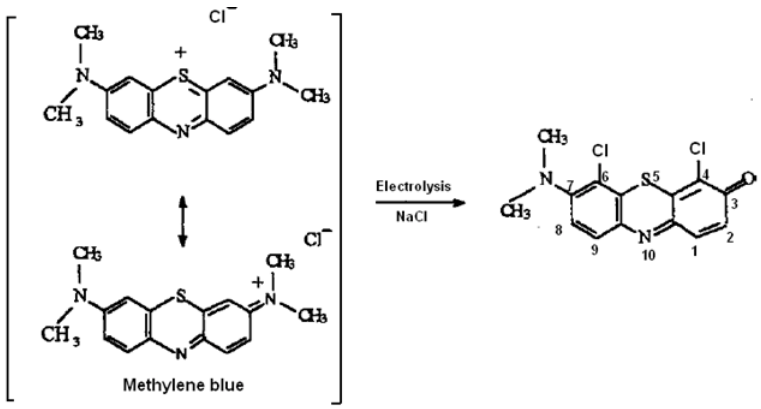


Fig. 2. Electrolysis of Methylene blue in the presence of NaCl with formation of novel compound [25]

Table 3
THE *p*H SOLUTIONS VALUES BEFORE AND AFTER 1 H OF ELECTROCHEMICAL PROCESS

Time, min	Sample	Membrane without commercial extract plant			Membrane with commercial extract plant		
0	Feed wastewater	7.62					
	Treatment wastewater	A	C	K	A	C	K
30		4.78	6.65	12.26	3.72	6.42	10.83
60		5.28	11.56	12.37	4.93	10.17	11.56

Methylene blue is a cationic dye which produces cations (C^+) and reduced ions (CH^+) in water.

From table 3 one may notice that the *p*H value of treated solution increases in the cathodic compartments possible due to the increase number of negatively charged site thus resulting in an increased dye adsorption. Moreover, the increase in *p*H solution can lead to an increase in deprotonated methylene groups which may favors the formation of methylene dichloride complex by strong electrostatic attraction between the positively charged cationic dye molecules [26-29]. The *p*H value of the treated solution for membrane with commercial extract was lower in comparison with *p*H value of treated solution for the reference membrane, possible due to surface complex, derived from Mehylene blue adsorption on the sites of adsorbed hydroxyde ions. This surface complex is possible not to be very steady and could be destroyed by lowering the *p*H value [30]. The presence of chloride ion in solution promotes the electrogeneration of active chlorine species as oxidant mediators. Several investigations have reported that at *p*H value > 9 more Methylene blue molecules are adsorbed on membrane surface and can be desorbed at *p*H value of 4.0 [26-30].

Determination of Methylene blue dye concentration

A stock solution of 10^{-5} mol/L of Methylene blue (MB) was prepared by dissolving accurately weighted dye in distilled water. From the stock solution, different volumes of methylene blue were introduced in six conical flasks with a capacity of 100 cm^3 in order to obtain the following concentrations $0.05 \cdot 10^{-5}$; $0.1 \cdot 10^{-5}$; $0.5 \cdot 10^{-5}$; $2 \cdot 10^{-5}$; $4 \cdot 10^{-5}$; $8 \cdot 10^{-5}$ mol/L. A Metertech SP-830 type spectrophotometer was used in order to determine the absorbance at the maximum absorbance wavelength (668 nm) of Methylene blue dye.

The calibration curve obtained by plotting the absorbance against concentration was linear as shown in figure 3.

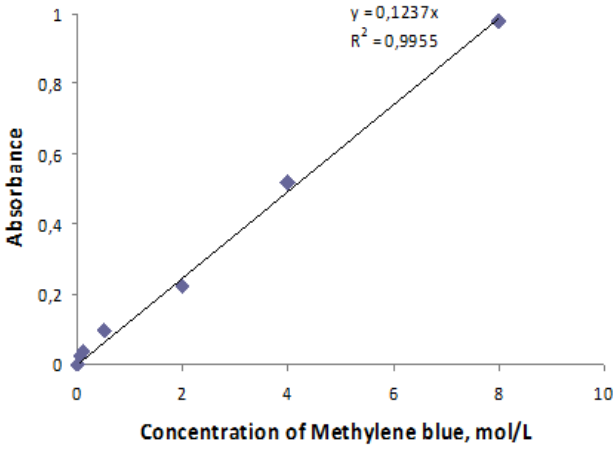


Fig. 3. Calibration curve for Methylene blue dye

After each experiment all samples from the central compartment were filtered using Whatmann filter paper with a pore size of 0.45 μm, in order to minimize the interference of fine particle in suspension with the analysis. The filtrates were analyzed for residual concentrations of Methylene blue using an UV-visible spectrophotometer Metertech SP-830 at a wavelength of 668 nm.

In order to evaluate the efficiency of electrochemical process in removing Methylene blue, the percentage of sorption (removal percentage) was determined according to the eq. (3) [8, 13, 27, 32]:

$$CR\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

where: C_o and C_t are the initial dye concentration and concentration of dye at time t in solution in the central compartment (mol/L), respectively.

The energy consumption (E.C.) during electrodialysis process is given by eq. (4) [13, 32, 33]:

$$E.C. = \frac{1}{V} \cdot \int_{t=0}^{t=t_{fin}} U(t) \cdot I(t) \cdot dt \quad (4)$$

where: E.C. is the energy consumption (kWh/m^3), I is the applied current intensity (A), E is the voltage (V), t is the time (h), t_{fin} is the final time (h) and V is the volume of cathodic compartment (m^3).

The values of CR % and E.C. are presented in table 4.

In comparison to common adsorption, where the process can be limited by diffusion into the pores of adsorbent, in the membrane process, convection mass transport through membrane pores may exceed this problem. The convection mass transport through membrane pores, allows adsorption and separation processes to be very fast [34].

In the presence of commercial gooseberry buds extract, the retention has been significantly increased to 89.17% in comparison to membrane without commercial gooseberry buds extract (42.6%), after 1 h, because the Methylene blue molecules are much smaller than the membrane pores (table 4). This retention could be assigned to the adsorption of Methylene blue dye at the surface or in the pores of membrane. Moreover, this confirms that complexes were formed due to binding of Methylene blue molecules on polymer membrane matrix through electrostatic interaction resulting in the enhancement of the electrochemical process. The efficiency of Methylene blue adsorption increases as the *p*H is increased.

From table 4 it can be seen that the E.C. values increased with increasing time. The E.C. value was higher after 60 min, probably due to ions transport in the presence of large dye macro-cations and increase of cell resistance. The E.C. value for membrane without commercial gooseberry buds extract was higher in comparison with membrane with commercial gooseberry buds extract possible due to the hydroxyl radicals consumption, diminishing the CR% and consequently, rising the energy consumption.

Time, min	Experiments without commercial plant extract		Experiments with commercial plant extract	
	CR, %	E.C., kWh/m^3	CR, %	E.C., kWh/m^3
30	11.56	21.01	44.38	18.25
60	42.60	32.90	89.17	30.13

Table 4
THE VALUE OF CR % AND E.C. AT DIFFERENT APPLIED CELL CURRENT INTENSITY AFTER 1 H OF TREATMENT

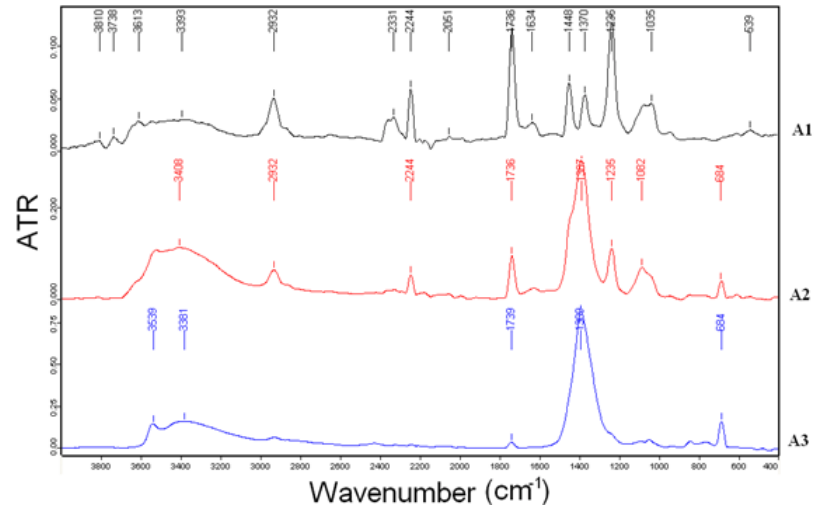


Fig. 4. FTIR-ATR spectra of membrane with commercial gooseberry buds extract before and after electrochemical process at various times

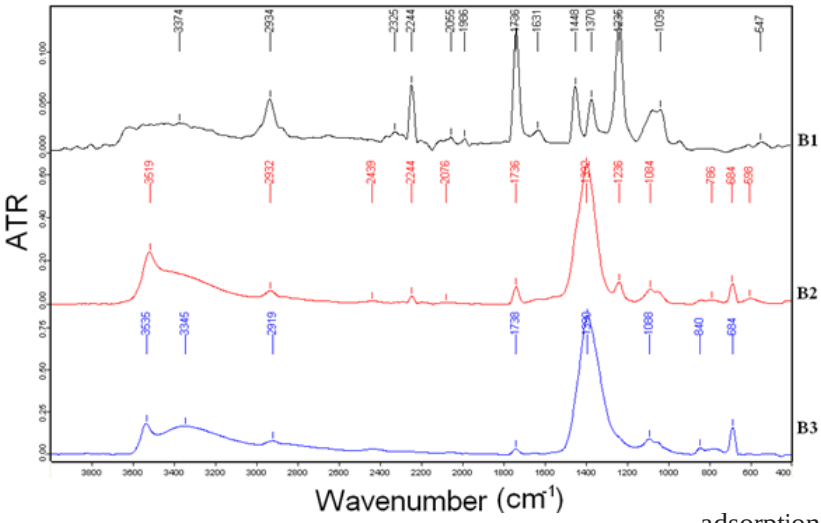


Fig. 5. FTIR-ATR spectra of membrane without commercial gooseberry buds extract before and after electrochemical process

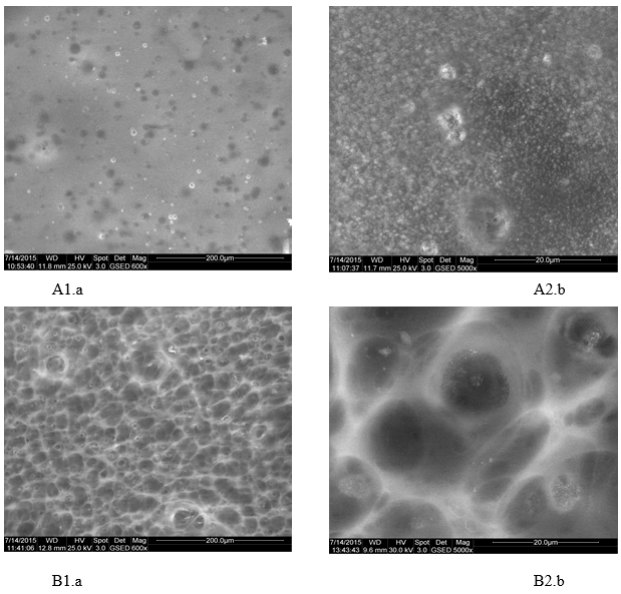


Fig. 6. SEM images of prepared membrane with (A1.a, b) and without plant extract (B1.a, b)

Characterization of membranes

The membranes samples were examined before and after the exposure to the electrochemical process (Figures 4 and 5).

FTIR spectrum showed peaks around 3000–3500 cm^{-1}, which corresponds to the stretching vibration of O-H. The peak observed at around 2932 cm^{-1} can be assigned to the aromatic C-H group (asymmetric stretching vibration) [13, 35]. This peak intensity is decreased after Mehylene blue adsorption which indicates that C-H bonds are less in the structure of membrane.

The specific peak at 2244 cm^{-1} could be assigned to –Ca≡N (absorption band of poly-acrylonitrile from copolymer). The peak at 2331 cm^{-1} is attributed to the formation of hydrogen bonds between the copolymer and the commercial extract. Moreover, thus indicating that the grafting reaction occurred successfully and the composite material is a crosslinked copolymer from raw materials.

The peaks that appears at 1736 cm^{-1} was assigned to –C=O stretching vibration and the peak at 1634 cm^{-1} is associated with the skeletal vibration of aromatic C-C bonds. The peak that appears at 1370 cm^{-1} is shifted to higher wave numbers (1390 cm^{-1}) which can be due to N-H deformation vibration [13, 35]. The peak at 1235 cm^{-1} that appears at time zero and 30 min was assigned to í(N–C) stretching vibrations. At 60 min this peak disappears possible due to the adsorption between the dye molecules and the polymer membranes. At this time the removal percentage of dye was higher.

The surface morphological of the prepared membranes before being used in the electrodialysis cell was determined using ESEM, and shown in figure 6.

From table 4 it can be seen that the E.C. values increased with increasing time. The E.C. value was higher after 60 min, probably due to ions transport in the presence of large dye macro-cations and increase of cell resistance. The E.C. value for membrane without commercial gooseberry buds extract was higher in comparison with membrane with commercial gooseberry buds extract possible due to the hydroxyl radicals consumption, diminishing the CR% and consequently, rising the energy consumption.

Characterization of membranes

The membranes samples were examined before and after the exposure to the electrochemical process (figs. 4 and 5).

SEM images of the top surface of prepared membranes are presented in figure 6 at different magnifications. It can be seen that irregular surface structure and many pores in the surface are depicted in the blank membrane. In figure A1.a,b it can be seen that the commercial plant extract reduced the amount of fissures and were distributed relatively uniform in the bulk of membrane matrix providing superior conducting regions [36]. The membrane containing commercial gooseberry buds extract showed compact cracks, which may be attributed to polystyrene crosslinked with divinylbenzene, polyvinyl alcohol and ethyl alcohol that caused the membrane to become more compact.

Conclusions

The mini-laboratory electrodialysis cell for removal of Methylene blue dye from synthetic solutions was successfully applied in conjunction with membrane enriched with commercial gooseberry buds extract. It was found that the *p*H value increases in the cathodic compartments possible due to the increase of negatively charged site number, leading to an increase of dye adsorption. The percentage of Methylene blue removal was over 89 % and the energy consumption of 30.13 kWh/m^3 after 1 h of electrodialysis, for membrane enriched with commercial gooseberry buds extract.

The peak at 2331 cm^{-1} in the FTIR-ATR, indicated that the plant extract was successfully incorporated in the membrane matrix. The surface morphologies showed that the extract reduced the amount of fissures, was compatible with polymer blend and was relatively uniform distributed in the bulk membrane matrix.

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