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Removal of Methylene blue from saline solutions by adsorption and electrodialysis

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Abstract. In this study, the removal of MB from saline solutions was evaluated by two methods by adsorption and electrodialysis; the adsorption of the mixture dye/salt on dried orange peel waste (OPW) was studied in batch method. In this study the biosorption of cationic dye by OPW was investigated as a function of initial solution pH, and initial salt (sodium chloride) concentration. The maximal dye uptake at pH ≥ 3.6 in the absence and in the presence of salt and the dye uptake diminished considerably in the presence of increasing concentrations of salt up to 8 g/L. The Redlich Peterson and Langmuir were the most suitable adsorption models for describing the biosorption equilibrium data of the dye both individually and in salt containing medium. As well, this work deals with the electrodialysis application to remove the dye. Synthetic solutions were used for the investigation of the main operational factors affecting the treatment performance; such as applied voltage, pH, initial dye concentration and ionic strength. The experimental results for adsorption and electrodialysis confirmed the importance of electrostatic interactions on the dye. The electrodialysis process with standard ion exchange membranes enabled efficient desalination of cationic dye solutions; there are two main factors in fouling: electrostatic interaction between cations of dyes and the fixed charged groups of the CEM, and affinity interactions.

Keywords: methylene blue; orange peel waste; adsorption; electrodialysis; fouling; interaction

1. Introduction

The textile industry produces large quantities of wastewaters heavily charged with organic dyes and high levels of toxic heavy metals. The dyeing and finishing industry also uses large quantities of salt besides metal-complex dyes in order to lower the dye solubility by increasing the degree of aggregation of the dye molecules. Some dyes require as much as 250–300 g/L of salt to enhance the bath dye exhaustion. NaCl is mainly used salt in dying processes. These salts when discharged in high concentrations are toxic to aquatic life and are harmful to the sewer system as well (Maurya *et al.* 2006, Ncibi *et al.* 2008). The conventional methods used for removing such heavy metals and dyes from wastewaters are precipitation, ion exchange, coagulation, electro-coagulation, adsorption, membrane process, etc. (Panswed and Wongchaisuwan 1986, Ciardelli *et al*. 2000, Irem *et al.* 2013, Chenna *et al.* 2016).

In the process of dye adsorption, several factors are reported to affect the adsorption. These factors include adsorbent dose, initial dye concentration, contact time, temperature, pH and ionic strength (Hosseini *et al.* 2011, Zhou *et al.* 2011, Hu *et al.* 2013). Among them, pH and ionic strength are two important factors affecting the adsorption processes. Solution pH affects the adsorption mainly through adjusting the electrostatic interactions between the dyes and the adsorbents (Saeeda *et al.* 2010, Jingfeng *et al.* 2010, Pavan *et al.* 2008). Solution pH affects not only the surface charge of the adsorbents, but also the ionization of the dyes. While the effect of ionic strength on the dye adsorption is more complicated and is not so clear (Li *et al.* 2010, Newcombe and Drikas 1997, Aksu and Balibek 2010). Ionic strength may affect not only the electrostatic interactions, but also the hydrophobic interactions (Hu *et al.* 2013, Li *et al.* 2010).

Although it is known that ionic strength may affect the electrostatic, very little is known about the detail of the effect. The present study represents an effort to gain a better understanding of this issue. The effect of ionic strength on the adsorption behavior of MB dye onto raw orange peel was investigated. The selected adsorbent has negatively charged and the selected dye of methylene blue (MB) has positively charged Therefore, MB, a cationic dye, has been extensively used in dyeing industry (Liu *et al.* 2012, Rehman *et al.* 2012).

Among membrane processes, the electrodialysis seems to be very viable technology for the desalination of solutions containing organic substances. A hybrid microfiltration (MF) and electrodialysis (ED) system was successfully employed to remove the color and contaminants of paper industry waste water (Nataraj *et al.* (2007), and that electrodialysis was also a promising technology for the treatment of textile effluents for TDS reduction to reuse the received water for production cycle (Chandramowleeswaran and Palanivelu (2006). The combined electrodialysis/column process to remove sulphur compounds adsorbed onto GAC and the use of the bipolar

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membrane makes it possible to regenerate the saturated adsorbent granules without adding chemical products. Since the only reagent was electricity, the projected economics are very attractive (Drouiche *et al.* 2009). The application of electrodialysis to remove fluoride and nitrate from synthesized photovoltaic industry wastewater was employed by Belkada *et al.* (2018). The synthetic solutions were used for the investigation of the main operational factors affecting the treatment performance; such as current intensity, initial pollutants concentration, and pH. Significant fluoride removal was obtained in an acidic or neutral medium after a relatively short treatment time of 6 min. Nitrate ions were also removed showing an efficiency of 98% after 18 min of treatment using a current intensity of 0.1 A and for an initial concentration of 1000 ppm.

Majewska-Nowak (2013) performed laboratory tests to determine the efficiency of dye solution desalination by electrodialysis, and it was found that the separation efficiency was strongly dependent on the dye molecular weight. Although such efforts were made to understand the feasibility of the dye desalting by ED, the dye-membrane interactions were not very clear in these processes. Dye molecules are usually ionized as anions (for all acid dyes, as well as some reactive dye and direct dyes) or cations (for all basic dyes and some direct dyes), and the affinities between the dye ions and the IEMs are very strong. These affinities caused serious membrane contamination during the desalting process, long process time, high energy consumption, as well as short membrane life.

The aim of this work is to study the evaluation of two processes for removal of MB dye solutions: The adsorption of the mixture dye/salt on dried OPW was evaluated as a function of pH, adsorbent dosage and contact time in a batch system and examined the proposed mechanism. The Electrodialysis of MB was carried out to investigate the fouling mechanism on/in the commercially available CEM. Two fouling factors of organic substance on CEM were taken up in this study: electrostatic interaction and affinity interaction between of the foulant and the membrane matrix.

2. Experimental

2.1 Adsorbent

Orange peel waste (OPW) used in this study was obtained from a juice shop in the center of Tunis (Tunisia). The peels were washed with distilled water several times to remove ash and other contaminants and then dried in an oven at 70°C for 24 h. The dried OPW was crushed and sieved through AFNOR sieves of 250 µm size and used as such.

The techniques used to characterize the OPW, include Brunauer Emmet Teller (BET), Fourier Transform infrared spectroscopy (FTIR), Boehm titration and pH point of zero charge (pH_{PZC}). The BET–N_2 adsorption/desorption experiments were carried out using a Quantachrome instrument model Autosorb-1. The FTIR analysis was done using a Fourier Transform Spectrophotometer model IRAffinty-1 SHIMADZU. The spectra of the OPW before and after adsorption were in a range of 4000−400 cm^{-1}.

Table 1 Various experimental conditions in adsorption

	Parameters			
	Concentration dye (mg/L)	pH	Adsorbent dosage (g/L)	Temperature (°C)
Effect of pH	40	2.5 – 10	2	25
Adsorption isotherm	20 – 120	8	2	25

Table 2 Fundamental properties of ion-exchange membranes. IEC: ion exchange capacity, BS: burst strength, R_m: membrane resistance, d: membrane thickness, FG: Functional group and t: transport number

	IEC (mmol/g)	BS (MPa)	R_m (Ω cm^2)	d (mm)	FG	t
PC–SK	~ 1	0.4	0.75–3	0.13	$-SO_3^-$	> 0.93
PC–SA	~ 1.5	0.5	1–1.5	0.09–0.13	$-NR_4^+$	> 0.96

2.2 Adsorbate

Methylene blue was purchased from Fluka, and was prepared by dissolving 1.0 g/L of the dye in distilled water. The dye solution pH was adjusted using 0.1M HNO_3 or 0.1M NaOH. Fresh dilutions of the desired dye concentrations were made at the start of each experiment.

2.3 Adsorption experiments

Sorption studies were performed by the batch technique; the experiments were carried out at 50 mg/L initial concentration of dye or dye and salt containing synthetic solutions at desired level of each component at the beginning of the adsorption with 0.1 g/50 mL OPW mass at 25°C for 3 h equilibrium time and the amount of dye adsorbed q_e (mg/g), onto OPW was calculated from the mass balance equation as follows

$$q_e = (C_i - C_e)\frac{V}{W} \tag{1}$$

Where C_i and C_e are the initial and final (equilibrium) concentrations of dye (mg/L), respectively. V is the volume of dye solution (L), and W is the weight of the adsorbent used.

The effects of the various experimental conditions in adsorption are summarized in Table 1.

2.4 Electrodialysis experiments

2.4.1 Electrodilysis system

The ED system used was "PCCell ED 64 002" unit supplied by PCA-Polymerchemie Altmeier GmbH and PCCell GmbH, Heusweiler, Germany) with the same membrane setup as previously described (Ali *et al.* 2013). The schematic of the ED system used in the experiments and a close-up of the ED stack and its components is illustrated in previous study (Ali *et al.* 2013). A DC electric potential was connected directly to the ED stack TiO_2-coated titanium electrodes. The stack consisted of three cation-exchange membranes and two anion exchange

Table 3 Various experimental conditions in electrodialysis.

	Parameters			
	Concentration dye (mg/L)	pH	Flow rate (L/h)	Ionic strength
Applied voltage (0 – 24V)	7.5	3	5	0.04
Effect of pH	5	2.9 – 9.8	5	0.04
Concentration dye (mg/L)	2 – 8.5	3	5	0.04
Ionic strength (mol/L)	10	3	5	0.01 – 0.04

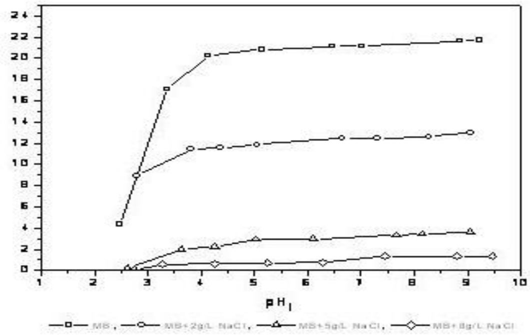


Fig. 1 Effect of initial pH on equilibrium MB sorption capacity of OPW in the absence and in the presence of salt (C_{0MB} =50mg/L, X_{OPW} = 2g/L, temperature: 25°C)

membranes, providing for each an available membrane area of 64 cm^2 (effective area) and the properties of the membranes were listed in Table 2.

2.4.2 Experimental protocol

During the experiments, the same solution was used as initial concentrate and dilute. Prior to the experiments, pH was adjusted by the addition of 0.1 M HCl and/or NaOH. In order to prevent the generation of chlorine or hypochlorite, which could be hazardous for the electrodes, 0.1 M Na_2SO_4 was used as electrode rinse solution circulating in electrode compartments. Flow rate of electrode rinse solution was fixed to 30 L/h for all experiments. Although, the flow rate of other solutions (dilute and concentrate) was fixed at the beginning of the experiment. Total voltage drop, including voltage drop in the membrane stack as well as on the electrodes, was measured in the experiments. Samples were collected at the inlet (before treatment) and outlet (after treatment) of ED cell at each experiment.

Cleaning solutions of 0.1 M HCl, 0.1 M NaOH and distilled water were circulated through the ED cell for 30 min each in order to remove any deposits after the completion of each experiment.

The demineralization rate (DR) from the diluate was calculated from conductivity values using the following equation

$$DR(\%) = \frac{(EC_{Di}^{0} - EC_{Di}^{t})}{EC_{Di}^{0}} \times 100 \quad (2)$$

Where EC_{Di}^0 and EC_{Di}^t are the conductivity of the dilute before and after treatment, respectively.

The percentage removal of dye was calculated as follows

$$\%\, Dye\ removal = \frac{C_i - C_t}{C_i} \times 100 \quad (3)$$

Where C_t is dye concentration (mol/L) in dilute compartment and C_i is the initial concentration of dye in the feed phase (mol/L).

The effects of the various experimental conditions in electrodialysis are summarized in Table 3.

2.4.3 Analytical methods

The pH, electrical conductivity (EC) and temperature of samples taken from the diluate and concentrate during each experiment were measured using a pH/Conductivity meter (Multi-parameter analyzer consort C 561, Belgium). UV–vis spectrophotometer (Shidmadzu Model UV-1601, Japan) was utilized to determine the absorbance of MB in experimental samples. MB was analyzed at a wavelength of 664 nm.

3. Results and discussion

3.1 Effect of ionic strength on dye adsorption

3.1.1 Effect of initial pH

The pH of dye solution plays an important role in the whole adsorption process and particularly in the adsorption capacity, influencing the surface charge of the adsorbent, the degree of ionization of the dye present in the solution and the dissociation of functional groups on the active sites of adsorbent, and the solution dye chemistries. Fig. 1 indicates the equilibrium dye uptake by dried OPW at various initial pH values ranging from 2 to 9.5 in single 50 mg/L dye and binary (50 mg/L dye and 2 g/L, 5 g/L and 8 g/L salt).

In the absence of salt, the adsorption capacity of MB increases significantly with increases in the pH solutions ranging from 2.5 up to 3.7. At pH value lower 3.7, the minimum amount of MB was observed at pH 2.5, which is probably due to the H^+ ions competing favourably with the cationic groups of the dye molecule for sorption sites on OPW. For pH values higher 3.6, the adsorption capacity was practically constant with increase in the pH solutions. This result could be explained considering the electrostatic attraction between the surface of the adsorbent, negatively charged, mainly due to COO^- species with the cationic dye MB. In order to confirm these results, the pH of zero charge of OPW determined, which value obtained was 3.6. At pH values lower than 3.6 the surface of OPW is positively charged, precluding the electrostatic attraction of MB, a cationic dye. On the other hand, for pH values higher than 3.6, the MB adsorption is facilitated.

In presence of salt, In Fig. 1, the results show the similar curves were obtained, evidently pH significantly affected the extent of adsorption of dye and did not affects the optimum pH for adsorption. The amount of dye decreased with increasing ionic strength of the aqueous solution at all pH values studied as shown though the decrease was significant at ionic strength. At pH 7, the removal of MB decreased from 21.17 to 12.45 mg/g at 2 g/L salt containing medium resulted in 41.2% reduction in adsorption capacity.

Table 4 Physical and chemical properties of the adsorbent

Physical properties	
BET surface area (g/cm^3)	1.026
Total pore volume (cm^3/g)	0.014
Pore diameter (nm)	53.77
Particle size (µm)	250
Chemical properties	
PH_{PZC}	3.6
Carboxylic groups (mmol/g)	1.62
Phenolic groups (mmol/g)	0.57
Lactonic groups (mmol/g)	0.06
Acidic groups (mmol/g)	2.25
Basic groups (mmol/g)	0.25
Total (mmol/g)	2.5

Table 5 Mathematical equations of the isotherm models used

Isotherm model	Equation	Linear expression	Plot
Langmuir	$q_e = \frac{q_m R_L\, C_e}{(1 + R_L C_e)}$	$\frac{C_e}{q_e} = \frac{1}{R_L\ q_{max}} + \frac{C_e}{q_{max}}$	$\frac{C_e}{q_e}\ vs\ C_e$
Freundlich	$q_e\ =\ K_F {C_e}^{1/n}$	$ln\, q_e = ln\, K_F + \frac{1}{n}\ ln\, C_e$	$ln\, q_e\ vs\ lnC_e$
Temkin	$q_e = \frac{RT}{A_T} ln(B_T\ C_e)$	$q_e\ =\ B_T\, ln\left(\frac{C_e}{q_e}\right) + A_T$	$q_e\ vs\ ln\frac{C_e}{q_e}$
Redlich-Peterson	$q_e\ =\ \frac{A_{RP}\ C_e}{1 +\ K_{RP}\ (C_e)^{\beta}}$	$ln\left(\frac{A_{RP}\ C_e}{q_e} - 1\right) =\ \beta lnC_e +\ lnK_{RP}$	$ln\left(\frac{A_{RP}\, C_e}{q_e} - 1\right) vs\ lnC_e$

However, MB uptake capacity of OPW decreased from 21.17 to 1.32 mg/g with increasing salt concentration up to 8 g/L resulted in 89.2% decrease in adsorption. This behavior may be due to the inhibition effect of salt. This effect of ionic strength on dye uptake suggests the possibility of ion exchange mechanisms being in operation in the adsorption process. It may be due to competition of Na^+ (present in salt used to change the ionic strength of dye solution) with positively charged dye molecules for the same binding sites on the adsorbent surface. Similar results were reported for Rhizopus arrhizus (Aksu and Balibek 2007).

MB have a relatively small molecular or ionic dimension (the width, depth, and thickness of MB are equal to 1.43, 0.61, and 0.4 nm, respectively) (Pelekani and Snoeyink 2000). These dimensions allow this dye to have easy access within the macro-porous structure of OPW, which has pores that are 53.77 nm in diameter.

In addition, the adsorption process is influenced by substituent groups present in OPW. The presence of surface functional groups plays an important role in the adsorption capacity and the removal mechanism of the adsorbates. As demonstrated by the Boehm method (Table 4), the main adsorption groups to be considered for the OPW are carboxylic acid, phenols, and carbonyls. On the other hand, due to the cationic properties of MB, its charge is delocalized throughout the chromophoric system, although it is probably more localized on the nitrogen atoms, the adsorption mechanism of MB on OPW should follow an electrostatic mechanism. As the pH_{PZC} for OPW is 3.6 (Table 4) solutions with pH upon to 3.6 favor electrostatic interactions between OPW and MB when the adsorbent acquires negative charges that the presence of Na^+ ions can screen the negative sites of the adsorbent, leading to the reduce of electrostatic attractive force.

Table 6 Effect of salt concentration on the Langmuir, Freundlich, Temkin and Redlich-Peterson adsorption constants of MB adsorption (Initial pH: 8, X_{OPW}=2g/L, temperature: 25°C, agitation rate: 22rpm)

Salt concentration	Langmuir isotherm			
	q_{max} (mg/g)		K_L (L/mg)	R^2
0	200		0.0279	0.997
2	142.8		0.0052	0.988
5	100		0.0019	0.999
8	38.4		0.0056	0.991
Salt concentration	Freundlich isotherm			
	K_F		n	R^2
0	16.36		2.38	0.923
2	2.27		1.56	0.972
5	0.46		1.30	0.993
8	0.17		1.06	0.812
Salt concentration	Redlich Peterson model			
	a_{RP} $(L/mg)^{\beta}$	K_{RP} (L/g)	β	R^2
0	0.0524	5.58	0.82	0.99
2	0.0052	0.74	1	0.993
5	0.0019	0.19	1	0.997
8	0.0073	0.21	0.95	0.988
Salt concentration	Temkin model			
	A_T		B_T	R^2
0	0.471		31.26	0.984
2	0.066		27.16	0.982
5	0.032		16.5	0.954
8	0.035		10	0.983

3.1.2 Isotherm data analysis

For the investigation of salt effect on MB adsorption, the (Langmuir 1918, Freundlich 1906, Temkin and Pyzhev 1940) and Redlich and Peterson 1959) equations were applied to the equilibrium data for single dye and dye-salt binary systems. The corresponding parameters of different isotherms at different salt levels estimated by non-linear regression analysis were listed in Table 5. The accuracy of each model is quantitatively determined based on the squared regression correlation coefficient (R^2).

The Langmuir isotherm assumes that adsorption occurs on a homogeneous surface containing sites with equal energy and that are equally available for adsorption. This is valid for the complete monolayer of adsorption. As seen

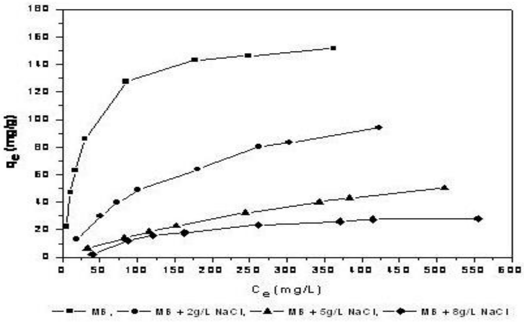


Fig. 2 Adsorption isotherms of MB in the absence and in the presence of salt (C_{0MB} =20 – 120 mg/L, X_{OPW}=2g/L, pH 8, temperature: 25°C)

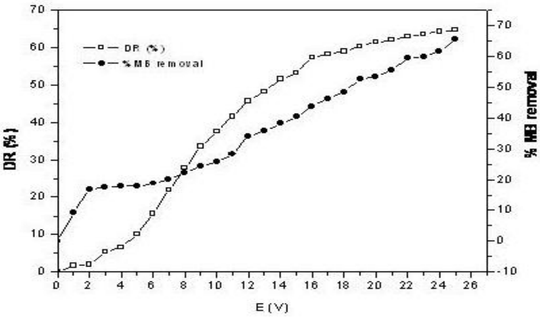


Fig. 3 Effect of applied voltage on the demineralization rate and dye removal

from Table 6, dried OPW exhibited the maximum adsorption capacity (q_{max}) for single MB adsorption. The addition of salt decreased the q_{max} value of MB adsorption insignificantly. The presence of 8g/L salt reduced the maximum MB uptake capacity from 200 to 38.4 mg/g compared to the mono-dye conditions. A high value of the other Langmuir parameter, b, indicates a steep desirable beginning of the isotherm which reflects the high affinity of the adsorbent for the sorbate. The highest b value obtained for mono-dye conditions also decreased with the addition of salt indicating its negative effect on MB adsorption.

The separation factor (R_L), an important parameter of the Langmuir isotherm, can be used to verify if the adsorption in the system studied is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Kadirvelu and Namasivayam 2003). In the initial dye concentration dye of 50 mg/L, the values between 0.910 and 0.417 indicate favorable adsorption in the MB-OPW system.

The Freundlich isotherm is an empirical model that can be used for heterogeneous systems with interaction between the molecules adsorbed. The n parameter, known as the heterogeneity factor is related to the distribution of bonded ions on the sorbent surface. In general n>1 illustrates that adsorbate is favourably adsorbed on an adsorbent, corresponds to a normal an L-type Langmuir isotherms, and the higher the n value the stronger the adsorption intensity. In particular, the value of n, which is significantly higher than unity, indicated that MB ios are favourably adsorbed under all the experimental conditions. The values of n at different salt concentrations also indicated that the salt added into adsorption affected the MB adsorption intensity contrarily. The constant K_F related to adsorption capacity, can be defined a sorption coefficient that represents the quantity of adsorbed dyes for unit equilibrium concentration. From the Table 6, the magnitude of K_F showed a relatively easy uptake of MB from aqueous solution with high adsorptive capacity of adsorbent in both single and binary systems. The highest K_F value was 16.36 in the absence of salt and the value of K_F decreased to 0.17 with the addition of 8 g/L salt which was consistent with the experimental observation.

The Temkin isotherm considers the interactions between adsorbate assuming that the adsorption heat of all molecules decreases linearly when the layer is covered and that the adsorption has a maximum energy distribution of uniform bond. The constant b_T is related to the heat of adsorption. The positive and highest b_T value was 31.26 in the absence of salt and the value of b_T decreased to 10 with the addition of 8 g/L salt which indicates an exothermic process. The fit to experimental data in Table 6 shows that the Temkin isotherm is less adequate to explain the adsorption of MB onto OPW, as compared to the Langmuir isotherms.

The Redlich-Peterson isotherm was developed to improve the fitting between the Langmuir and the Freundlich equations. The value of parameter g shows whether the Langmuir isotherm (β=1) or the Freundlich isotherm (β = 0) is preferable for the system. Related adsorption parameters were also calculated according to the three-parameter isotherm of Redlich-Peterson using non-linear regression method for MB adsorption at different salt levels and are tabulated in Table 6. Redlich-Peterson constant K_{RP} indicated that the adsorption capacity of biosorbent also diminished with increasing salt concentration. It is noted that β normally lies between 0 and 1, indicating favorable adosorption. The value of β is equal to 1.0 for 2 and 8 g/L salt containing medium and tends to unity for other salt concentrations studies that is the isotherms approach the Langmuir form.

The adsorption isotherms of MB adsorption in the absence and the presence of increasing concentrations of salt are shown in Fig. 2. The equilibrium of BM uptake increased with increasing initial dye concentration up to 600 mg/L for all cases studied. The amount of MB adsorbed at equilibrium suggests that saturation of cell-binding sites of OPW occurred at the higher concentrations of this dye. The equilibrium uptake of MB diminished regularly with the raising salt concentration. The inhibitory effect of salt on the equilibrium MB uptake was dominant at higher salt concentrations.

3.2 Effect of ionic strength on electrodialysis

3.2.1 Effects of applied voltage

To study the effect of applied voltage, the ionic strength, pH, MB concentration of feed solution and the inlet velocity were fixed respectively to 0.04 M, 3, 7.5 mg/L and 5 L/h.

The influences of applied voltages on the demineralization rate and dye removal are shown in Fig. 3. These shows that the demineralization rate increases with an increase of the applied voltage. There are three distinguished parts in this curve. In the first part (E < 4 V)

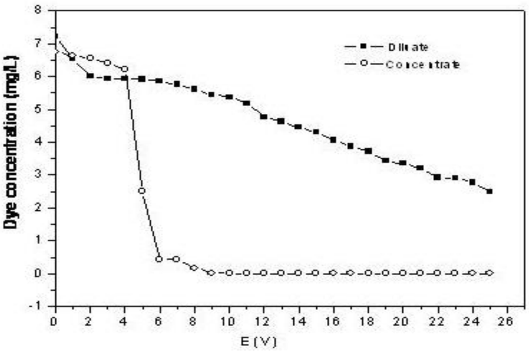


Fig. 4 Dye concentration in diluate and concentrate of ED

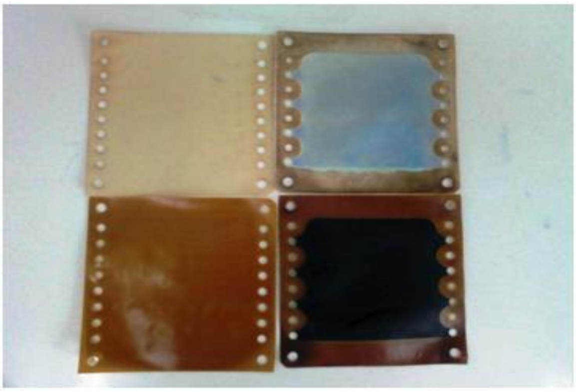


Fig. 5 Picture of a clean (right) and scaled (left) ion-exchange membrane

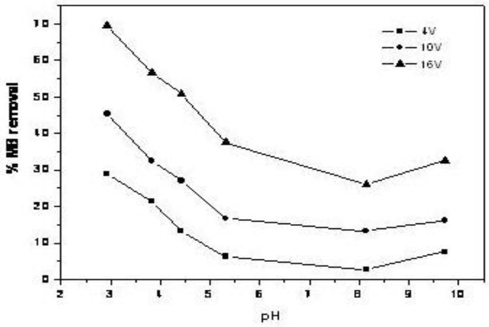


Fig. 6 Effect of pH of the feed solution on the removal of MB (feed flow rate 5 L/h; ionic strength 0.04 M, MB concentration 5 mg/L)

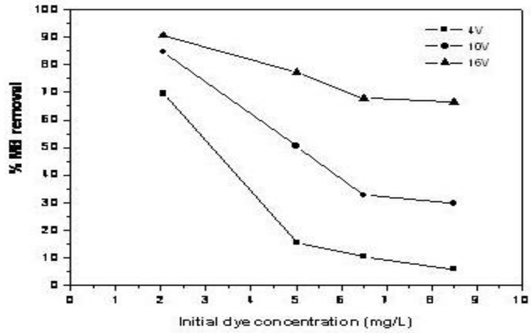


Fig. 7 Effect of initial dye concentration on the MB removal (feed flow rate 5L/h, pH = 3, ionic strength 0.04M)

DR increases only marginally with the increasing voltage drop.

Previous work (Ben Sik Ali *et al.* 2010, Fadel *et al.* 2016) showed that in this region the resistance of the stack is relatively high. The applied voltage is not so important to overcome the resistance of membranes and to induce the transport of several ions. At these conditions there are few transports of ions between the dilute and concentrate compartments.

Fig. 4 gives the plots of dye concentration in diluate and concentrate as function of the applied voltage of electrodialysis process with standard ion-exchange membranes. According to these plots, the dye concentration in the diluate was decreasing with increasing drop voltage, although, the dye concentration in the concentrate was also decreased with increasing drop voltage until 9 V. After this voltage, the dye concentration was maintained zero. It can be concluded that no migration of dyes particles into concentrate cells. This is also confirmed in Fig. 5. The behavior of MB indicates that dye particles are subjected to membrane sorption phenomena. The dye molecules adsorbed onto the membrane surface since the PC-SK membrane surface is negatively charged. The behavior is observed to the desalination by electrodialysis for water salt solution containing various anionic dyes (Majewska-Nowak 2013).

3.2.2 Effect of initial pH

The removal of MB was studied at different pH values ranging from 2.9 to 9.8 and a fixed initial MB solution of 5 mg /L. Effects of pH of the feed solution on the removal of MB are illustrated in Fig. 6. As seen in Fig. 6, a clear dependence of the dye transport and removal vs. the pH of a solution is observed. So, in a pH range of 3 to 5.5, the dye removal is lowers sharply and it's virtually constant when pH exceeds 5.5. It was thought that these results were due to the nature of MB in aqueous solutions. Mainly, they were due to the presence of spices charged MB in the solution. MB is a cationic dye which exhibits two major absorption bands in dilute aqueous solutions and different MB species were found on the MB: the monomer (MB^+), the protonated monomer (MBH^{2+}), the dimer ($(MB^+)_2$) and the trimer ($(MB^+)_3$). Only monomer and dimer species were present in aqueous solution (Ben Douissa *et al.* 2013).

3.2.3 Effect of MB initial concentration

The effect of initial feed concentration on removal performance of MB from aqueous solution was investigated using aqueous solutions at various concentrations of MB. The ionic strength, the pH and the flow rate of feed solution were initially fixed respectively to 0.04 M, 3 and 5 L/h. Three voltage (4, 10 and 16 V) was respectively applied across the entire assembly for each experiment.

As shown in Fig. 7, the MB removal has a considerable dependency on the feed solution in this range of concentration. The maximum iron removal is obtained for 2 mg/L as initial concentration. An increase of the initial concentration leads to the decrease of the MB removal. Effectively at some hydrodynamique and electrical conditions the number of dyes transported through the

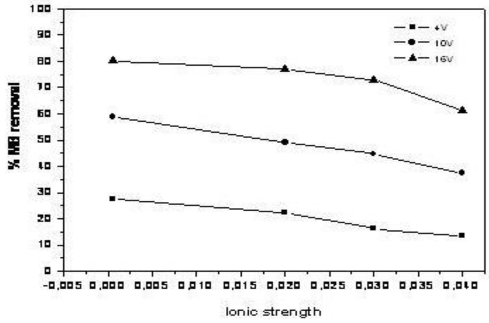


Fig. 8 Effect of the ionic strength of feed solution on the MB removal (feed flow rate 5 L/h; pH = 3; MB concentration 10 mg/L)

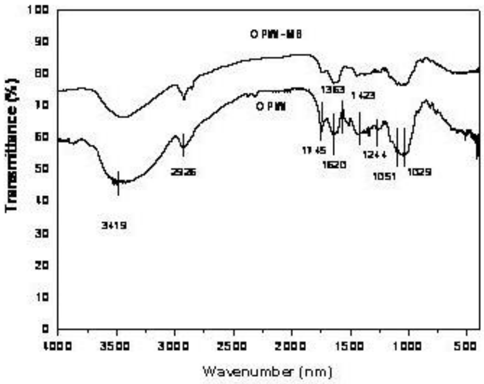


Fig. 9 FTIR spectroscopy of MB on OPW

membranes are almost the same but total amounts of MB are quite different from the different treated solution.

3.2.4 Effects of ionic strength

The effect of the feed solution ionic strength on the removal of dye was investigated using aqueous solutions at various concentrations of NaCl salt. The ionic strength of feed solution was varied from 2 10^{-2} M to 4 10^{-2} M.

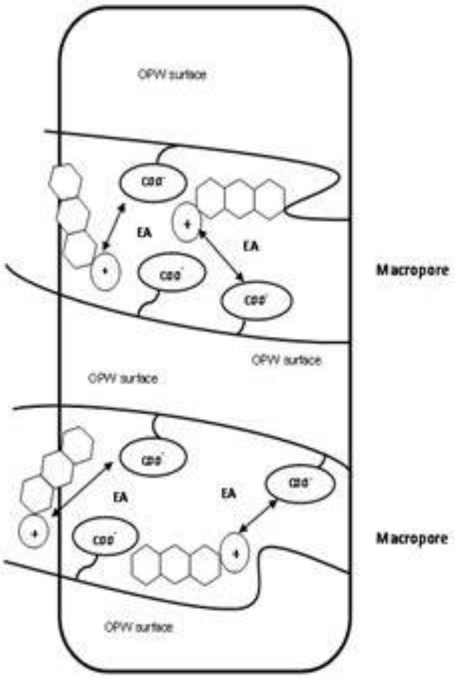
The pH and MB concentration of prepared solution are fixed respectively to 3 and 10 mg/L. The flow rate of dilute and concentrate were fixed to 6 L/h. 4, 10 and 16 V was respectively applied across the entire assembly.

Fig. 8 represents the effects of the ionic strength of feed solution on ED performances. As shown in Fig. 8, the initial salt concentration didn't have a significant effect on the MB removal. But, the increase of concentration of salts in the solution leads to an increase of the conductivity of solution. As consequence the electric current induced was bigger.

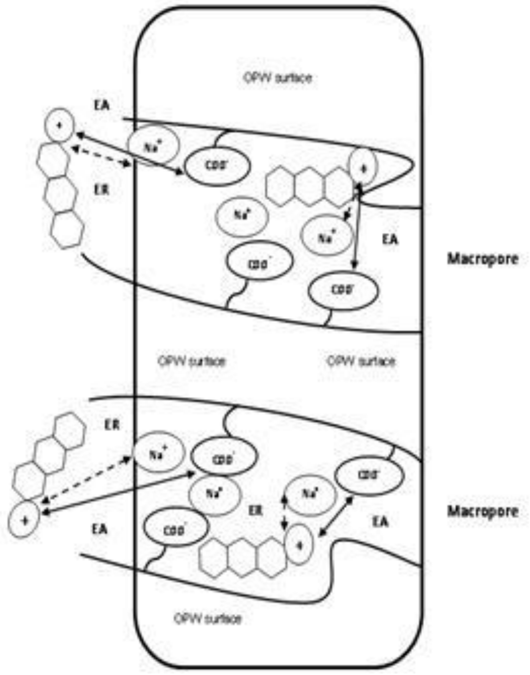
3.3 Comparison of interaction results

The FTIR spectroscopy of OPW, OPW−MB are shown in Fig. 9. From these figures, it is possible to verify the complex nature of this material. The OPW is composed basically of polysaccharide lignin, and pectin, containing hydroxyl and carboxylate groups.

In OPW spectrum, the broad and intense absorption peaks observed from 3000 cm^{-1} to 3600 cm^{-1} indicating the presence of free or hydrogen bonded O−H groups (alcohols, phenols and carboxylic acids) as in pectin, cellulose and lignin on the surface of the adsorbent (Gnanasambandam and Protor 2000). The O–H stretching vibrations occur within a broad range of frequencies indicating the presence of "free" hydroxyl groups and bonded O–H bands of carboxylic acids. The peaks observed at 2926 cm^{-1} are attributed to the C−H bonds of aliphatic acids (Li *et al.*



(a) In the absence of salt



(b) In the presence of salt

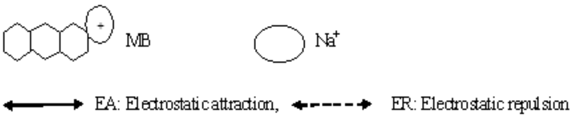


Fig. 10 Suggested mechanism of MB on adsorption

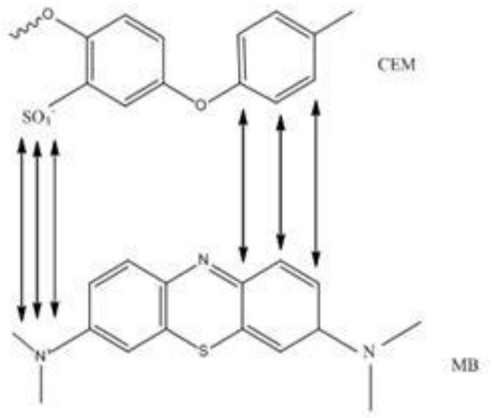


Fig. 11 Suggested mechanism of MB and cation-exchange membrane

2007). The Peak observed at 1745 cm^{-1} is the stretching vibration of C=O bond due to non-ionic carboxyl groups (–COOH, –COOCH$_3$), and may be assigned to carboxylic acids or their esters (Farinella *et al.* 2007). Asymmetric and symmetric stretching vibrations of ionic carboxylic groups (–COO$^-$) respectively, appeared at 1620 cm^{-1} and 1423 cm^{-1}. The peaks at 1363 cm^{-1} may be assigned to symmetric stretching of –COO$^-$ of pectin, and aliphatic acids group vibration at 1244 cm^{-1} to deformation vibration of C=O and stretching formation of −O–H of carboxylic acids and phenols, and at 1051 cm^{-1} can be assigned to the stretching vibration of C–O–H of alcoholic groups and carboxylic acids (Guibaud *et al.* 2003).

It is well indicated from FTIR spectrum of OPW that carboxyl and hydroxyl groups were present in abundance. These groups in biopolymers may function as proton donors; hence deprotonated hydroxyl and carboxyl groups may be involved in coordination with dyes. FTIR spectra of MB-OPW showed that the peaks expected at 3419, 1745, 1620, 1423, 1363, 1244 and 1051 cm^{-1} had shifted, respectively, to 3417, 1737, 1641, 1435, 1377, 1246 and 1068 cm^{-1} due to dye sorption. These shifts may be attributed to the changes in counter ions associated with carboxylate and hydyroxylate anions, suggesting that acidic groups, carboxyl is predominant contributors in dye uptake (Iqbal *et al.* 2007). These FTIR results corroborated by the amount of carboxylic and carbonyl groups on the material and with the elemental analysis (see Table 4) indicated that the OPW presented functional groups such as, OH, COO− and CO, that could be potential adsorption sites for interaction with the cationic MB dye. The Fig. 10 suggested mechanism of MB on adsorption in the absence and in the presence of salt.

In Fig. 11, electrically charged membranes are used together with electrodialysis in the separation, traditionally, ion exchange membranes are classified into anion exchange membranes and cation exchange membranes depending on the type of ionic groups attached to the membrane matrix. Cation exchange membranes contain negatively charged groups such as (-SO$_3$H, -PO$_3$H, -COOH, -NH$_3$OH, etc.), fixed to the membrane backbone and allow the passage of cations but reject anions. Anion exchange membranes contains positively charged groups, such as -NH$_3^+$, -NRH$_2^+$, -NR$_2$H$^+$, -NR$_3^+$, -PR$_3^+$, -SR$_2^+$, etc., fixed to the membrane backbone and allow the passage of anions but reject cations. According to the connection way of charge groups to the matrix or their chemical structure, ion exchange membranes can be further classified into homogenous and heterogeneous membranes, in which the charged groups are chemically bonded to or physically mixed with the membrane matrix, respectively. However, most of the practical ion exchange membranes are rather homogenous and composed of either hydrocarbon or fluorocarbon polymer films hosting the ionic groups (Xu 2005).

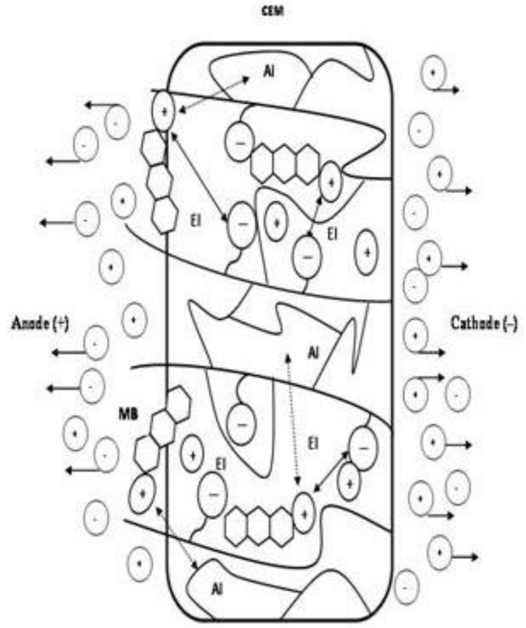


Fig. 12 Suggested mechanism of MB fouling behavior: EI, electrostatic interaction between MB and membrane fixed charge; AI, affinity interaction between MB and membrane matrix

All ion-exchange membrane materials can be divided into three large classes, namely, high molecular membranes based on polymers containing functional ion-exchange groups, inorganic membrane materials, and hybrid materials of the organic/inorganic type (Yaroslavtsev and Nikonenko 2009).

High-molecular ion-exchange membranes are constructed on the basis of flexible polymer chains, repeating units of which–on the basis of aliphatic, cyclic, aromatic (involving the structures containing heteroatoms, oxygen, nitrogen, etc.), and hydrocarbon fragments or perfluorinated units-contain functional groups.

Almost, all cationic-exchange membranes CEM have been obtained by the co-poly condensation or copolymerization of monomers and introducing sulfuric groups acids as fixed charges in to polymer. Fig. 12 shows the structure of a commercially available CEM and a suggested mechanism for fouling by MB. There are two main factors in fouling: interaction between cations and the fixed charged groups of the CEM and affinity interactions such as π–π interactions between the membrane matrix and aromatic compounds. Hence, aromatic CEM will have potentially high organic fouling properties.

4. Conclusions

In the present study, two methods were used to removal of MB: The adsorption process was applied successfully for the removal of MB, sorption dye was dependent on initial pH of solution in the absence and the presence of salt, adsorption at pH>3.7 enhanced the efficiency of adsorption process, while the adsorbent dosage up to 20 g/L had an increasing effect on the adsorption capacity of OPW in absence and the presence of salt.

The electrodialysis process with standard ion exchange membranes enabled efficient desalination of cationic dye solutions, therefore the removal of MB from the dye/salt depending on the applied voltage, the ions of dyes are not transported from diluate to concentrate compartment, these ions are adsorbed on the surface of standard cation exchange.

The experimental results demonstrated that electrostatic interactions are very important for the adsorption. Electrostatic attraction promotes the adsorption; on the contrary, electrostatic repulsion suppresses the adsorption. With increasing ionic strength, more Na^+ ions can screen the charged sites of the adsorbent, leading to a reduction of the electrostatic interactions and the between the CEM and MB, there are two factors: electrostatic interaction between cations of dyes and the fixed charged groups of the CEM, and affinity interactions such as π–π interactions between the membrane matrix and dye.

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