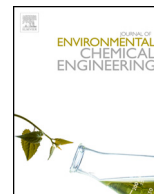




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## Can electrochemical oxidation techniques really decontaminate saline dyes wastewater?

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## ABSTRACT

Formation of toxic chlorinated organic byproducts is of great concern when selecting electrochemical oxidation (EO) as decontamination technology for saline dye wastewater, but still not verified. To test the applicability of EO, methyl orange (MO) was used as a model dye for anodic contact glow discharge electrolysis (CGDE) and conventional electrolysis (CE) in the presence of chloride. The degradation kinetics and organic intermediates were analyzed. In the presence of chloride, the rates of dye degradation were significantly increased as CGDE and CE were applied. CE resulted in higher mineralization efficiency than CGDE which needs much energy input. Several refractory chlorinated aromatic and even aliphatic compounds were identified during MO degradation, as well as the other anthraquinone dye, alizarin red S (AR). Therefore, the issues of toxic chlorinated byproducts and energy cost should be preferentially evaluated prior to the selection of EO technologies.

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## Introduction

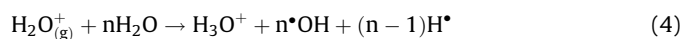
The electrochemical oxidation (EO) technologies have been greatly developed for its alternative use for industrial wastewater treatment, owing to the improved performance of electrode materials and optimization of reactor geometry [1]. In general, these EO technologies are considered environmentally compatible, because their main reagent, the electron, is a clean reactant. Pollutant in EO can be removed by direct electrolysis or indirect electrolysis in which some electro-active species act as electron shuttles between anode and the organic compounds [2–5]. Among anodically generated oxidizing chemical, active chlorine ( $\text{Cl}_2/\text{HClO}$ ) is the most widely employed, in particular for treatment of saline wastewater, such as textile and tannery effluents.

High content of NaCl is one of the important characteristic of textile wastewater, because large amounts of NaCl ( $50\text{--}80\text{ g L}^{-1}$ ) are used in dyeing processes to improve dye fixation and completion [6]. With the use of abundant NaCl in saline wastewater to produce on-site chlorine, chloride-mediated electrolysis offers a promising approach for the treatment of dyeing wastewater [7]. Direct oxidation of chloride ions at the anode leads to yield soluble chlorine (Eq. (1)), which can be rapidly

hydrolyzed to be disproportionated to hypochlorous acid/hypochlorite ion ( $\text{HClO}/\text{ClO}^-$ ,  $pK_a = 7.55$ ) (Eqs. (2) and (3)).



$\text{HClO}/\text{ClO}^-$  is the major oxidizing agent for dye degradation in conventional electro-oxidation (CE). Hydroxyl radical and other reactive species also participate in electrochemical advanced oxidation processes (EAOPs), such as anodic contact glow discharge electrolysis (CGDE) [8–10]. Recently, our group [11] and other colleagues [8–10,12–14] reported that using CGDE with applied voltage (580 V) a series of  $\cdot\text{OH}$  (Eq. (4)),  $\text{Cl}\cdot/\text{Cl}_2\cdot$  (Eqs. (5–9)) and chlorine species, would be present which could enhance organic pollutant degradation.



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In spite of success of EO methods in fast decolorization of dye, the electrochemical and chemical reactions that take place in  $\text{Cl}^-$ -containing solution are complex and not entirely known. Similar to other advanced oxidation technologies [15–22], CGDE and CE are likely to form chlorinated organic compounds during electrolysis of chloride-rich solutions [11], leaving the treated matrix more polluted and toxic. Conversely, some authors argued that no chlorinated organics were formed in degradation of small organics [23] and reactive blue 19 [18]. Hence until now whether chlorinated byproducts are formed is still under debate. Since the formation of undesirable chlorinated organic byproducts is a major concern when EO is applied, it is of great significance to identify the organic intermediates formed in saline water as EO, such as CE and CGDE, is used.

With this perspective, the aim of this study is to investigate the effects of Cl ions on the degradation of structurally different dyes (alizarin red S (AR), anthraquinone dye; methyl orange (MO), azo dye) treated by anodic CGDE and CE. The degradation kinetics of MO with Cl ions were compared and attempts were made to identify and compare the byproducts formed.

## Experimental

### Chemicals

Alizarin red S (AR) purchased from Acros (certified pure) and methyl orange (MO) from Sigma–Aldrich (ACS reagent), were used as model dyes.  $\text{Na}_2\text{SO}_4$ , NaCl,  $\text{H}_2\text{SO}_4$  and NaOH were laboratory reagent grade. LC–MS grade methanol was purchased from Fisher Chemical and diethyl ether (extra pure) was purchased from Honeywell Burdick & Jackson. Barnstead UltraPure water (18.3 M $\Omega$  cm) was used throughout the study.

### Experimental procedures

The electrolytic reactor setup has been reported elsewhere [11]. The potential difference applied between the electrodes was 580 V

and the current used was 80 mA. An ice bath was used to maintain the temperature at  $25 \pm 5^\circ\text{C}$  in the reactor. CE was carried out in the same reactor vessel with terminal voltage across the electrodes maintained at a constant value of 9 V. The anode was immersed to a depth of about 1 cm in the electrolyte so that the current was 80 mA.

The simulated dye wastewater samples were freshly prepared before each degradation experiment. The chemicals used were described in Supporting Material. One mole  $\text{Na}_2\text{SO}_4$  and 1 M NaCl was used to make up the electrolyte to a conductivity equivalent to 7.5–150 mM  $\text{Na}_2\text{SO}_4$  prior to pH adjustment with 1 M  $\text{H}_2\text{SO}_4$ . An acidic environment was chosen because: (1) dyes degradation is more favorable under acidic pH, as suggested by our previous studies [11]; (2) the characteristic absorption peak of MO does not shift at pH 3.0 during degradation process, thus favoring the accurate evaluation of dye degradation.

### Methods and analysis

The pH and conductivity of the samples were measured with a Multi WTW 340i instrument (Germany). The MO degradation was monitored by measuring the absorbance at 507 nm with a UV–vis spectrophotometer (Hitachi Model U-2910). Total organic carbon (TOC) content of the samples was determined using a Shimadzu TOC analyzer (model TOC-VCPH/CNP). GC–MS analysis was carried out on an Agilent 7890A gas chromatography equipped with an Agilent 19091J-433 capillary column, HP-5 5% Phenyl Methyl Siloxan (30 m  $\times$  320  $\mu\text{m}$   $\times$  0.5  $\mu\text{m}$  film thickness), interfaced to a mass spectrometer (MS) (5975A inert XL MSD with a Triple-Axis Detector) (see details in Supporting Material).

## Results and discussion

### Degradation kinetics

Degradation kinetics of MO in the presence of chloride were examined using CGDE and CE at the same applied current (80 mA). The rate constant  $k$  ( $\text{min}^{-1}$ ) for the MO decoloration were estimated from the slope of the graph of  $\ln(C_0/C)$  as a function of time (Fig. 1a). In the absence of chloride, CE resulted in the minimal dye degradation ( $k = 0.0025 \text{ min}^{-1}$ ,  $R^2 = 0.995$ ), suggesting the direct oxidation/reduction of MO at the electrode surfaces was negligible. In contrast, enhanced degradation during anodic CGDE ( $k = 0.06 \text{ min}^{-1}$ ,  $R^2 = 0.98$ ) in Fig. 1a should be attributed to the

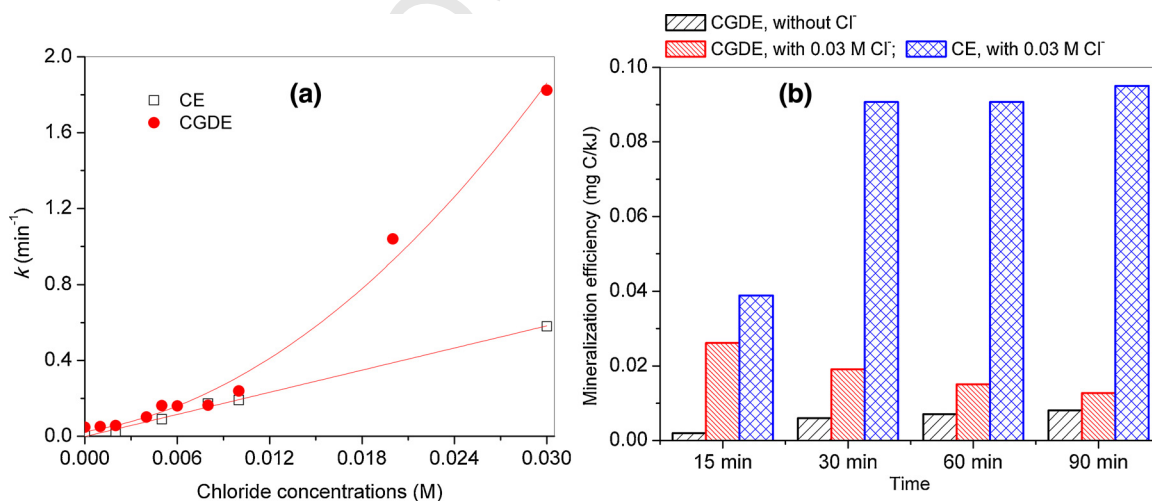


Fig. 1. Effect of Cl ions on (a) MO degradation and (b) mineralization efficiency by CE and CGDE (sample volume = 100 ml, dye concentration = 0.05 mM, initial pH = 3, current = 80 mA).

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