Efficient removal of Indigo Carmine dye by a separation process
Simona Caprarescu, Alexandra Raluca Miron, Violeta Purcar, Anita-Laura Radu, Andrei Sarbu, Daniela Ion-Ebrasu, Leonard-Ionuț Atanase and Marius Ghiurea

ABSTRACT
This study is aimed at developing an innovative approach for Indigo Carmine dye removal from synthetic solutions by electrodialysis, carried out using ion exchange membranes. The batch electrodialysis system was operated at various current intensities: 0.05, 0.1 and 0.15 A. The pH and conductivity of solutions were measured before and after using electrodialysis process. The colour removal efficiency (CR %) was determined by spectrographic analysis and the energy consumption (EC) was calculated. The obtained results show that the pH of treated solution increases due to the increase in solution conductivity. Moreover, the values of CR % and EC increase when increasing current intensity. The optimal value was obtained at 0.15 A (CR > 97%). The membranes were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy.

Key words | dye, environment, Indigo Carmine, membrane, separation process, wastewaters

INTRODUCTION
Synthetic dyes are extensively used in various fields and their presence in water and wastewater represents a serious environmental issue and an important health threat due to their high occurrence, persistence and toxic impact. In addition, dyes have direct and indirect toxic effects on humans as they are associated with cancer, jaundice, tumours, skin irritation, allergies, headaches, concentrating troubles, nausea, dizziness, breathing difficulty, irregular heart beat, and/or seizures (Hansa et al. 1999; Forgacs et al. 2004; Banerjee et al. 2007; Manu 2007; Secula et al. 2011; Karthik et al. 2014).

Many researchers have studied different techniques for Indigo Carmine and other dyes’ removal from wastewater including: adsorption (Forgacs et al. 2004; Mittal et al. 2006; Miron et al. 2015), ultrafiltration (Forgacs et al. 2004; Karthik et al. 2014), several oxidation processes (Banerjee et al. 2007; Manu 2007; Secula et al. 2011; Karthik et al. 2014),...

Coagulation or flocculation combined with flotation and filtration, precipitation, and electroflocculation, can all be used for removal of dyes from wastewater, but frequent problems are the high consumption of electrical energy and chemical reagents. Ultrafiltration and nanofiltration, filtration and separation processes, can be used for dye removal from wastewater, but fouling can cause difficulties in the membrane resulting in a decrease of the flux (Mozumder & Islam 2010; El-Ashtoukhy 2013; Karthik et al. 2014). Electrocoagulation has attracted great attention as an eco-friendly and cost-effective process, but its drawback is that it produces metallic hydroxide flocks inside the wastewater by electro dissolution of an iron or aluminium soluble anode (Bayramoglu et al. 2007; Secula et al. 2011; Garcia-Morales et al. 2013). The conventional biological wastewater treatment process is unsatisfactory in treating dye-containing wastewater due to low biodegradability of dyes (El-Ashtoukhy 2013). The advanced oxidation processes indicate good results for removal of dyes from wastewater, but are expensive. Methods like adsorption, ion exchange, chemical oxidation, and membrane filtration processes (nanofiltration, reverse osmosis, electrodialysis) are more expensive than biological treatment but are used for the removal of pollutants consisting in dyes that are not easily removed by biological methods (Forgacs et al. 2004; Mittal et al. 2006; El-Ashtoukhy 2013; Alqaragully 2014; Karthik et al. 2014). Reverse osmosis can be advantageously used for the treatment of textile wastewater taking into account several limitations such as design, pre-treatment stringency, and operating parameters are strictly adhered to avoid fouling of membrane modules (Abid et al. 2012).

Electrophoresis is a separation technique, defined as the differential movement of charged species (ions) by attraction or repulsion in an electric field, which can be used for the separation of a range of reactive dyes in textile wastewater. This powerful technique is reasonably easy and inexpensive, but all electrophoresis separations depend upon the charge distribution of the molecules being separated (Hansa et al. 1999).

Indigo Carmine or 5,5'-indigodisulfonic acid sodium salt is a dark blue, water-soluble powder. The molecular structure and some characteristics of Indigo Carmine are given in Table 1 (Bayramoglu et al. 2007; Secula et al. 2011). Indigo Carmine is used in the textile industry for the dyeing of denim and polyester fibbers and, in food industries, cosmetics industries, and pharmaceuticals industries as a diagnostic aid, as a redox indicator in analytical chemistry, and as a microscopic stain in biology (Mittal et al. 2006; Secula et al. 2011; Dogan & Turkdemir 2012; El-Ashtoukhy 2015).

Recently, electrochemical methods were used for wastewater treatment as they offer certain advantages, the main one consisting of environmental compatibility (due to the fact that its main reagent, the electron, is a clean reagent). Among other important advantages, we can mention: versatility, low energy consumption, the catalyst/electrode is immobilized (i.e. there is no need for the catalyst separation from the reaction mixture), variables (such as current and potential) are easily controlled allowing for automation of the process (Dogan & Turkdemir 2012; El-Ashtoukhy 2013; Karthik et al. 2014).

Traditional wastewater treatment technologies such as activated sludge processes were found to be substantially ineffective for manipulating wastewater containing synthetic textile dyes as a result of high chemical stability of these pollutants. The processes that involve chemical oxidation were reported to be very effective but the efficiency strongly depends on the nature of dye (Forgacs et al. 2004; Banerjee et al. 2007; Karthik et al. 2014).

Electrodialysis is an isothermal separation process based on charge transfer by using membranes and an electric field as the driving force. The use of electrodialysis is

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Indigo Carmine (3,3'-dioxo-2,2'-bis-indolyden-5,5'-disulfonic acid disodium salt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IUPAC name</td>
<td>3,3'-dioxo-2,2'-bis-indolyden-5,5'-disulfonic acid disodium salt</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C16H8N2Na2O8S2</td>
</tr>
<tr>
<td>Molecular structure</td>
<td><img src="image" alt="Molecular structure" /></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>466.36 g/mol</td>
</tr>
<tr>
<td>Absorption maximum (water)</td>
<td>608–612 nm</td>
</tr>
<tr>
<td>Composition</td>
<td>Dye content, ~85%</td>
</tr>
<tr>
<td>Reactive group</td>
<td>Amines, phosphines, and pyridines; ketones; hydrocarbons, aliphatic unsaturated; salts, basic</td>
</tr>
</tbody>
</table>
becoming more and more attractive because of several advantages such as operability at ambient temperature, ion-exchange membranes tolerate a higher level of chlorine and extreme pH-values, easy replacement of membranes, maximize water recovery with the minimum amount of energy and chemical usage, etc. Electrodialysis and ion exchange membranes are very much used in water and wastewater treatment, as well as in the food and chemical processing industries (Caprarescu et al. 2015). The electrodialysis was successfully employed for removing the anionic dye and mineral salt from aqueous solutions (Majewska-Nowak 2013). In comparison with reverse osmosis, electrodialysis systems become less economical when extremely low salt concentrations in the product are required. The current utilization efficiency typically decreases as the feed salt concentration becomes lower. In electrodialysis systems, investment and energy costs depend strongly on the feed water salt concentration (Strathmann 2013).

The textile dyes wastewaters contain high amount of salts and organic substances. In the membrane-based processes the salts are unable to pass through the membrane and remain in the concentrate. It was found that the salt rich permeate can be reused in the preparation of dye baths but the major problems are a drop in flux and membrane fouling. To overcome these problems and to achieve a high quality separation, different separation methods are combined. (Banerjee et al. 2007; Abid et al. 2012; Karthik et al. 2014; Liang et al. 2014)

The present study was aimed at investigating the ability of removing a cationic dye (Indigo Carmine) from synthetic solutions using an electrodialysis cell of our own construction device based on polymer membranes containing polyvinyl alcohol, acrylonitrile, vinyl acetate, dimethyl sulfoxide and small amounts of ion exchange resin (Purolite A500 with quaternary ammonium groups) and Hypersol-Macronet MN500 (with sulfonate acid groups). The prepared membranes were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

**EXPERIMENTAL**

**Materials and methods**

The experiments were carried out in an electrodialysis cell (Figure 1) consisting of three polypropylene compartments (anodic, central and cathodic) in configuration with two parallel pure lead electrodes and two different types of ion exchange membranes. The cell consists of a dilute compartment (central) and a concentrate compartment (anodic) formed by an anion exchange membrane placed next to the anodic compartment and a cation exchange membrane placed next to the cathodic compartment. In this electrodialysis process, the dye degradation occurred in the central compartment, indicated by the low values of dye concentration registered here.

The membrane surface area was approximately 16 cm². Each electrode surface area was approximately 16 cm². Each compartment has an inside diameter of approximately 4.5 cm, external diameter of approximately 8.9 cm, thickness with silicone gaskets of approximately 1.4 cm and thickness without silicone gaskets of approximately 1.1 cm. All the compartments (approximate total volume of 53 cm³) were filled with synthetic solutions of 5 × 10⁻⁵ M Indigo Carmine. Electrodialysis was carried out at different current intensity values: 0.05 A, 0.1 A and 0.15 A. The operation time was 1 h for each experiment. All the experimental tests were performed at room temperature (25 °C ± 1 °C).

Indigo Carmine stock solution with an initial concentration of 5 × 10⁻⁵ M (Sigma-Aldrich), used in an electrodialysis cell, was prepared by dissolving the dye in ultrapurified water. In order to adjust the solution conductivity, 1 g/L sodium chloride (NaCl) was dissolved into dye synthetic solutions. NaCl was used as support electrolyte to increase
solution conductivity and conductance and therefore resistance in the experimental tests was reduced.

The ion exchange membranes were made from vinyl acetate, acrylonitrile, polyvinyl alcohol, dimethyl sulfoxide (DMSO) provided by Fluka and ion exchange resin (Purolite A500 and Hypersol-Macronet MN500, Purolite, Romania). All chemicals used in the current study were of analytical grade.

A laboratory model DC power supply apparatus (Protek, Germany) was used to maintain DC current constant. The conductivities in milli-Siemens per centimeter (mS/cm) were measured for all the samples using an autoranging conductivity meter (PIERRON, France). After each experiment, pH of the samples was measured by a pH-meter supplied by HANNA Instruments (Germany). A stainless steel digital calliper with Metric/SAE/Inch-Fractions (China) was utilized to measure the membrane thickness and dimensions of the electrodialysis cell.

UV-Vis spectra (SP-830 Metertech) were recorded when using different dye concentrations. Solutions of different concentrations in Indigo Carmine dye solution were scanned at maximum absorption wavelength, namely 610 nm.

Preparation of membranes

The polymer membranes were obtained by wet-phase inversion method.

Firstly, the blend solution was prepared by dissolving 3 g of acrylic copolymer (80% acrylonitrile: 20% vinyl acetate), 0.8 g polyvinyl alcohol and 0.5 g of ion exchange resin powder (Purolite A500 or Hypersol-Macronet MN500, Purolite, Romania) in 42 mL dimethyl sulfoxide under constant and uniformly stirring at 100 °C during 2 h. The ion exchange resin powder was gradually added to the solution. After stirring, the homogeneous solution was kept at room temperature (25 °C ± 1 °C) for around 12 h in order to remove air bubbles. The polymer solution obtained was cast at room temperature onto a glass plate (70, 110, and 4 mm) using a casting knife. Afterwards, the glass plate with polymer solution on it was immersed in the coagulation bath (80% isopropyl alcohol: 20% distilled water) at room temperature until the membrane was detached from the glass plate. Prior to use, the prepared membranes were kept in the above-mentioned bath at room temperature for 24 h, in order to stabilize their structure.

The commercial resin Purolite A500 type is a macroporous type I strong base anion exchange resin with quaternary ammonium groups, whereas commercial resin MN500 type Macronet (hyper-crosslinked) is an adsorbents resin having sulfonic acid functional groups. Both ion exchange resins exhibited a polymer structure consisting of functionalized polystyrene crosslinked with divinylbenzene. The typical physical and chemical characteristics of these ion exchange resins used in the preparation of the membranes are presented in previous work (Caprarescu et al. 2015).

The morphologies of the prepared membrane (SEM) before being used in the electrodialysis system were observed by FEIQuanta 200 electron microscope. SEM images were recorded in low vacuum mode (Figure 2).

The SEM images of the top surface of prepared membranes are presented in Figure 2 with 20,000× magnification. It can be seen that the ion exchange resin particles (i.e. functional groups) were distributed relatively uniform on the surface and in the bulk of membrane matrix. This uniformity provides superior conducting regions in the membranes. Also, the ion exchange resin particles interactions can enhance the compatibility of particles and binder in order to reduce the amount of fissures between the binder and particles in the membrane matrix (Klaysom et al. 2011; Hosseini et al. 2012). The prepared membrane shows compact cracks, which may be attributed to polystyrene crosslinked with divinylbenzene and polyvinyl alcohol that caused the membrane to become more compact.

If the polymer solution is cast in thin film, denser membranes are obtained because the solvent in the thinner film can be removed easier at the given drying time. Denser membranes possess better selectivity (Klaysom et al. 2011; Hosseini et al. 2012).

Membranes (see Table 2) were examined before and after the exposure to electrodialysis process.

Membrane thickness does not affect their investigated features.

Characterization of membranes

Membranes were characterized by various techniques such as FTIR and TGA.

Figure 2 | SEM image of prepared membrane before use in the electrodialysis cell.
Membranes FTIR spectra were recorded using a Tensor 37 device (Bruker) and the attenuated total reflectance (ATR, Golden Gate United) technique. The wavelength range was from 4,000 to 400 cm\(^{-1}\) at 64 scans per spectrum, with a resolution of 4 cm\(^{-1}\).

Thermal stability of the membranes was investigated using TGA curves (recorded on a NETZSCH STA 449 F1 Jupiter-Simultaneous TGA-DSC device) under nitrogen flow of 20 cm\(^3\)/min at a heating rate of 10 °C/min in the temperature range of 25–850 °C.

**RESULT AND DISCUSSION**

**Electrodialysis experiments**

Electrochemical methods use electrons as the main reagent, but may also require the presence of supporting electrolytes, which increases the conductivity of the solution and reduces the electrolysis time.

During the electrolysis of NaCl aqueous solution, the following reactions occur (Secula et al. 2011; El-Ashtoukhy 2013):

\[
\text{Anode: } 2\text{Cl}^- - 2e^- \rightarrow \text{Cl}_2 \quad (1)
\]
\[
\text{Cathode: } 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (2)
\]

In the solution bulk, the Cl\(_2\) hydrolysis takes place as follows:

\[
\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCI} + \text{H}^+ + \text{Cl}^- \quad (3)
\]

\[
\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \quad (4)
\]

The Cl\(_2\) ions are replaced by hydroxide ions which can be oxidised to oxygen at the anode according to the reaction:

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad (5)
\]

The generated hypochlorite ions act as main oxidizing species in dye degradation present in the effluent according to the reaction (Bayramoglu et al. 2007):

\[
\text{Dye} + \text{OCl}^- \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{Cl}^- + \text{H}_2\text{O} \quad (6)
\]

In the literature, studies done by other researchers (De Urzedo et al. 2013) highlighted that, in the presence of hypochlorite, the degradation of Indigo Carmine in aqueous solution is quickly promoted.

Based on results, we propose a plausible route for the degradation of Indigo Carmine by NaCl in aqueous solution (Figure 3).

As the literature suggested and our research confirmed, the pathway for Indigo Carmine degradation includes: the formation of hydroperoxide intermediate occurred via an initial electrophilic addition of HOCl (hypochlorous acid), which is in equilibrium with its conjugated base OCl\(^-\) (hypochlorite anion) in aqueous solution, towards the exocyclic C=C bond of the anionic form of Indigo Carmine dye to yield the chlorohydrins intermediate. Chlorohydrins’ intermediate continuous formation due to its much less extensive \(\pi\)-electron conjugation system than the anionic form of Indigo Carmine may be the main cause for the quick and intense solution colour removal, as experimentally observed.

The next step in dye degradation mechanism is possible to imply the replacement of Cl\(^-\) by OH\(^-\) in chlorohydrins’ intermediate structure. This step in the degradation dye mechanism represents an easy and quick stage that occurs mainly in basic aqueous solution, in order to generate a dihydroxylated intermediate.

Dihydroxylate and chlorohydrins intermediate presents high instability and a very short-lived character. The mechanism for dihydroxylate intermediate conversion to hydroperoxide intermediate is possible to involve the chlorination of the indolic nitrogen in the dihydroxylate intermediate structure, yielding to an unstable intermediate.

Simultaneous nucleophilic attacks of the hydroxyl groups at both the carbonyl carbons of unstable intermediate, causing rupture of the indolic rings and the consequent

<table>
<thead>
<tr>
<th>Membrane sample</th>
<th>Notation</th>
<th>Thickness of sample, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane with ion exchange resin, blank</td>
<td>A</td>
<td>0.0429 0.0411</td>
</tr>
<tr>
<td>Membrane with ion exchange resin, tested at applied current intensity of 0.05 A</td>
<td>B</td>
<td>0.0417 0.0413</td>
</tr>
<tr>
<td>Membrane with ion exchange resin, tested at applied current intensity of 0.1 A</td>
<td>C</td>
<td>0.0420 0.0415</td>
</tr>
<tr>
<td>Membrane with ion exchange resin, tested at applied current intensity of 0.15 A</td>
<td>D</td>
<td>0.0423 0.0416</td>
</tr>
</tbody>
</table>
formation of expanded six-membered rings, followed by the elimination of two molecules of HCl will lead to the transient species. Finally, we suggest that hydroperoxide intermediate is formed via the insertion of two molecules of H2O at the C=N bonds of the transient species.

Finally, it is proposed that decomposition of hydroperoxide intermediate via cleavage of the exocyclic C=C single bond yielded to the formation of 1-hydroxy-3,4-dioxo-3,4-dihydro-1H-benzo[c][1,2]oxazine-6-sulfonic acid and 2-(2-amino-5-sulfophenyl)-2-oxoacetic acid.

Final pH and conductivity

pH and conductivity values from anodic compartment (A), central compartment (C) and cathodic compartment (K), after 1 h of electrodialysis process, are shown in Table 3.

Table 3 | The pH and conductivity solutions values before and after 1 h of electrodialysis process

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Conductivity, mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed wastewater</td>
<td>6.35</td>
<td>3.3</td>
</tr>
<tr>
<td>Treated wastewater after electrodialysis from compartments:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>4.85</td>
<td>3.9</td>
</tr>
<tr>
<td>C</td>
<td>11.72</td>
<td>2.7</td>
</tr>
<tr>
<td>K</td>
<td>12.12</td>
<td>5.1</td>
</tr>
<tr>
<td>0.05 A</td>
<td>4.93</td>
<td>2.65</td>
</tr>
<tr>
<td>0.1 A</td>
<td>5.68</td>
<td>3.3</td>
</tr>
<tr>
<td>0.15 A</td>
<td>11.87</td>
<td>4.1</td>
</tr>
<tr>
<td>0.05 A</td>
<td>12.28</td>
<td>10</td>
</tr>
<tr>
<td>0.1 A</td>
<td>12.35</td>
<td>11.5</td>
</tr>
<tr>
<td>0.15 A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
From Table 3, one may notice that the pH value of treated solution increases in the central and cathodic compartments due to the solution conductivity increase. Also, the increase in solution pH during electrodialysis can be attributed to the increase of hydroxide ions ($\text{OH}^-$) concentration that is generated from water reduction at the cathode. The addition of $\text{Cl}^-$ ions into solutions leads to an increase of the anodic dissolution rate. The chloride ions might be discharged at the anode and generate $\text{Cl}_2$ that is dissolved into solution. Also, the increase in the solution pH decreases the reaction rate, which could be connected with the dissociation of $\text{HOCl}$ to $\text{OCl}^-$. The $\text{H}_2$ bubbles that occurred at the cathode can contribute to the improvement of mass transfer rate and mixing conditions at the lead anode with a consequent increase in the rate of dye oxidation (Secula et al. 2011). A change in the solution pH was observed after 1 h of electrodialysis process, after contact of Indigo Carmine with ion exchange membrane. After treatment, it is possible for $\text{Cl}^-$ ions, compensating positive electric charge of quaternary ammonium groups from the anion exchanger resin, to be interchanged with the ions from Indigo Carmine structure, which start to form ion pairs with these groups.

Moreover, variation in the solution pH possibly affects the surface charge potential of the adsorbent. Because the solution pH increased with the decrease of surface charge potential, the electrostatic attraction between surface of adsorbent (cation exchange membrane) and the positively charged dye (Indigo Carmine) was lowered, and this may lead to a decrease in the rate of adsorption.

**Indigo Carmine dye concentration determination**

The dye concentration was determined by UV-visible spectrophotometry using the calibration method at maximum wavelength of 610 nm. The colour removal efficiency (CR %) in the treatment experiments was calculated according to the relation (Bayramoglu et al. 2007; Secula et al. 2011):

$$CR\% = \frac{C_0 - C_t}{C_0} \times 100$$  \hspace{1cm} (7)

where $C_0$ and $C_t$ are the initial dye concentration and concentration of dye at time $t$ in solution from central compartment (mol/L), respectively.

All samples from the central compartment were filtered using polytetrafluorethylene filters with a pore size of 0.45 $\mu$m (Whatman Labware). The dye concentration was measured in triplicates and data were presented as means ± standard deviation.

The energy consumption (EC) during electrodialysis process is given by Equation (8) (Majewska-Nowak 2013; Stergiopoulos et al. 2014):

$$EC = \frac{1}{V_D} \int_{t=0}^{t_{f\text{n}}} U(t) \cdot I(t) \cdot dt$$  \hspace{1cm} (8)

where EC is the energy consumption (kWh/m$^3$), $I$ is the applied current intensity (A), $E$ is the voltage (V), $t$ is the time (h), $t_{f\text{n}}$ is the final time (h) and $V_D$ is the volume of dilute compartment (m$^3$).

The values of CR % and EC are presented in Table 4. From Table 4 it can be seen that the CR % values of 78.92 ± 0.03, 96.05 ± 0.04 and 97.66 ± 0.03% corresponded to current intensity values of 0.05, 0.1 and 0.15 A, respectively (current density values approximately of 31.25, 62.5 and 93.75 A/m$^2$, respectively, after 1 h of electrodialysis). This increase occurred because at higher values of current density, the anodic dissolution rate increases in agreement with Faraday’s law. The bubbles generated at higher currents improve the mixing of Indigo Carmine dye and further enhance the separation of the flocs by electrodialysis. The current intensity determines the bubble production, the floc size and growth (Secula et al. 2011; El-Ashtoukhy 2013). The rate of dye removal, associated in this electrodialysis process with colour removal efficiency, increased with increasing applied current intensity due to the amount of hypochlorite (El-Ashtoukhy 2013).

El-Ashtoukhy investigated removal of Indigo Carmine dye from synthetic wastewater by electrochemical oxidation in a new cell with horizontally oriented electrodes. Electrochemical unit consists of Pb/PbO$_2$ anode and stainless steel screen as cathode. Under optimum operating conditions, the final dye removal yield was 88.2%.

From Table 4, it can be seen that the EC values increase with the increasing current intensity. The EC value is low (6.77 kWh/m$^3$) at a current intensity of 0.05 A (current density value approximately of 31.25 A/m$^2$) possibly due to the reduction of stack resistance. The EC was higher at a current intensity of 0.05 A probably due to the hampered ion

<table>
<thead>
<tr>
<th>Current intensity, A</th>
<th>CR, %</th>
<th>E.C., kWh/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>78.92 ± 0.03</td>
<td>6.77</td>
</tr>
<tr>
<td>0.1</td>
<td>96.05 ± 0.04</td>
<td>42.40</td>
</tr>
<tr>
<td>0.15</td>
<td>97.66 ± 0.03</td>
<td>106.04</td>
</tr>
</tbody>
</table>
transport in the presence of large dye macro-anions and increasing cell resistance (Majewska-Nowak 2013). The results obtained were comparable with the existing literature. Stergiopoulos et al. (2014) investigated removal of Indigo Carmine from textile wastewater, by integrating electrocoagulation, electrooxidation and advanced electrochemical oxidation using the electro-Fenton process. The electro-Fenton treatment operated at current densities of 3.3 and 6.6 A/m² indicate an EC value of $4.75 \times 10^{-3}$ and $5.23 \times 10^{-3}$ kWh/m³ of treated solution, respectively. The electrocoagulation treatment with iron electrodes and the electrooxidation process with Ti/Pt electrodes operated at applied current density of 50 A/m² indicate an EC value of 0.511 and 0.825 kWh/m³, respectively. El-Ashtoukhy (2013) investigated removal of Indigo Carmine dye from synthetic wastewater by electrochemical oxidation. The results show that the energy consumption was 11.1 kWh/kg dye removed at applied current density of 88.5 A/m².

Majewska-Nowak investigated the efficiency of dye solution desalination by electrodialysis. A standard anion-exchange and cation-exchange membranes or monovalent selective anion-exchange membranes were used in the electrodialysis stack. The best results for standard ion-exchange membranes were achieved for the desalination of Direct Black solution. The recovery of dye and salt solutions – the dye concentration in the dilute remained constant irrespective of the molecular weight of anionic dyes, whereas the salt recovery remained very high (99.5%). Also, the energy consumption was 0.40 kWh/m³ at an applied current density of 1.56 A/m².

Characterization of membranes

Fourier transform infrared spectroscopy

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

From Figure 4, it can be seen that the broad $\nu$(O–H) peak from bound water appeared around 3,389 cm⁻¹. A dramatic reduction of this peak was observed when membranes were used in electrodialysis cell, under NaCl (presumably because of functional sites).

The peak at around 2,932 cm⁻¹ corresponded to the aromatic $\nu$(C–H) stretching. The peaks appearing at 1,734 cm⁻¹ (for membrane with anion exchange resin, blank), assigned to C=O carbonyl groups, disappear in the case of the

![Figure 4](https://iwaponline.com/wst/article-pdf/74/10/2462/457326/wst074102462.pdf)
membranes with anion exchange resin tested at various current intensity.

The peak that appears at 1,369 cm\(^{-1}\) is shifted to higher wave numbers (1,392 cm\(^{-1}\)) which can be due to N-H deformation vibration (ammonium salts NH\(_4^+\)) (Vinodh et al. 2010; Xu et al. 2010; Wang et al. 2011; Garcia-Vasquez et al. 2014; Caprarescu et al. 2015).

The peak at 1,238 cm\(^{-1}\) was assigned to \(\nu(N-C)\) stretching vibrations from the quaternary ammonium functional sites. FTIR spectra for anion exchange membranes (A500) tested at different current intensity presented a peak at 684 cm\(^{-1}\), due to \(\nu(C-Cl)\) wagging when the adjacent C atom had a chlorine atom attached (Vinodh et al. 2010; Xu et al. 2010; Garcia-Vasquez et al. 2014).

From Figure 5 it can be seen that the broad \(\nu(O-H)\) peak from bound water was present from 3,200 to 3,600 cm\(^{-1}\). Peaks located at 1,029, 1,038 and 1,085 cm\(^{-1}\) were attributed to \(\nu(S-O)\) modes, corresponding to \(-SO_3^-\) functional groups. Stretching peak belonging to polyvinyl alcohol, i.e. \(\nu(C-Cl)\) at 684 cm\(^{-1}\), was observed as well. The absorbance intensity decreased for bands attributed to the sulfonate groups, which indicated a partial degradation of functional sites. The colour removal of 97.66 ± 0.03% obtained after 1 h, at applied current intensity of 0.15 A is very high and suggests that Hypersol-Macronet MN500 with very good adsorption characteristic is a promising adsorbent for textile dye removal. The peak observed at 1,369 cm\(^{-1}\) was attributed to SO\(_2^\) asymmetric stretching vibration, corresponding to aliphatic sulphonyl chlorides. The peak that appears at 1,736 cm\(^{-1}\) was assigned to C=O carbonyl stretching vibration. The specific peak at 2,244 cm\(^{-1}\) could be assigned to –C≡N (absorption band of poly-acrylonitrile from copolymer). The peak that appears at 2,931 cm\(^{-1}\) was shifted to higher wave numbers (2,935 cm\(^{-1}\)) and was due to asymmetrically CH\(_2\) stretching vibration (Vinodh et al. 2010; Xu et al. 2010; Wang et al. 2011; Garcia-Vasquez et al. 2014; Caprarescu et al. 2015).

These studies demonstrated that the adsorption between the dye molecules and the ion-exchange membranes were attributed both charge interactions, and hydrophobic interaction and hydrogen bonding.

Ion exchange resins are manufactured for extended use. Ion exchange membranes are usually visibly cracked when they are frequently used or improperly stored. As long as ion exchange based membranes do not dry out, they can be reused 4–5 times. If they dry out, they must be discarded immediately, since they will crack when rewetted. High salt sample content can reduce the lifetime of a membrane.
Thermogravimetric analysis

The characteristic TGA curves for ion exchange membrane are presented in Figures 5 and 6.

The first mass loss appeared at 25–180 °C, being assigned to the removal of bound water and solvent from the membrane phase (Figure 6). The second stage, from 180 to 330 °C, might correspond to the dehydrochlorination of acrylic copolymer and polyvinyl alcohol. Also, the decomposition of the membrane sample may be due to the loss of aliphatic component grafted onto the polymer backbone followed by the hydroxyl groups of membrane matrix (dye interaction with quaternary ammonium groups). The third stage, from 330 to 450 °C, corresponded to the loss of the quaternary ammonium groups. Up to around 450 °C, the degradation step might correspond to the degradation of the acrylic copolymer and polystyrene crosslinked with divinylbenzene. The final stage of weight loss, starting from 450 °C, was also ascribed to the degradation of the polymer residues (Vinodh et al. 2010; Xu et al. 2010; Li et al. 2013; Garcia-Vasquez et al. 2014; Caprarescu et al. 2015). The mass loss for every stage is given in Table 5.

In literature (Garcia-Vasquez et al. 2014; Vinodh et al. 2010; Xu et al. 2010; Caprarescu et al. 2015), quaternary ammonium groups in anion exchange membranes were reported to start degrading at 250 °C. Vinodh found that the polymer backbone of polystyrene copolymers substituted with quaternary ammonium degrades at 460 °C.

The first step from 25 to 200 °C was assigned to the loss of bound water (Figure 7). The second stage from 200 to 340 °C was attributed to dehydrochlorination of acrylic copolymer and polyvinyl alcohol. Also, the secondary degradation can be attributed to aliphatic component grafted onto the polymer backbone (dye interaction with sulfonic acid groups). The third stage from 340 to 440 °C corresponded to degradation of the functional sites (sulfonic acid groups). Up to 440 °C, it was ascribed to the degradation of polystyrene crosslinked with divinylbenzene and polyvinyl alcohol back bones.

Polystyrene crosslinked with divinylbenzene chains broke, possibly due to the subtraction of a weak hydrogen atom from the aliphatic polystyrene chain by hydroxyl radicals. These chain scissions can cause the dragging out of sulfonic acid groups and a reduction of the ion-exchange sites concentration (Wang et al. 2011; Li et al. 2013; Garcia-Vasquez et al. 2014). The mass loss for every stage is presented in Table 6.

**Table 5** The value of mass loss for anion exchange membrane

<table>
<thead>
<tr>
<th>Membrane sample</th>
<th>Temperature, °C</th>
<th>Mass loss, %</th>
<th>Residue (850 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25–180</td>
<td>1.52</td>
<td>25.64</td>
</tr>
<tr>
<td></td>
<td>180–330</td>
<td>25.64</td>
<td>34.47</td>
</tr>
<tr>
<td></td>
<td>330–450</td>
<td>25.64</td>
<td>20.50</td>
</tr>
<tr>
<td></td>
<td>450–850</td>
<td>25.64</td>
<td>38.15</td>
</tr>
<tr>
<td>B</td>
<td>25–180</td>
<td>1.46</td>
<td>12.74</td>
</tr>
<tr>
<td></td>
<td>180–330</td>
<td>12.74</td>
<td>17.84</td>
</tr>
<tr>
<td></td>
<td>330–450</td>
<td>12.74</td>
<td>11.04</td>
</tr>
<tr>
<td></td>
<td>450–850</td>
<td>12.74</td>
<td>62.85</td>
</tr>
<tr>
<td>C</td>
<td>25–180</td>
<td>1.11</td>
<td>19.30</td>
</tr>
<tr>
<td></td>
<td>180–330</td>
<td>19.30</td>
<td>28.83</td>
</tr>
<tr>
<td></td>
<td>330–450</td>
<td>19.30</td>
<td>15.25</td>
</tr>
<tr>
<td></td>
<td>450–850</td>
<td>19.30</td>
<td>48.14</td>
</tr>
<tr>
<td>D</td>
<td>25–180</td>
<td>1.36</td>
<td>24.03</td>
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<tr>
<td></td>
<td>180–330</td>
<td>24.03</td>
<td>37.79</td>
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<tr>
<td></td>
<td>330–450</td>
<td>24.03</td>
<td>23.52</td>
</tr>
<tr>
<td></td>
<td>450–850</td>
<td>24.03</td>
<td>35.66</td>
</tr>
</tbody>
</table>
These studies demonstrated that the ion-exchange resin powder not only provided functionality from the colour removal efficiency point of view (more over 97%), but can also increase the final ion exchange membrane thermal stability (the degradation starts over 300 °C) even at low amounts (0.5 g).

CONCLUSIONS

The removal of Indigo Carmine dye from aqueous solutions can be carried out effectively by applying electrodialysis with different type of ion-exchange membranes. After 1 h of experiment, it was found that the pH values of treated solution increases due to the increase in the conductivity of solution. The values of CR % and EC increase with increasing current intensity. The highest value of dye removed was obtained at 0.15 A (over 97%) with a high energy consumption of 106.04 kWh/m³.

Membranes were characterized by FTIR-ATR, TGA and SEM. The FTIR-ATR spectra showed peak at 1,238 cm⁻¹ corresponding to ν(N–C) stretching vibrations from the quaternary ammonium functional sites (anion exchange membranes). Peaks located at 1,029, 1,038 and 1,085 cm⁻¹ were attributed to ν(S–O) modes, corresponding to −SO₃⁻ functional groups (cation exchange membranes). The colour removal of 97.66 ± 0.03 % obtained after 1 h, at applied current intensity of 0.15 A is very high and suggests that Hypersol-Macronet MN500 with very good adsorption characteristic is a promising adsorbent for textile dye removal. TGA curves showed that the ion exchange membranes started to decompose up to 300 °C. The surface morphologies (SEM) showed that the ion exchange resin particles are compatible with polymer blend and were distributed relatively uniformly on the surface and in the bulk of membrane matrix. TGA curves showed that the ion-exchanger resin powder increases the final ion exchange membrane thermal stability (the degradation starts over 300 °C) even at low amounts (0.5 g) providing a colour removal efficiency over 97%.

ACKNOWLEDGEMENTS

The work has been funded by the Romanian National Authority, project number PN.16.31.03.04.02 and also it was supported by the Sectoral Operational Programme Human Resources Development 2007–2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398

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First received 31 March 2016; accepted in revised form 4 August 2016. Available online 13 September 2016.