



The separation of mineral salt from a dye-salt aqueous mixture by electro dialysis

Arif Eftekhari Ahmed*, Katarzyna Majewska-Nowak, Moutaz Ahmed, Martyna Grzegorzek

Faculty of Environmental Engineering, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, Tel.: +48713203639; email: arif.eftekhari.ahmed@pwr.edu.pl (A.E. Ahmed), Tel.: +48713204120; email: katarzyna.majewska-nowak@pwr.edu.pl (K. Majewska-Nowak), Tel.: +48729405109; email: moutazahmed42@gmail.com (M. Ahmed), Tel.: +48713203639; email: martyna.grzegorzek@pwr.edu.pl (M. Grzegorzek)

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ABSTRACT

The efficiency of desalination of reactive dye solutions with the addition of a fixed amount of mineral salt was evaluated using standard ion-exchange membranes in the electro dialysis (ED) process. Five reactive dyes (Reactive Orange 16, Remazol Brilliant Blue R, Reactive Orange 20, Reactive Black 5, Reactive Red 120), varying in molecular weight, were used in the study. The model solutions were prepared by varying the dye concentration (20, 50 and 100 mg/L) and adding mineral salt (2 g/L of NaCl) to each dye solution. It was observed that the salt was successfully separated from dye solutions with the efficiency of 97.6%–98.5%. The migration of dye molecules from dilute to concentrate compartments was negligible. The dye concentration in the concentrate compartments amounted to 0.6–0.85 mg/L, irrespectively of the process parameters. However, significant deposition of dye particles in the membrane matrix was noted. Around 26%–31% of the initial dye mass was adsorbed, and this effect was strongly influenced by the dye reactivity. It can be concluded that the ED process with standard ion-exchange membranes is quite a promising method for reactive dye and mineral salt separation. This will enable further usage of the obtained dye and salt streams in a variety of technological processes.

Keywords: Reactive dye; Desalination; Electromembrane process; Ion-exchange membrane

1. Introduction

In the textile industry, huge volumes of exhausted dye baths containing unfixed dyes and other auxiliary chemicals (salts, acids, hydroxides, dispersing and complexing agents, etc.) are generated. These effluents are extremely harmful to aquatic ecosystems; thus, it is unquestionable that they should be treated before being discharged to water bodies. More recently, due to the new concept of the circular economy, water recovery as well as separation and reuse of organic dyes and the minerals in the dyeing baths are of great interest. It is hard to treat the dye-containing

effluents by conventional methods (anaerobic/aerobic biodegradation, coagulation, electrocoagulation, adsorption, photocatalytic oxidation) to adhere to the requirements of the circular economy. Thus, membrane processes seem to be a viable technology in textile wastewater treatment aimed at dyes, salts, and water recovery for reuse in technological processes. Some membrane systems, involving mainly reverse osmosis (RO) and/or nanofiltration (NF), for dye-house effluent treatment have already been proposed [1,2]. It seems that the NF process is the most efficient in organic dye separation, although the rejection of multivalent salts also occurs in the course of this process. Thus, the separation of salts from dyes is challenging.

* Corresponding author.

Another group of membrane processes (besides pressure-driven membrane processes) that can be potentially used in valorization of textile wastewater is a group of electromembrane processes. Xue et al. [3] applied the electro-dialysis (ED) process in desalination of Acid Blue 9 (AB9) solution. They found that almost all SO_4^{2-} ions and 98% of Cl^- ions were removed from the dye solution. The residual chloride ion concentration was only 130 mgCl/L (in comparison to 3.3 gCl/L at the process beginning), whereas dye concentration in the final product amounted to 200 g/L. The authors found that the AB9 anions were not only adsorbed on the anion-exchange membrane surface, but these anions were also able to move into the anion-exchange membrane matrix. Fortunately, the formation of a dye layer on the membrane surface was reversible, and dye desorption was accomplishable in a well-designed cleaning procedure. The energy demand in the proposed ED system was estimated at 4 kWh/m³, and the overall operating cost was calculated as 0.091 \$/kg of dye solids, which was considered economically competitive. However, this idea of dye solution purification by the ED process was only implemented in dye production technology. Targeting textile dye-bath desalination, Lafi et al. [4] applied conventional electro-dialysis to separate salt (NaCl) from a solution containing a cationic dye (Methylene Blue, MB). The initial dye concentration was rather low (2–8.5 mg/L), whereas the ionic strength of dye solution varied from 0.01 to 0.04 mol/L (approximately 0.6–2.4 gNaCl/L). They found that the ED with standard ion-exchange membranes enabled the efficient desalination of the cationic dye solution. The MB ions were not transported from diluate to concentrate compartments; however, these ions were adsorbed on the surface of the standard cation-exchange membranes. Due to the identical initial composition of solutions in the diluate and concentrate compartments, the usefulness of the obtained results appears questionable. Nevertheless, this study confirmed that electrostatic interactions between the dye cations and the fixed charge groups of the cation-exchange membranes play a crucial role in desalination of MB solutions by ED.

Majewska-Nowak [5] proposed an integrated ultrafiltration–electrodialysis (UF-ED) system for recovery of valuable substances (direct dyes, salts) and water reuse. By applying ion-exchange membranes and the electric field, separation of dye macroparticles from mineral salts was possible; however, some small fractions of dye penetrated into the membranes. It was found that the separation efficiency was heavily dependent on the dye's molecular weight. The concentration of low-molecular-weight dyes (<1,000 Da) in the diluate decreased with operation time, which was attributed to the sorption of dye particles in the membrane structure. Lafi et al. [6] verified the usability of the integrated UF-ED system for treatment of real textile wastewater (after primary treatment) with the sole aim of water reuse. UF was used for separation of the macromolecules and colloids, as well as for colour diminishing, whereas ED allowed for the separation of ionic species. The removal efficiency of the total dissolved solids amounted to 94.2%, and the wastewater conductivity was decreased by 97.1%. The specific energy demand for wastewater desalination was estimated at 0.9 kWh/m³. The treated textile wastewater can be reused

as process water in textile factories. An innovative approach for textile wastewater valorisation was delivered by Ye et al. [7]. They implemented a loose NF membrane as the anion conductive membrane in the ED stack for dye and salt separation. Due to the loose surface structure, the NF membrane with a low molecular weight cut-off (678 Da) exhibited a high permeation for NaCl with a satisfactory retention (>99.2%) of reactive dyes. It was proved that the loose NF membrane used as an anion conductive membrane in the NF-based ED process resulted in a superior fractionation of dye/NaCl binary mixtures with reduced fouling when compared to the conventional anion-exchange membrane. This was explained by the intrinsic negative surface charge of the loose NF membrane, which acted as an effective barrier to repel the dye particles from entering the membrane matrix via electrostatic repulsion. Unfortunately, the performance of the proposed integrated system in separation of multivalent salts from dye particles was not verified.

Most recently, the ED with bipolar membranes has been employed in the valorisation of textile wastewater. Lin et al. [8] proposed an integrated, tight ultrafiltration (TUF) and bipolar membrane electro-dialysis (BMED) process for treatment of highly saline textile wastewater with the aim of resource recovery. Due to the application of TUF membrane with a low molecular weight cut-off (5 kDa), it was possible to retain reactive and direct dyes with high efficiency (99.7%), whereas mineral salts (Na_2SO_4 and NaCl) freely passed to the permeate. The low dye concentration in the permeate (approximately 3 mg/L) allowed for the subsequent BMED operation without fouling the membrane. Additional benefits of this integrated TUF-BMED process consisted of salt conversion into an acid and base for further direct usage in dye-houses. It was also emphasized that pure water was received from the TUF permeate in the BMED stack, which seems to be rather controversial (the risk of undesirable increase of the stack resistance). The proposed, integrated TUF-BMED system exhibited some drawbacks, that is, severe proton leakage, low acid production yield, and the necessity of external pH control.

According to the above short literature review, it can be deduced that separation of dyes from mineral salts generates a huge challenge in textile effluent valorisation. As in the pressure membrane processes, besides dye rejection, some salts can also be rejected, and electro-dialysis seems to be more suitable for dye-bath fractionation. Thus, the aim of the study was to evaluate the desalination efficiency of dye-salt mixtures *via* electro-dialysis with standard ion-exchange membranes. 5 reactive dyes varying in molecular weight were chosen for the study. Reactive dyes are widely used for dyeing cotton fibres and fabrics; however, they have rather low affinity for cotton, requiring high amounts of salts in the dyeing baths (even up to 30 g/L) [9,10]. For this reason, efficient fractionation of dye-salt mixtures can be expected. Moreover, due to low fixation rate, approximately 10%–50% of the initial reactive dye load in the dye bath remains unused [11]. Reactive dyes are regarded as very problematic among other dyes, as their removal from textile effluents by conventional treatment systems is not effective [12]. Therefore, treatment methods focused on reactive dye recovery and reuse seem to be an economically and environmentally viable approach.

2. Materials and methods

2.1. Reagents and experimental solutions

The electro dialysis process was carried out for model dye solutions containing mineral salt (NaCl). Five reactive, anionic dyes, varied in molecular weights, were used in the experiments (Table 1). Reactive Black 5 and Reactive Orange 20 were purchased from the Boruta Company (Poland), whereas Remazol Brilliant Blue R, Reactive Orange 16, and Reactive Red 120 were supplied by Merck Polska. All tests were performed for solutions containing single dye and sodium chloride (2 g/L). The concentration of each dye in model solutions amounted to 20, 50, and 100 mg/L. The dye concentration range was adjusted on the assumption that the ED process can be alternately preceded by UF pre-treatment with tight polymeric membranes enabling reactive dye rejection by 80%–97% [13].

2.2. Membranes and experimental installation

The study on the desalination of dye-salt mixtures was conducted with the use of a lab-scale electro dialysis system (PCCell BED-1 produced by PCCell GmbH, Germany) equipped with commercial ED membranes. Standard PC-SK cation-exchange and PC-SA anion-exchange membranes

(PCA GmbH, Germany) were applied. The membrane characteristics is shown in Table 2. Each membrane had an effective area of 64 cm². Before using the ion-exchange, membranes were subjected to the cycling process with the use of 0.1 N HCl and 0.1 N NaOH solutions.

The ED stack (PCCell 64002 model) consisted of 10 cell pairs. Each cell pair included a diluate and a concentrate compartment, therefore 10 anion-exchange and 11 cation-exchange membranes were set in the stack. The thickness of each electro dialytic cell was equal to 0.5 mm.

Three independent circulation loops (diluate, concentrate, electrode solution) can be distinguished in the ED system. Each loop enabled circulation of a given solution at a flow rate in the range of 10–100 L/h. The electrode solution loop was equipped with an internal tank (9 L), whereas diluate and concentrate loops had external tanks (2 L each). The ED system also incorporated a DC power supply, which was characterized by a maximum output voltage of 24 V and an amperage of 5 A.

2.3. Methodology

The desalination of reactive dye solutions by ED was preceded by desalination of water salt solution (2 gNaCl/L) for comparison purposes.

Table 1
Characteristics of experimental dyes

Dye	Molecular weight, Da	Classification/reactive group/ number of reactive group	Dye symbol	λ_{\max}^a , nm	Structural formula
Reactive Orange 16	617.53	Reactive/vinyl sulfone/1	RO16	486	C ₂₀ H ₁₇ N ₃ Na ₂ O ₁₁ S ₃
Remazol Brilliant Blue R	626.53	Reactive/vinyl sulfone/1	RBB	594	C ₂₂ H ₁₆ N ₂ Na ₂ O ₁₁ S ₃
Reactive Orange 20	682.18	Reactive/monochlorotriazine/1	RO20	491	C ₂₃ H ₁₆ ClN ₇ O ₁₀ S ₃
Reactive Black 5	991.8	Reactive/vinyl sulfone/2	RB5	533	C ₂₆ H ₂₁ N ₅ Na ₄ O ₁₉ S ₆
Reactive Red 120	1,469.98	Reactive/dichlorotriazine/2	RR120	624	C ₄₄ H ₂₄ Cl ₂ N ₁₄ Na ₆ O ₂₀ S ₆

^aWavelength corresponding to maximum absorbance of the dye solution.

Table 2
Properties of the ion-exchange membranes (according to PCCell ED 64002 manual)

Parameter	Membrane	
	Cation-exchange PC-SK	Anion-exchange PC-SA
Producer	PCA GmbH (Germany)	
Thickness, μm	90–130	
Ion-exchange capacity, mmol/g	Approx. 1.2	Approx. 1.1
Electrical resistance, $\Omega\cdot\text{cm}^2$	1–3	1–3
Thermal stability, $^{\circ}\text{C}$	Maximal 60	Maximal 60
Chemical stability (pH range)	0–9	0–9
Burst strength, MPa	0.4	0.5
Permselectivity (transfer number)		
$t\text{-K}^+$	>0.95	
$t\text{-Cl}^-$		>0.93
Ionic form	Na ⁺	Cl ⁻
Functional group	Sulfonic acid	Quaternary ammonium

In all ED experiments the volume of diluate and concentrate amounted to 2 L. The initial sodium chloride concentration in the diluate and concentrate loops was always 2 g/L, whereas the desired amounts of reactive dyes were added to the diluate feed solutions only. The initial dye concentration varied, and 3 series of experiments were made: for the initial dye concentration of 20, 50, and 100 mg/L. A solution of sodium chloride (0.05 mol/L) was used as an electrode rinsing bath.

All ED desalination experiments were performed at a constant current intensity (0.15 A) and the current density amounted to 2.35 mA/cm². The ED system operated in batch mode, that is, both diluate and concentrate circulated in the stack until the end of the desalination process. The ED process was terminated immediately when voltage reached 24 V, and voltage variation was monitored every 10 min.

At the beginning of the process, the flow rate of diluate and concentrate was fixed to 90 L/h. The cleaning procedure of the ED stack by distilled water was performed (for about 30 min) upon completion of the experiments with a given dye. The cleaning procedure of the ED system was also carried out when the diluate and/or concentrate flow rate decreased by approximately 20%. Water cleaning enabled recovery of the initial flow rate of solutions in the diluate and concentrate loops.

In the course of the ED process, the quality of both diluate and concentrate was evaluated every 10 min. The concentration of organic dyes was determined by absorbance measurements at the wavelengths given in Table 1. A spectrophotometer UV-Vis U-1900 (Hitachi, Japan) was used to determine the dye solution absorbance. The salt concentration was estimated indirectly by measuring the electrical conductivity of diluate and concentrate samples. A conductivity meter Elmetron CC-411 was used for this analysis.

The dye retention (R_d , %) in the diluate compartment, that is, the percentage of the initial dye amount which remained in the diluate was calculated using Eq. (1):

$$R_d = \frac{C_{td}}{C_{id}} \times 100\% \quad (1)$$

where C_{td} – actual dye concentration in diluate (mg/L), C_{id} – initial dye concentration in diluate (mg/L).

The desalination efficiency (R_s , %) was calculated according to Eq. (2):

$$R_s = \frac{C_i - C_s}{C_i} \times 100\% \quad (2)$$

where C_s – actual conductivity of diluate solution (mS/cm), C_i – initial conductivity of diluate solution (mS/cm).

The limiting current density was evaluated theoretically using the simplified formula given by Rautenbach and Albrecht [14]:

$$i_{lim} = \frac{k \cdot C_D^+ \cdot F}{T_m^+ - T^+} \quad (3)$$

where i_{lim} – limiting current density (A/m²), k – mass transfer coefficient (L/m²·s), C_D^+ – concentration of cations (Na⁺)

in diluate after desalination (eq/L), F – Faraday constant (96,500 As/eq), T_m^+ – transfer number of cations in membrane (0.95), T^+ – transfer number of cations in solution (0.45).

It was assumed that the final salt concentration in the diluate should be lower than 5%–10% of the initial salt concentration (i.e., lower than 0.1–0.2 gNaCl/L).

The electrical energy consumption (EC) and the specific electrical energy consumption (E_v) were evaluated using Eqs. (4) and (5):

$$EC = I \int_0^t U dt \quad (4)$$

$$E_v = \frac{EC}{V_d} \quad (5)$$

where EC – energy demand for ED process (kWh), I – current intensity (A), U – voltage (V), t – time of process (h), E_v – specific electrical energy consumption (kWh/m³), V_d – volume of treated solution (diluate, 2 L).

The only energy utilized for ion transport across the membranes was included in the calculation of energy consumption (EC). The energy required to pump the streams of diluate and concentrate through the ED stack was not considered.

The mass balance towards dyes was calculated in order to evaluate the dye susceptibility for adsorption in the ion-exchange membranes and in the ED system. The mass of the deposited dye was calculated according to Eq. (6):

$$M = (V_{id} C_{id} + V_{ic} C_{ic}) - (V_{fd} C_{fd} + V_{fc} C_{fc}) \quad (6)$$

where M – mass of dye accumulated on/in the ion-exchange membranes (mg), V_{id} , V_{fd} – initial and final volume of diluate, respectively (2 L), V_{ic} , V_{fc} – initial and final volume of concentrate, respectively (2 L), C_{id} , C_{fd} – initial and final concentration of dye in diluate, respectively (mg/L), C_{ic} , C_{fc} – initial and final concentration of dye in concentrate, respectively (mg/L).

3. Results and discussion

3.1. Desalination of dye salt-mixtures by ED

The aim of the study was to successfully separate salt from the dye-salt mixture. The applied electrical current density was constant (2.35 mA/cm²), and it was established theoretically [14] in such a way as to not exceed the limiting current density. The limiting current density was calculated according to Eq. (3) and was equal to 6.56 or 3.28 mA/cm², assuming 90% or 95% desalination of sodium chloride solution (2 gNaCl/L), respectively. The recommended operational current density should not exceed $0.8i_{lim}$; thus, the applied current density of 2.35 mA/cm² seemed to be reasonable for conducting the ED desalination with high efficiency.

The effect of dye concentration on the desalination efficiency for various reactive dyes is shown in Figs. 1–3. The obtained salt removal was high (97.6%–98.5%), regardless of the dye type and dye amount in the treated solution. One can assume that this high desalination efficiency was

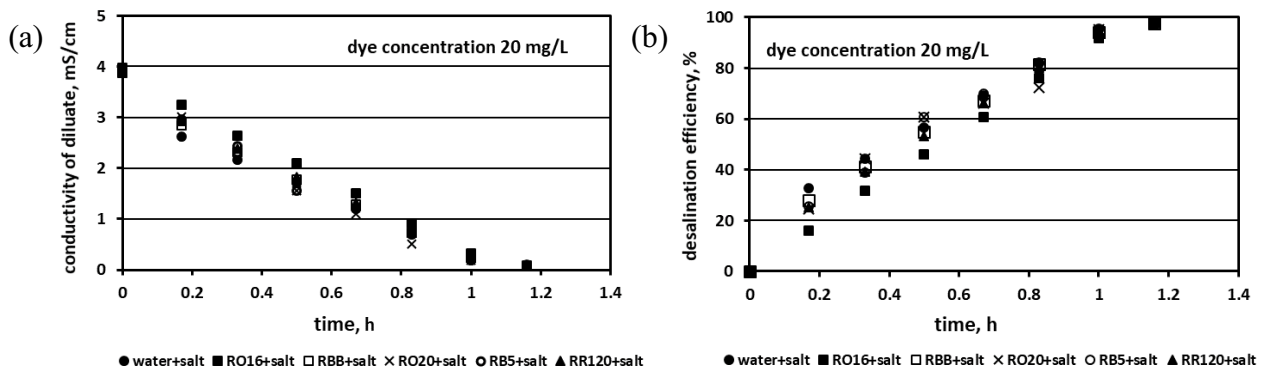


Fig. 1. Variations of diluate electrical conductivity (a) and desalination efficiency (b) in the course of ED desalination of dye-salt mixtures (initial dye concentration: 20 mg/L; initial NaCl concentration in diluate and concentrate: 2 g/L).

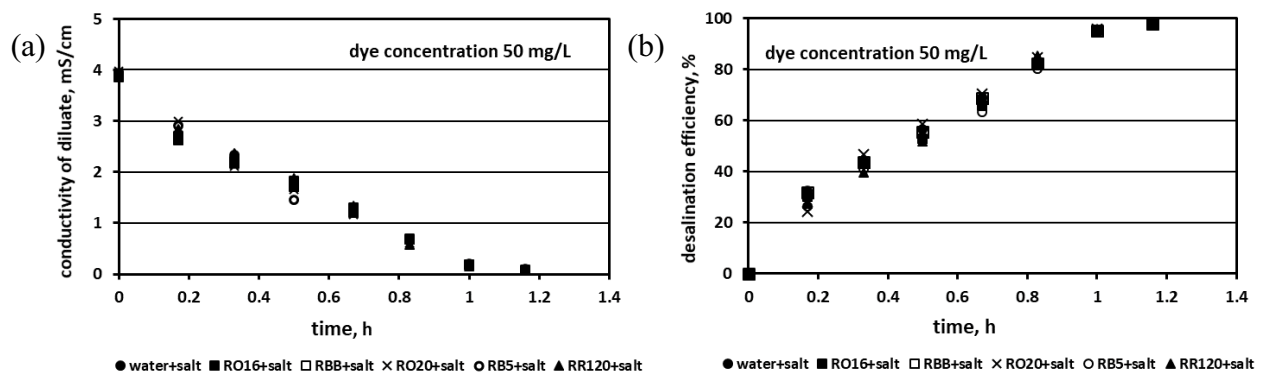


Fig. 2. Variations of diluate electrical conductivity (a) and desalination efficiency (b) in the course of ED desalination of dye-salt mixtures (initial dye concentration: 50 mg/L; initial NaCl concentration in diluate and concentrate: 2 g/L).

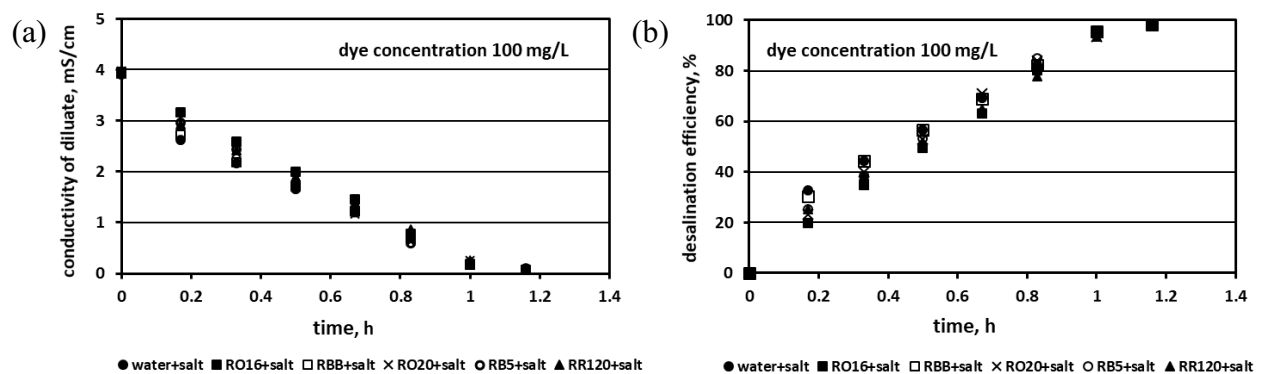


Fig. 3. Variations of diluate electrical conductivity (a) and desalination efficiency (b) in the course of ED desalination of dye-salt mixtures (initial dye concentration: 100 mg/L; initial NaCl concentration in diluate and concentrate: 2 g/L).

possible because sodium chloride was the only mineral salt (in addition, monovalent) in the dye solution, and there was no competition in the ion migration through the ED membranes. The final conductivity of the diluate varied in a rather raw range from 0.06 to 0.09 mS/cm. The operational time to reach this low diluate conductivity was similar for all tested dye solutions, and amounted to approximately 70 min. These observations were in accordance with Faraday's law. According to this law, the time of the ED process is directly proportional to the initial salt concentration. Since the initial

concentration of sodium chloride was always 2 g/L, it was not surprising that the dye type and dye concentration had no significant impact on the ED process duration. The trajectories of the diluate conductivity and desalination efficiency vs. time were quite similar for all tested dye solutions (Figs. 1–3). However, it should be mentioned that when only salt solution (2 gNaCl/L, no dye) was treated by ED at the same electrical current density (2.35 mA/cm²), the desalination process lasted slightly shorter (60 min) in comparison to the duration of the ED series with dye-salt mixtures

(approx. 70 min). The ED process was terminated earlier due to a faster increase of voltage to 24 V (in comparison to the ED courses of dye-salt mixtures). As a consequence, the final conductivity of diluate was slightly higher (0.18 mS/cm) than in the case of desalination of dye-salt solutions (0.06–0.09 mS/cm). The presence of dye particles in the diluate compartments can somewhat hinder the free movement of salt ions to the concentrate compartments, especially when dyes have the potential to be adsorbed by the ion-exchange membranes.

3.2. Behaviour of reactive dyes in the course of the ED process

Besides the successful desalination of dye-salt mixtures, an equal goal of the study was to obtain separate diluate streams reached in reactive dyes for possible reuse in the dyeing process. Therefore, dye particles should not migrate through the ion-exchange membranes, and the dye concentration in the diluate should remain constant at a level close to the initial dye concentration.

The variations of dye concentration in the diluate and concentrate streams in the course of the ED treatment are given in Figs. 4–6. It was observed that the dye concentration in the diluate compartments was systematically

decreasing with increasing operational time. This phenomenon was noted for all experimental dyes, irrespective of their initial concentration. The highest decrease in dye concentration at the end of the ED process was stated for Reactive Orange 16 (RO16), which is characterized by the lowest molecular weight among tested reactive dyes (617.53 Da). In turn, the lowest drop of dye concentration in diluates with process time was observed for Remazol Brilliant Blue R (RBB) (molecular weight: 626.53 Da) and Reactive Orange 20 (RO20) (molecular weight: 682.1 Da). On the other hand, analysis of the dye concentration in concentrate compartments concluded that there was only slight migration of dye particles through the ion-exchange membranes. Moreover, the dye concentration in the concentrate compartments was kept on a constant, low level (below 0.9 mg/L) irrespective of the dye type and dye concentration. Such behaviour of reactive dyes during electrodialysis (i.e., continuous decreasing of dye concentration in the diluate cells with minor dye migration into the concentrate cells) indicates that dye molecules are easily adsorbed by the ion-exchange membranes. The calculated dye retention coefficient (Fig. 7), as well as the deposited dye mass in the course of the electrodialysis of dye-salt mixtures (Fig. 8), are the reflection of this phenomenon. As can be seen from Fig. 7, the retention of dyes

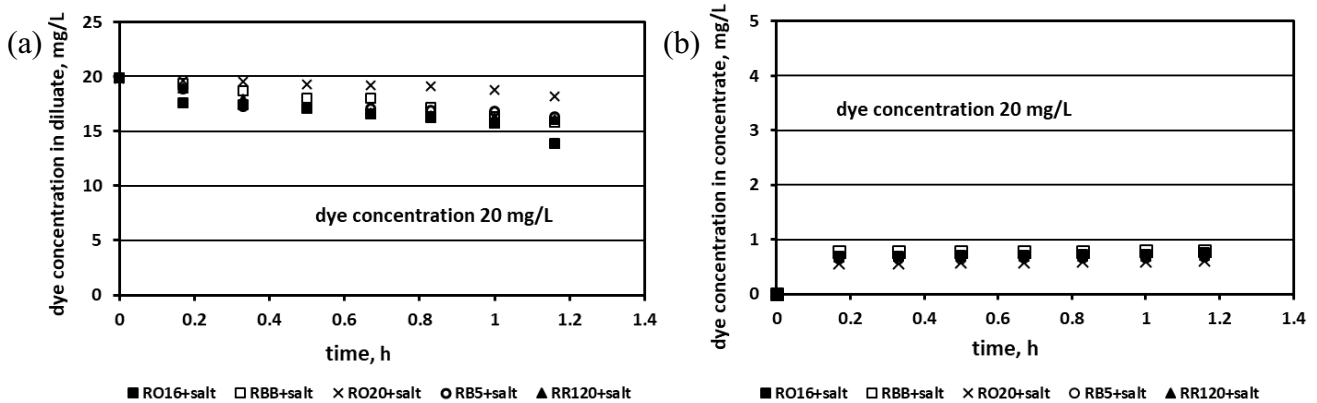


Fig. 4. Variations of dye concentration in diluate (a) and concentrate (b) in the course of ED desalination of dye-salt mixtures for various reactive dyes (initial dye concentration: 20 mg/L; initial NaCl concentration in diluate and concentrate: 2 g/L).

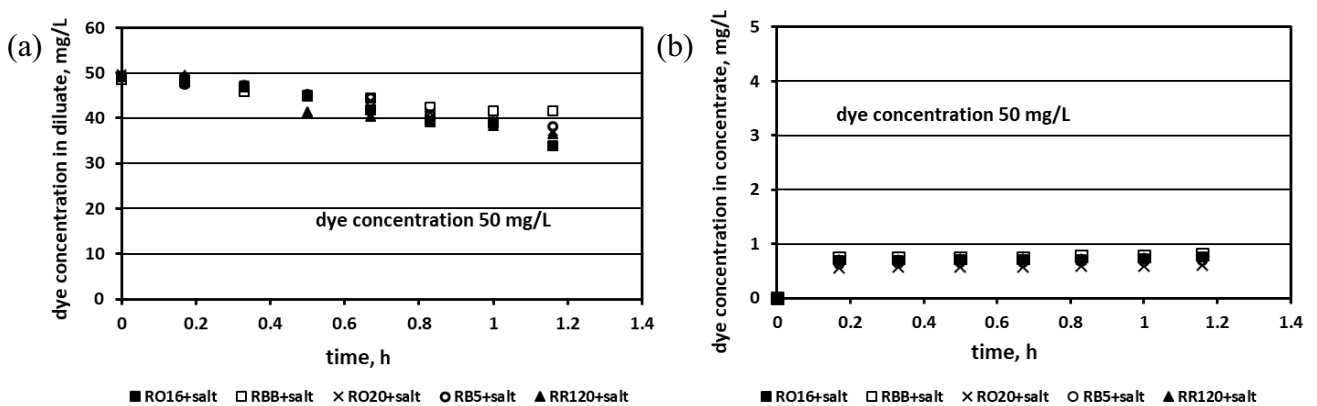


Fig. 5. Variations of dye concentration in diluate (a) and concentrate (b) in the course of ED desalination of dye-salt mixtures for various reactive dyes (initial dye concentration: 50 mg/L; initial NaCl concentration in diluate and concentrate: 2 g/L).

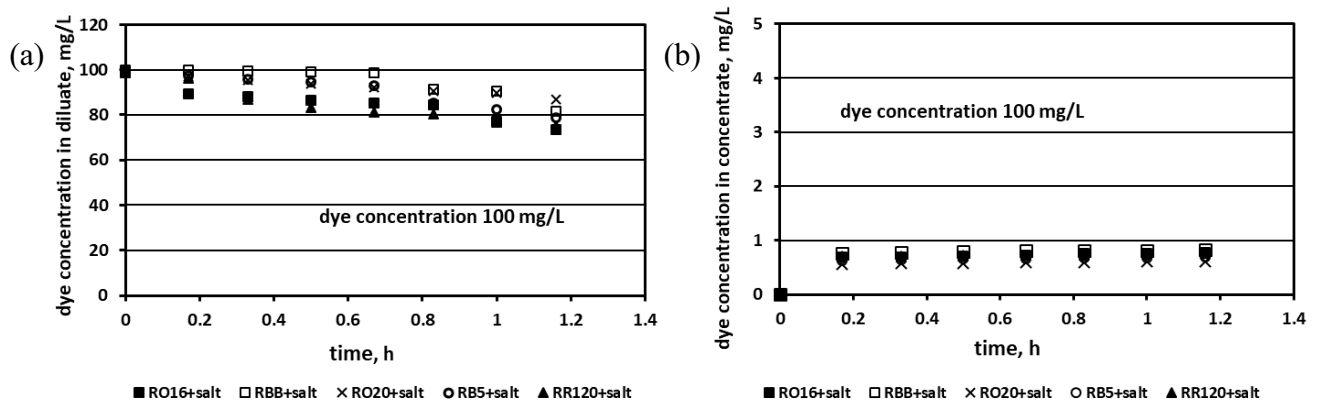


Fig. 6. Variations of dye concentration in diluate (a) and concentrate (b) in the course of ED desalination of dye-salt mixtures for various reactive dyes (initial dye concentration: 100 mg/L; initial NaCl concentration in diluate and concentrate: 2 g/L).

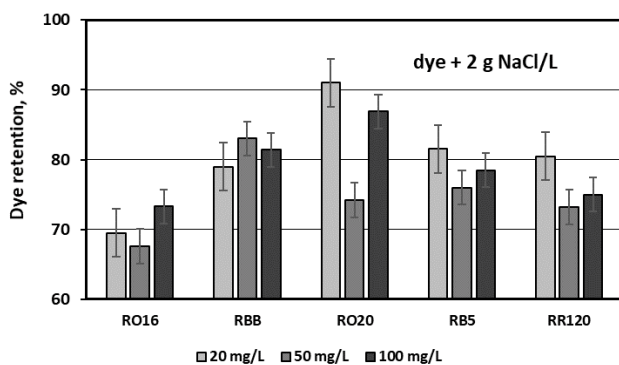


Fig. 7. Dye retention in diluate compartments for variable initial dye concentration (20, 50, and 100 mg/L).

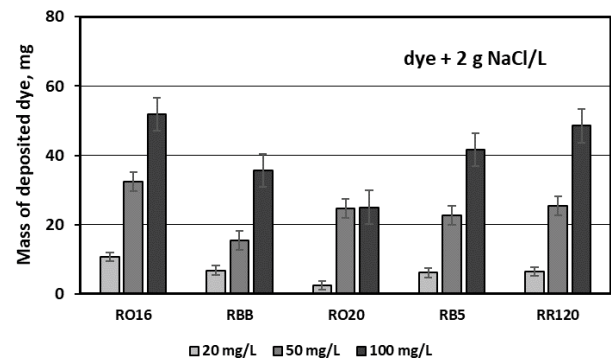


Fig. 8. Mass of dye accumulated on/in the ion-exchange membranes in relation to the initial dye concentration (20, 50, and 100 mg/L).

in the diluate compartments after ED treatment varied from 68% to 91%. The lowest dye retention was observed for Reactive Orange 16 (RO16), whereas the highest dye retention was detected for Reactive Orange 20 (RO20), especially for the lowest and the highest dye concentration (20 and 100 mg/L, respectively) in the treated solution. There was no distinct relationship between the initial dye concentration and the percentage of dye that remained in the diluate compartments at the end of the ED process; however, for a few dyes (RO20, RB5, and RR120), the lowest dye concentration brought about the best dye retention. Instead, a strong correlation was observed between the initial dye concentration and the amount of dye deposited on and/or in the ion-exchange membranes – the higher the dye concentration (i.e., the higher the total dye mass in the ED system), the more dye particles were adsorbed/absorbed by the ion-exchange membranes (Fig. 8). It was interesting to note that for Reactive Orange 16, the mass of deposited dye constituted even 32% of the total initial amount of this dye in the diluate cells. Other tested dyes were deposited in the ED stack to a lesser extent: the percentage of the deposited dye mass varied from 6% to 25%. Although Reactive Orange 16, which had the highest susceptibility for adsorption, was characterized by the lowest molecular weight (617.53 Da) among all tested dyes, it seems that the dye's molecular weight is not

a critical parameter influencing the degree of reactive dye deposition in the membrane matrix. Even though Reactive Red 120 was characterized by the highest molecular weight (1469.98 Da), this dye also exhibited significant susceptibility for accumulation on and/or in the ion-exchange membranes (Fig. 8): the deposited mass of RR120 comprised 16%–25% of the initial dye amount in the ED system. Therefore, the simple relationship between the dye molecular weight and the intensity of dye accumulation in the membrane matrix, as it was observed in the case of ED desalination of direct dye solutions [5], does not occur when reactive dye solutions are treated by ED. In light of their chemical reactivity, the behaviour of reactive dyes in the course of the electro dialysis should be considered.

Commercially available reactive dyes are characterized by different reactivities because they contain various reactive groups, such as vinyl sulfone, chlorotriazine, trichloropyrimidine, and difluoro-chloropyrimidine. These reactive groups react chemically with the substrate (textile polymer fibre) to form covalent bonds. The covalent bond can be formed between the reactive group and, for example, amino groups of polymers [12]. It can be anticipated that in the course of the electro dialysis of reactive dye-salt solutions, the anionic dye particles (having great negative charge density) will easily be electrically attracted by the positively

charged anion-exchange membranes [15]. It is therefore highly likely that the intensity of this phenomenon will be the result of both the dye reactivity and the dye molecule size. Considering that the reactivity of the reactive groups can be arranged such as monochlorotriazine < vinyl sulfone < dichlorotriazine [16], the experimental results given in Fig. 8 become more understandable. As previously mentioned, the highest susceptibility for adsorption was observed for RO16 dye. Indeed, this dye contains the moderate reactive group (vinyl sulfone), although has the lowest molecular weight, which can facilitate dye accumulation in the membrane matrix. The high deposited amount of RR120 dye can be attributed to the presence of 2-dichlorotriazine groups in the dye molecule. RB5 exhibited lower vulnerability to adsorption (than RR120) – it also contains 2 reactive groups, but of a lower reactivity (vinyl sulfone groups). RBB and RO20 were adsorbed to a lesser extent due to containing merely 1 reactive group (vinyl sulfone and monochlorotriazine, respectively). This deduction seems to be in accordance (to some extent) with the results obtained by Won et al. [15]. They investigated the adsorption mechanism of reactive dyes (Reactive Orange 16, Reactive Yellow 2, and Reactive Blue 4) on protonated waste biomass, and found that the solution pH strongly influenced the binding mechanism of reactive dyes. At acidic pH, the electrostatic attraction was the main bonding mechanism, whereas under alkaline conditions, the dye uptake by the biomass occurred according to their reactivity (chemical bonding existed between the waste biomass and dye molecules). Owing to the fact that, in the course of the ED, the pH of the diluate solution was mostly alkaline with a minor drop in value around 6.4–6.9 at the end of the process, and it could be supposed that the dye reactivity was the dominant factor influencing their accumulation in the membrane matrix.

The proposed idea of reactive dye-salt mixture fractionation by electrodialysis can mainly be implemented in dye-houses as a method of resource recovery. Due to rather small volumes of the exhausted dye baths, a batch mode of ED operation seems to be the most suitable. It can be anticipated that the problem of dye accumulation on and/or in the ion-exchange membranes (in industrial ED systems) will exist to a similar degree as in the reported study, and the percentage loss of reactive dyes will be proportional to the initial dye content in the treated dye baths. Lafi et al. [6] applied electrodialysis in a batch mode for treatment of real textile wastewater with the sole aim of water recovery. In turn, Praneeth et al. [21] proved that membrane washing with HCl (2% solution) after each batch enabled the restoration the ED performance in terms of the ion transport rate and permselectivity during a 3-month treatment of the RO retentate of textile industrial effluents.

3.3. Energy demand for desalination of dye-salt mixtures

Energy demand is always important for practical applications of any technological process, and it should also be taken into account in the electromembrane treatment. The power demand for conventional ED desalination can comprise even 30% of operating costs [17].

The specific electrical energy consumption (E_e) in the course of the ED desalination of dye-salt mixtures was

calculated with the use of Eqs. (4) and (5). It should be noted that the pumping energy was not involved in the calculations. The obtained E_e values for ED of solutions containing various amounts of dyes are given in Fig. 9. It can be seen from the data given in Fig. 9 that the specific energy consumption during the ED tests with dye solutions varied in the range of 0.68–0.98 kWh/m³. When only the salt solution was treated, the energy demand was markedly lower and amounted to 0.64 kWh/m³. According to Faraday's law, the energy demand in the ED process is directly proportional to the applied current and salt content. Thus, some fluctuations in the energy consumptions were not expected – all ED tests were performed for solutions containing 2 gNaCl/L at a constant current intensity (0.15 A). However, it should not be forgotten that, in the case of reactive dye-salt mixtures subjected to the ED process, the salt ion migration through the ion-exchange membranes could be affected not only by the dye adsorption (due to their reactivity) in the membrane matrix. The ion transport from the diluate to the concentrate cell may be also influenced by such phenomena as: the shielding effect of salt on reactive dye (influencing the degree of dye interactions with membranes), or the formation of a negatively charged layer due to the electrostatic interactions between the anionic dye and the anion exchange-membrane, especially under alkaline condition (due to the negative surface charge of dye molecules) [18]. Possibly, the above-mentioned interactions between dye molecules, mineral salt and ion-exchange membranes brought about slight variations in the specific energy consumption under variable dye concentration in the treated solutions (Fig. 9). As previously discussed, (section 3.1 – Desalination of dye salt-mixtures by ED), the impact of dye concentration on the desalination efficiency was negligible.

Generally, the energy consumption needed for desalination of dye solutions was higher than the energy demand necessary for desalination of NaCl solutions (with no dye). This increased energy demand can be attributed to the hampered ion transport, due to the presence of large dye macro-anions in the diluate compartments as well as in the membrane matrix (dye deposition). Consequently, the electrical resistance of the ED stack could have increased. Similar conclusions were found by Lee et al. [19] in the course of their study on organic fouling of anion-exchange membranes. The presence of negatively charged foulants (humate, bovine

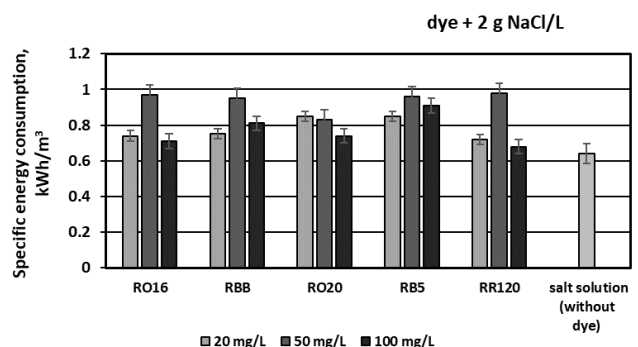


Fig. 9. Specific electrical energy consumption in the course of ED desalination of dye-salt mixtures at variable initial dye concentration (20, 50, and 100 mg/L).

serum albumin and sodium dodecyl benzene sulfonate) in desalted solutions led to an increase in membrane resistance (from 2.15 $\Omega\cdot\text{cm}^2$ for fresh membrane to 2.3–2.6 $\Omega\cdot\text{cm}^2$ for fouled membranes). Consequently, the power consumption increased by 10%–25% in comparison with the power consumption calculated for ED of salt solutions free of foulants. More recently, Zhao et al. [20] performed detailed experiments on the anion-exchange membrane fouling with the use of five negatively charged organic compounds varying in chemical structure. They observed an extremely high increase in membrane resistance (from 2.5 $\Omega\cdot\text{cm}^2$ for fresh membrane to even 120–140 $\Omega\cdot\text{cm}^2$ for fouled membranes) due to the presence of anionic surfactants (sodium dodecyl sulfate, and sodium dodecyl benzene sulfonate) in the NaCl solution treated by the ED process. It was also concluded that the organics with benzene rings caused more severe fouling of the anion-exchange membranes compared with organics with aliphatic chains.

4. Conclusions

- Electrodialysis (ED) with standard ion-exchange membranes enables efficient desalination of reactive dye solutions. The mineral salt (NaCl) can be removed to a high degree (up to 97.6%–98.5%) irrespective of the dye type and dye concentration in the treated solution. The final diluate solutions (containing retained dyes) are characterized by a low electrical conductivity (0.06–0.09 mS/cm).
- In the course of the electrodialysis, a systematic decrease of the reactive dye concentration in the diluate cells with increasing operational time is observed. This phenomenon occurs irrespective of the dye type and the initial dye concentration in the treated solution, and is accompanied by a minor dye migration into the concentrate cells. The dye concentration in the concentrate cells does not exceed 0.9 mg/L.
- The reactive dyes are easily adsorbed by the ion-exchange membranes in the course of the electrodialysis process. A strong correlation is observed between the initial dye concentration and the amount of dye deposited on and/or in the anion-exchange membranes – the higher the dye concentration, the more dye particles can be adsorbed/absorbed in the ED system.
- It can be supposed that the dye reactivity is the dominant factor influencing the degree of their accumulation in the membrane matrix. The mass of deposited dye constitutes 6%–32% of the total initial amount of the dye in the diluate cells. As a consequence, the retention of reactive dyes in the diluate cells after the ED treatment varies markedly (from 68% to 91%).
- The energy consumption needed for desalination of reactive dye solutions is higher than the energy demand necessary for desalination of solutions containing only salt (NaCl, 2 g/L). This increased energy demand can be attributed to the hampered ion transport due to the presence of large dye macro-anions in the diluate compartments as well as in the membrane matrix (dye deposition).
- An integrated, tight ultrafiltration-standard electrodialysis (TUF-ED) process has potential as a valorisation method of exhausted dye baths containing reactive dyes.

However, some losses of dyes in the course of the electrodialysis and the ion-exchange membrane fouling should be taken into consideration.

Symbols

C_{ic}, C_{fc}	–	Initial and final concentration of dye in the concentrate, respectively, mg/L
C_{id}, C_{fd}	–	Initial and final concentration of dye in the diluate, respectively, mg/L
C_{td}	–	Actual dye concentration in diluate, mg/L
C_r, C_s	–	Initial and actual conductivity of diluate solution, respectively, mS/cm
C_D^+	–	Concentration of cations (Na^+) in diluate after desalination, eq/L
EC	–	Electrical energy consumption, kWh
E_v	–	Specific electrical energy consumption, kWh/m ³
F	–	Faraday constant, 96,500 As/eq
I	–	Current intensity, A
i_{lim}	–	Limiting current density, A/m ²
k	–	Mass transfer coefficient, L/m ² ·s
M	–	Mass of dye accumulated in membranes, mg
R_d	–	Dye retention, %
R_s	–	Desalination efficiency, %
t	–	Process duration, h
T^+	–	Transfer number of cations in membrane (0.95)
T^m	–	Transfer number of cations in solution (0.45)
U	–	Voltage, V
V_d	–	Volume of treated solution, L
V_{ic}, V_{fc}	–	Initial and final volume of concentrate, respectively, L
V_{id}, V_{fd}	–	Initial and final volume of diluate, respectively, L

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