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Parameter evaluation of the anodic oxidation of phenol in wastewater using a Ti/RuO_2-IrO_2 anode

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ABSTRACT

The influence of different operational parameters (i.e., applied current density, chloride concentration, stirring rate, initial pH and temperature) on the electrochemical oxidation of phenol in a chloride-rich synthetic wastewater by a Ti/RuO_2-IrO_2 anode was investigated in a lab-scale batch reactor. A design of experiments (DoE) was developed to define the most important parameters in the process. It was observed that the initial pH, chloride concentration and the applied current density had the highest influence on the relative COD removal. The use of sulphate as a supporting electrolyte only resulted in a limited improvement of COD removal: only 10% more COD was degraded after 3 h of treatment. On the contrary, in the presence of chloride, already 90% of the initial COD was degraded after a reaction time of only 90 min. A kinetic and energetic evaluation of the electrochemical oxidation process showed that a high current density, applied in combination with a high initial pH, high chloride concentration and low initial COD concentration results in a fast degradation of phenol. In terms of energetic feasibility, a low applied current density combined with a high initial pH, high chloride concentration and low initial COD concentration was shown to be the most appropriate.

Keywords: Design of experiments; Electrochemical oxidation; Phenol; Ti/RuO_2-IrO_2 anode

1. Introduction

The presence of recalcitrant, non-biodegradable components in industrial wastewater and the increasingly stringent legislation puts a high pressure on the wastewater treatment facilities [1].

One specific problematic group of components are phenol and its derivatives, which cause severe environmental damage when emitted to natural waters because of their toxicity and low biodegradability [2]. Phenol is produced in various industrial sectors, as it is encountered in the production of pharmaceuticals, pesticides, textile, dyes and in petroleum refineries [2–4].

In the literature, phenol is widely used as a model pollutant for evaluating the efficiency of (physico) chemical methods to degrade recalcitrant components in wastewater [5].

Chemical oxidation by advanced oxidation processes (AOP) is of high interest to treat non-biodegradable components in wastewater. An AOP is based on the formation of highly reactive hydroxyl (·OH) radicals, which effectively degrade a wide variety of organics. ·OH radicals are most often produced from a precursor such as hydrogen peroxide (H_2O_2) or ozone (O_3), in combination with a catalyst such as ferrous iron (Fe^{2+}) or UV light. However, for some types of wastewater, the operational costs for the complete mineralisation of the organic pollutants are high (mostly due to the need for chemicals dosing and/or energy to power the UV-lamps) [6,7]. In those cases, a partial oxidation is advisable as a pre-treatment to increase the biodegradability and reduce the toxicity of the wastewater, so it can be further purified in a biological (aerobic or anaerobic) process.

An alternative approach for a typical AOP is the use of electrochemical advanced oxidation processes (eAOP). In these techniques, oxidation is achieved by applying a volt-

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age over a set of electrodes that are submerged in the wastewater. The oxidation reaction taking place at the anode is the driving force behind the degradation. Three possible mechanisms have been identified [8]: direct oxidation at potentials below the minimal standard cell potential for water electrolysis (E^0 = 1.23 V vs. SHE), direct oxidation at higher voltages and indirect oxidation via mediators such as chloride ions.

The first type of direct oxidation, which takes place at a potential below the minimal standard cell potential for water electrolysis (E^0 = 1.23 V vs. SHE), is achieved by direct electron transfer after adsorption of the organic pollutant at the anode. This type of oxidation is not interesting for practical application due to the very slow degradation kinetics, especially for more complex molecules. Also, electrode fouling occurs at low applied potentials, resulting in an inactivation of the electrode's surface [9,10]. Considering these drawbacks, oxidation at a higher voltage than the standard cell potential for water electrolysis is applied more frequently. In this case, oxidation is achieved by physically ($MO_x(\cdot OH)$) or chemically (MO_{x+1}) adsorbed hydroxyl radicals, which are themselves formed at the anode's surface (MO_x) [Eqs. (1), (2)]. This mechanism requires an electrocatalytic effect, which implies the use of proper anode materials to catalyse the production of these radicals.

The use of so-called 'non-active' anodes (e.g., boron doped diamond (BDD) and mixed metal oxide electrodes containing PbO_2 or SnO_2) stimulates the production of physically adsorbed hydroxyl radicals, which react very fast with the organic pollutant [Eq. (3)]. On the other hand, 'active' anodes such as Ti/Pt and Ti/RuO_2-TiO_2 anodes, have a lower oxidative power. Therefore, this type of anodes reacts with the chemically adsorbed hydroxyl radicals to the formation of a higher oxidation state of the anode material (MO_{x+1}). The anode then becomes capable of directly oxidising the adsorbed organics [Eq. (4)] [8].

$$MO_x + H_2O \rightarrow MO_x(\cdot OH) + H^+ + e^- \tag{1}$$

$$MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e^- \tag{2}$$

$$R + MO_x(\cdot OH) \rightarrow MO_x + mCO_2 + nH_2O + H^+ + e^- \tag{3}$$

$$R + MO_{x+1} \rightarrow RO + MO_x \tag{4}$$

The last mechanism is called indirect oxidation, which implies the involvement of external mediators (e.g., chlorides, ferric irons or silver ions). These inorganic mediators are responsible for the oxidation of organics in the bulk of the solution [11,12]. Special attention is paid to the indirect oxidation mechanism with chlorides because these are abundantly present in many industrial wastewaters. Chloride ions are electrochemically converted into Cl_2 (E^0 = 1.36 V vs. SHE), which is in turn rapidly oxidised into HClO at a pH between 2 and 7.5. When the pH is above 7.5, HClO (E^0 = 1.63 V vs. SHE) dissociates into H^+ and ClO^- (E^0 = 0.89 V vs. SHE) (Eq. (5)–(7)). Via this mechanism, in situ active chlorine (a collective term for all types of chlorine based oxidisers) is generated, which oxidizes organic components in the wastewater (Eq. (8)). This type of indirect oxidation is much faster than the indirect oxidation with OH-radicals because the reaction does not only take place in the proximity of the anode's surface but actually occurs in the bulk solution. However, this type of oxidation has the drawback of chlorinated organics production during oxidation, as well as the production of chlorites and chlorates, which can be harmful for microorganisms. At increased reaction times, chloro-organics are further oxidized and disappear again, as exemplified in some previous studies [4,13].

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{5}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{6}$$

$$HClO \rightarrow ClO^- + H^+ \tag{7}$$

$$R + ClO^- \rightarrow ROCl \tag{8}$$

Table 1 provides an overview of some reported experiments for the electrochemical oxidation of phenol with anode materials similar to those used in this study (i.e. Ti/RuO_2-IrO_2 anode).

The aim of this paper is to investigate the indirect oxidation of phenol by using a chloride-rich synthetic wastewater matrix. Ti-based electrodes were used, with the anode coated with a mixture of RuO_2 and IrO_2. The electrode material is chosen with respect to its low cost, its stability in a chloride-rich environment (RuO_2 electrodes are often used in the chloro-alkali industry) and its high service life (e.g., PbO_2 electrodes may cause a contamination of the wastewater with Pb, and SnO_2 has a very low service life) [18]. The influence of several operational parameters is investigated: anode material, applied current density (J), concentration of chlorides (C_{NaCl}), pH, temperature (T) and stirring rate. A design of experiments (DoE) is developed to highlight the most important parameters in the electrochemical oxidation process. Furthermore, more specific experiments are conducted and the concentration of phenol and COD are reported as a function of time for the most significant parameters. With these data, a kinetic and energetic evaluation is carried out.

2. Materials and methods

2.1. Characteristics of the synthetic wastewater

All experiments were carried out using a solution of phenol (Acros Organics, 99%) as sole organic pollutant, inultra-pure water (Millipore Milli-Q of specific resistance >18,2 MΩ.cm). The initial phenol concentration was 63 mg/L (COD = 150 mg O_2/L), 105 mg/L (COD = 250 mg O_2/L) or 210 mg/L (COD = 500 mg O_2/L).

NaOH (VWR, 99.5 %) or H_2SO_4 (Fischer Chemical, 95 %) was added to the water to investigate the influence of the pH on the phenol degradation. The influence of sulphate or chloride ions in the wastewater was investigated by adding Na_2SO_4 (Merck, anhydrous 99%) or NaCl (Acros Organics; 99.5 %) at different concentrations (0.5 g/L; 1.5 g/L or 2.5 g/L).

Table 1
Overview of electrochemical phenol degradation by other authors

Reference	Anode material	Electrolyte	Type of reactor	Most important observations
[14]	$Ti/Ti_{0.7}Ru_{0.3}O_2$ and BDD	Cl^-	Continuous	Addition of Cl^- to the water improves degradation rate Faster degradation of phenol with $Ti/Ti_{0.7}Ru_{0.3}O_2$ comparing to BDD with Cl^- as electrolyte
[15]	Pt, Ti/RuO_2 and $Ti/Sb\text{-}SnO_2$	SO_4^{2-}	Batch	Pseudo zeroth order kinetics with Pt and Ti/RuO_2 at high phenol concentrations Pseudo first order kinetics with $Ti/Sb\text{-}SnO_2$ and with Ti/RuO_2 and Pt at low phenol concentrations
[4]	Ti/RuO_2	SO_4^{2-} and Cl^-	Continuous	Only effective phenol degradation with Cl^- electrolyte Chlorophenol formation but also fast degradation in time No electrocatalytic loss during accelerated life test in Cl^- solution
[16]	$Ti/SnO_2\text{-}Sb$, Ti/RuO_2 and Pt	SO_4^{2-}	Batch	Slow degradation with Ti/RuO_2 and Pt anodes
[17]	$Ti/RuO_2\text{-}Pt$ and $Ti/IrO_2\text{-}Pt$	SO_4^{2-} and Cl^-	Continuous	Only effective phenol degradation with Cl^- electrolyte Faster oxidation at $Ti/RuO_2\text{-}Pt$ anode
[15]	$Ti/TiO_2\text{-}RuO_2\text{-}IrO_2$	SO_4^{2-} and Cl^-	Batch	Only effective phenol degradation with Cl^- electrolyte Chlorophenol formation but also fast degradation in time

2.2. Experimental lay-out

All experiments were carried out in a lab-scale batch reactor, equipped with a water jacket connected to a thermostatic bath for temperature control. The active reactor volume was 500 mL and the solution was mixed by a magnetic stirrer. Parallel plate electrodes (Ti cathode and $Ti/RuO_2\text{-}IrO_2$ anode, provided by Magneto Special Anodes B.V., The Netherlands) having an active surface area of 32 cm² (rectangular, 8 cm by 4 cm) and mounted at a fixed distance of 1 cm with polyamide screws, were submerged in the reaction mixture. A constant current (galvanostatic conditions) was applied using a lab-scale power supply (Elektro Automatik EA-PSI 8160-04 DT). The total reaction time was set at 1 h and samples for COD and phenol measurements were taken at fixed times during the experiment. Both parameters were used as response parameters in the design of experiments.

2.3. Analytical techniques

Phenol concentration was measured using a HPLC (Agilent 1100 Series) equipped with a reversed-phase C18 column (Agilent, Zorbax Eclipse Plus C18 4,6×100 mm; 3,5 μm) and a UV detector (270 nm). The mobile phase was a mixture of methanol and water (37/63%) and the injection volume was 3 μL. The COD was measured using the closed reflux colorimetric method (Method 5220 D, APHA) with test tubes from Machery-Nagel and a Nanocolor 500 D photometer [19]. When the concentration of added chlorides exceeded 1.5 g/L, the samples were diluted with ultra-pure water before analysis to avoid interference. The pH of the solution was measured using a Mettler Toledo SevenEasy pH meter and the conductivity of the water was measured using a Hach Lange conductivity sensor (CDC401 sensor connected to a HQ40d portable meter).

2.4.Design of experiments

A screening design was chosen to investigate the most significant parameters since it is especially effective when investigating four or more parameters [20,21]. In this work, five parameters (electrolyte type, electrolyte concentration, initial pH, applied current density and initial phenol concentration) were investigated using a non-geometric screening design. This design is used to characterize the most significant parameters in the process whereas small, negligible interactions are neglected [20]. The conditions for each experiment and the corresponding results are depicted in Table 2. Three centre points were added to the design to detect the presence of nonlinearities in the model. Based on the chosen experimental design, 15 experiments were conducted in a random order. A Pareto chart of the standardized effects was generated to evaluate the response parameters (i.e., relative COD and phenol removal after 1h of treatment) for each experiment after electrochemical oxidation. This chart represents the main influencing parameters of the process by graphically dis-

Table 2
Experimental conditions based on the screening design of experiments

J (mA/cm²)	pH (–)	Stirring rate (RPM)	T (°C)	C_{NaCl} (g/L)	$COD/COD_{0,1h}$ (–)	$C/C_{0,1h}$ (–)
5	3	250	20	0.5	0.98	0.95
20	9	250	20	2.5	0.24	0.00
5	9	250	37	2.5	0.83	0.27
20	9	750	20	2.5	0.14	0.00
5	3	750	37	2.5	1.00	0.29
5	9	250	20	0.5	1.00	0.27
5	3	750	20	2.5	0.88	0.05
20	9	750	37	0.5	0.53	0.50
12.5	6	500	28.5	1.5	0.74	0.00
5	9	750	37	0.5	0.79	0.92
12.5	6	500	28.5	1.5	0.74	0.00
12.5	6	500	28.5	1.5	0.75	0.00
20	3	750	20	0.5	0.96	0.66
20	3	250	37	0.5	1.00	0.45
20	1	250	37	2.5	0.38	0.00

playing the standardized effects (i.e., the ratio between the coefficient of each parameter and the standard error for this coefficient) of each parameter. When the standardized effect of a parameter exceeds the value of the reference line, this parameter is classified as a significant one in the process. This reference line is drawn at the (1-α/2) quantile, where α represents the significance level of a student-t distribution with the degrees of freedom equal to the degrees of freedom of the error term [20].

Also, a predictive model is compiled based on the results of each experiment, which enables prediction of values for these response parameters under known applied process conditions.

2.5. Kinetic evaluation

Generally, the indirect electrochemical oxidation of organic matter can be described by a second order reaction rate equation as shown in Eq. (9) [8]:

$$\frac{d[COD]}{dt} = -k * [COD] * [mediator] \tag{9}$$

with *k* the kinetic constant (L/(mg·s)), [COD] the COD concentration (mg O_2/L)) (in the case of component removal, to be replaced by [C] in mg/L) and [mediator] the concentration of the mediator (mg/L) or electrochemically formed oxidative species.

In most cases, oxidative species such as ClO^- are highly reactive and their concentration depends on the operating regime (electrolyte type and concentration, current density and anode material), which leads to the assumption that their concentration is constant at these conditions. Hence the above equation is simplified by using a steady state approximation, as expressed in Eq. (10) [8,22]:

$$\frac{d[COD]}{dt} = -k' * [COD] \tag{10}$$

with *k*′ the apparent or observed kinetic constant (1/s), including the concentration of ClO^-. In some cases, even a zeroth order reaction is observed, with the introduction of a pseudo zeroth order reaction constant k″ (mg/(L.s)) [Eq. (11)]:

$$\frac{d[COD]}{dt} = -k'' \tag{11}$$

This is the case whenever the applied current density is smaller than the limiting current density in combination with relatively high values for the COD. The process is then called current controlled and COD degradation follows zeroth order kinetics as described by Eq. (11) [8,22,23].

3. Results and discussion

3.1. Influence of electrolyte type

Fig. 1 depicts the decrease in COD as a function of time for the Ti/RuO_2-IrO_2 anode when Na_2SO_4 and NaCl are used as supporting electrolyte.

As illustrated in this figure, about 90% of the initial COD was removed after 90 min for the coated anode in a chloride environment. With sulphate as supporting electrolyte, only a limited degradation was observed after 3 h of treatment (+/− 10% COD removal). These results indicate that anodic oxidation of organics with the use of Ti/RuO_2-IrO_2 anodes is only useful in a chloride rich environment. These observations are in accordance with the literature where this type of Ru and Ir based ‘active’ electrode materials show nearly no phenol oxidation without the presence of chlorides (cf. Table 1) [4,14,17].

3.2. Design of experiments (DoE)

To investigate the efficiency of the electrochemical oxidation process for phenol degradation, the Pareto chart of the standardized effects for the five process parameters was

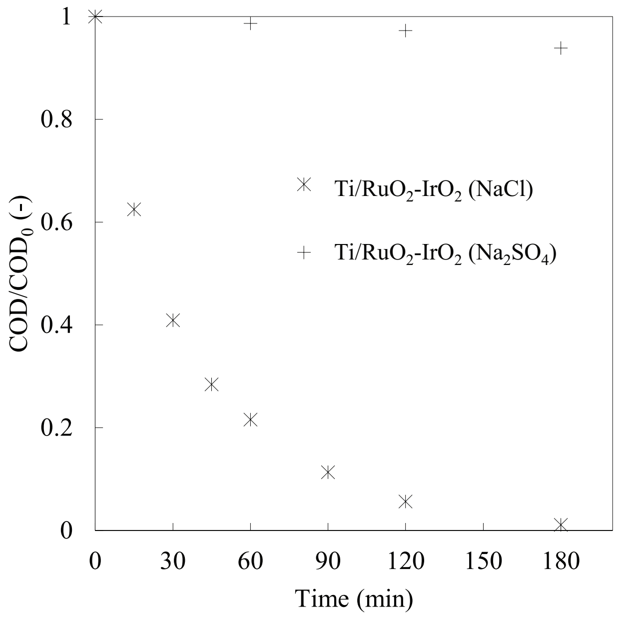

Fig. 1. Evolution of normalized COD in function of time for a Ti/RuO$_2$-IrO$_2$ anode in different supporting electrolytes. Conditions: J = 20 mA/cm², pH 6, T = 20°C, Stirring rate= 250 RPM, $C_{electrolyte}$ = 2.5 g/L and COD_0 = 150 mg O_2/L.

calculated with the relative decrease (COD/COD_0) after a treatment time of 1 h as response parameter. The relative decrease in phenol concentration (C/C_0) after 1 h was not used for this analysis since the values for this response parameter were zero for several experiments. The chart is depicted in Fig. 2. The effect values for the current density, pH and chloride concentration of this response parameter exceeded the reference line value of 2.262 (calculated based on a 95% confidence interval), and are indicated as significant parameters. It was seen that the current density had the largest influence on the relative COD decrease. This is explained by the direct relationship between the applied current density and the kinetics of the electrochemical reaction at the anode; in this case, the conversion of chloride to active chlorine (cf. Faraday's law, which states that the mass quantity of produced species at an electrode is directly proportional to the applied current). The second most important parameter is the initial pH of the wastewater. A higher value for this process parameter results in a faster degradation of the phenol. At a pH value higher than 7.5, ClO^- is predominantly present. However, this type of active chlorine has a lower oxidizing power than its non-dissociated form HClO, which is present at lower pH values [12]. The influence of pH on the oxidation rate is further discussed in 3.4. The 3rd significant parameter is the initial chloride concentration, which influences the mass transfer of electroactive species to the anode's surface and directly affects the degradation rate. A higher initial concentration, therefore, provides a faster COD degradation. The temperature and stirring rate did not significantly influence the COD degradation.

A linear model, which allows the prediction of COD degradation after a treatment time of 1h, is represented in Eq. (12):

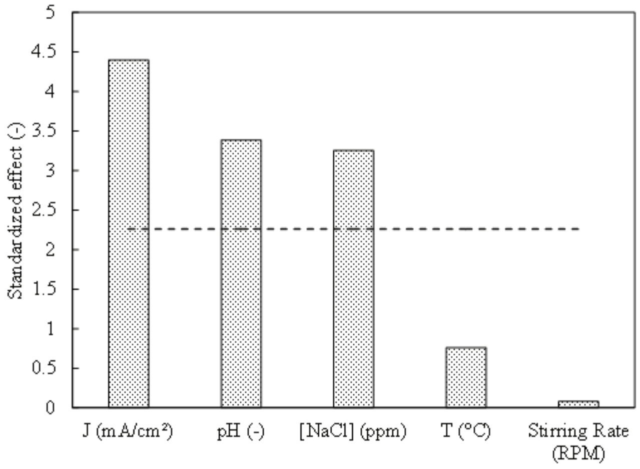

Fig. 2. Pareto chart of the standardized effects.

$$\frac{COD}{COD_0} = 1.572 - 0.02579 * J - 0.0496 * pH - 0.1431 * [NaCl] \quad (12)$$

where J is the applied current density (mA/cm²), pH is the initial pH value of the wastewater and [NaCl] is the initial chloride (g/L).

In Fig. 3, the results predicted by the model are compared to the experimental data. The first bisecting line (solid line) is also shown in this figure. The two dashed lines represent the upper and lower boundaries for a 95% confidence interval. The root mean square deviation (RMSD) for the predicted and measured results was 0.12, which means that there is an overall 12% deviation between the predicted and experimental values for COD/COD_0.

A positive effect of current density, pH and chloride concentration on the COD removal was observed, which is in accordance with previously reported observations [1,4,17].

3.3. Effect of applied current density

Fig. 4 illustrates the effect of the applied current density on the COD degradation and on the degradation of phenol, respectively. Both degradation curves show an exponential relation between the COD or phenol concentration and the reaction time. This exponential fit is related to first order kinetics and its equation for each condition is presented in these figures.

For each current density, the phenol concentration decreases exponentially with reaction time: the higher the applied current density, the faster the decrease in phenol concentration. Also, the relative COD decrease for the higher values of the applied current density follows pseudo first order kinetics, which is in accordance with Eq. (10). When the applied current density is 5, 12.5 or 20 mA/cm², the reaction rate constants are 0.006 s^{-1}, 0.013 s^{-1} and 0.025 s^{-1} for COD removal, as they are 0.079 s^{-1}, 0.195 s^{-1} and 0.618 s^{-1}, for relative phenol degradation, respectively. At these conditions, mass transfer limited the overall reaction rate, so the process is mass transfer controlled [15,22,24,25]. A higher current density increases the rate of the electrochemical conversion of chlorides to active chlorine, according to Faraday's law [1,4,11,21,24]. However, for the lowest value of the applied current density, the relative COD and phenol decrease are nearly linear. The pseudo first order reaction rate constants are, therefore, almost identical in the case of an exponential or linear decrease ($0.006\ s^{-1}$ vs. $0.005\ s^{-1}$ for relative COD removal and $0.079\ s^{-1}$ vs. $0.049\ s^{-1}$ for relative phenol removal). As stated before, the combination of a low current density and a relatively high COD content may imply pseudo zeroth order reaction kinetics [Eq. (11)]. The process is then called current controlled. These components block further oxidation of phenol and, therefore, cause pseudo zeroth order reaction kinetics with a lower pseudo reaction rate constant, which is the negative constant in the exponential fit.

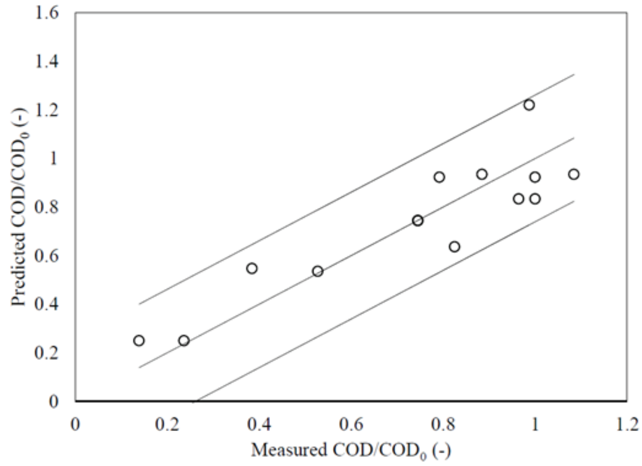

Fig. 3. Predicted and measured values for COD/COD$_0$ for the experiments from the DoE.

3.4. Effect of initial pH

To identify the effect of the (initial) pH on the degradation kinetics of phenol, experiments were conducted with an initial COD of 150 mg O_2/L, current density of 20 mA/cm², a constant temperature of 20°C, a constant stirring rate of 250 rpm, a chloride concentration of 2.5 g/L and with varying the pH between 3 and 9. Fig. 5 depicts the results of these experiments with respect to COD removal. A small positive effect was observed on the degradation at higher pH values, which confirms previous literature findings [1]. Phenol degradation under the applied conditions occurred very fast (results not shown): the concentration already dropped to 0 within a reaction time of 10 min. The pH dependence of the degradation rate could be explained by the predominant form of the chlorine oxidiser that is present in the solution. At low pH values, chlorine gas remains in solution (at pH just above 2 it starts to hydrolyse to HClO). At higher pH (above 7.5) ClO^- is formed by the dissociation of HClO. However, HClO is the most effective oxidiser among these three chlorine based oxidisers (ClO^- is the weakest chlorinating agent) [1,12]. Despite the high oxidation potential at near neutral pH values, due to the abundant presence of HClO, slightly faster oxidation of the organic species was detected at higher pH values. In the conducted experiments (Fig. 5), the reaction follows pseudo first order kinetics and, therefore, the pseudo reaction rate constant, which contains the concentration of mediator as presented in Eq. (10), is affected by a change in initial pH of the solution with pseudo reaction rate constants of $0.018\ s^{-1}$, $0.025\ s^{-1}$ and $0.026\ s^{-1}$ for an initial pH of 3, 6 or 9, respectively. As can be concluded from these reaction rate constants, there is only limited difference between pH values of 6 and 9. Therefore, the relation between the pH of the solution and the value of the reaction rate constants, cannot be attributed to the oxidative strength of the different chlorine species. However, at higher pH values, dissociation of

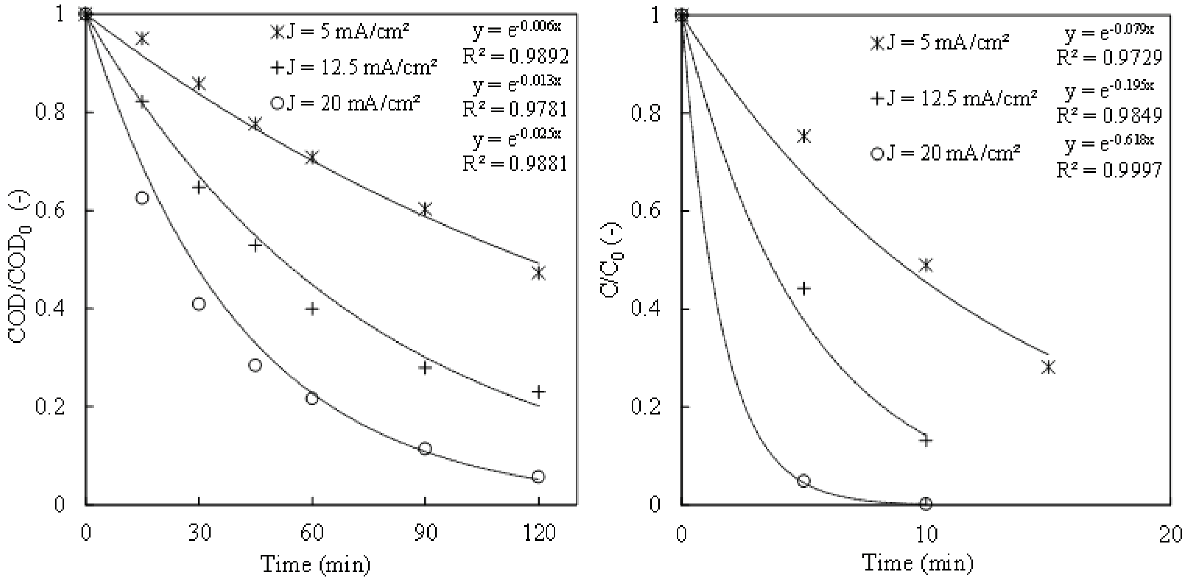

Fig. 4. Effect of applied current density on the organic matter and phenol degradation. Conditions: pH 6, T = 20°C, Stirring rate = 250 RPM, C_{NaCl} = 2.5 g/L and COD$_0$ = 150 mg O_2/L.

phenol into phenolate occurs, which may explain the limited effect of pH on phenol degradation. This dissociation, which was not further investigated in this study, could interfere with the kinetic evaluation of phenol degradation.

3.5. Effect of chloride concentration

Increasing the chloride concentration in the water does not only reduce the energy consumption of the process in galvanostatic conditions due to an increase in conductivity, but also provides a faster degradation of COD, as illustrated in Fig. 6. An increase in chloride concentration from 1.5 to 2.5 g/L increased the observed reaction rate constant from 0.015 to 0.025 s^{-1}. This is attributed to the improved mass transfer of these electroactive species to the anode's surface and, therefore, the higher amount of Cl_2, HClO or ClO^- that are electrochemically produced and react with the phenol. Also, a change in initial chloride concentration changes the reaction regime (i.e., current or mass transfer controlled) and, therefore, affects the pseudo first order reaction rate constant [14,22,24].

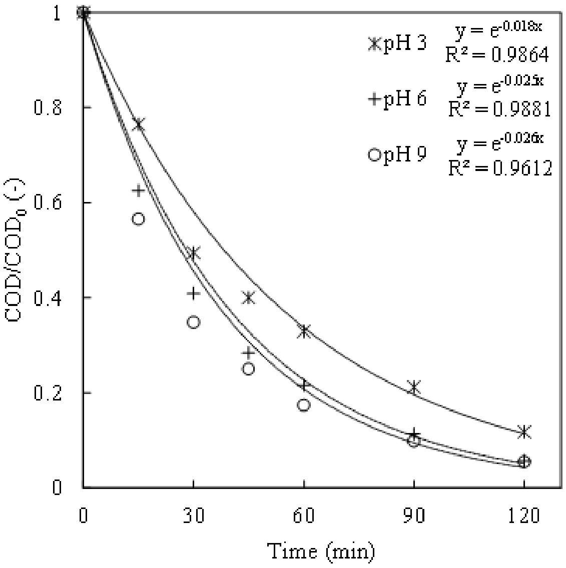

Fig. 5. Effect of initial pH on the organic matter degradation. Conditions: J = 20 mA/cm², T = 20°C, Stirring rate = 250 rpm, C_{NaCl} = 2.5 g/L and COD_0 = 150 mg O_2/L.

3.6. Effect of initial phenol concentration

Several authors reported an influence by the initial substrate concentration on the indirect oxidation process [13,23,26,27]. All agree that an increase in substrate concentration decreases the relative COD removal for a certain residence time in the electrochemical reactor. As illustrated in Fig. 7, an increase in initial COD and phenol concentration causes a decrease in reaction rate constant. In the case of COD removal, this constant decreases from 0.025 s^{-1} to 0.013 s^{-1} and to 0.004 s^{-1} when the initial COD of the wastewater increases from 150 to 250 and 500 mg/L, respectively. Also, for phenol removal, this decrease in pseudo reaction rate constant from 0.0618 s^{-1} to 0.177 s^{-1} and finally 0.051 s^{-1} with an increase in initial phenol concentration from 63 ppm to 105 ppm and 210 ppm, respectively, is observed.

However, in absolute values, the total amount of COD removed in this time interval is higher compared to experiments where the initial substrate concentration is lower. The ratio of organic matter to active chlorine concentration also influences which molecules are oxidized first. The higher this ratio, the more likely that phenol molecules, which are present in a higher concentration than the intermediate product, are degraded faster than their degrada-

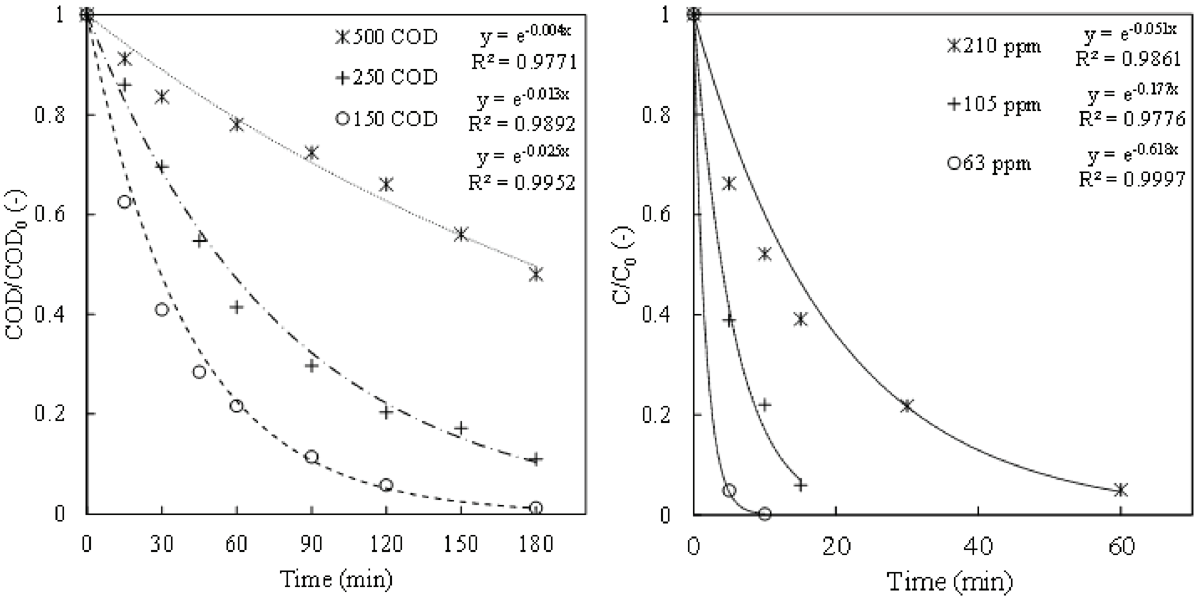

Fig. 6. Effect of chloride concentration on the organic matter degradation. Conditions: J = 20 mA/cm², pH = 6, T = 20°C, Stirring rate = 250 rpm and COD_0 = 150 mg O_2/L.

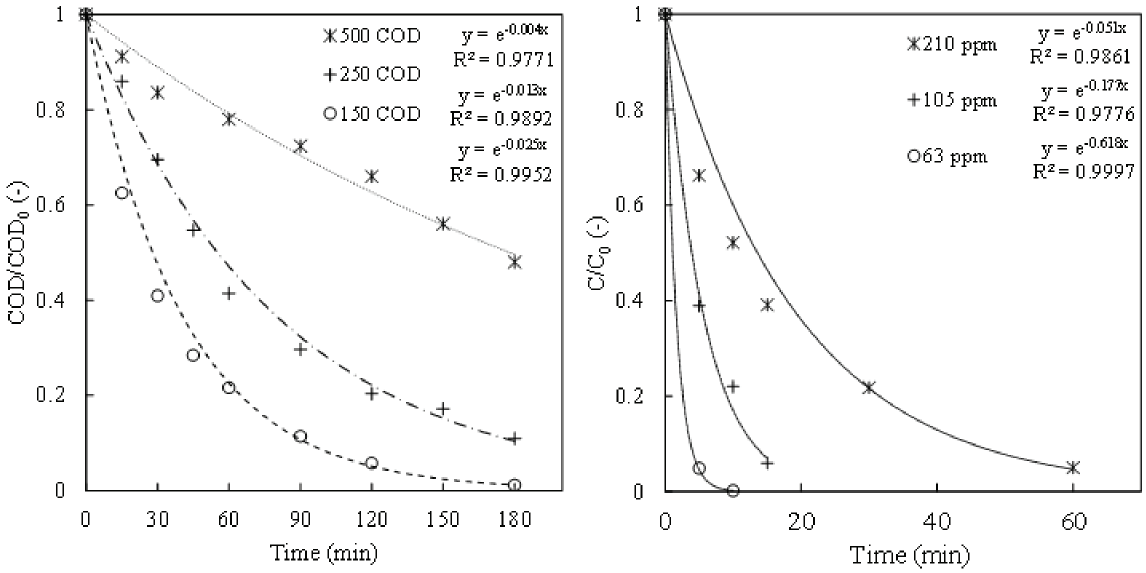

Fig. 7. Effect of initial phenol concentration on the organic matter and phenol degradation. Conditions: *J* = 20 mA/cm², pH = 6, T = 20°C, stirring rate = 250 rpm and C_{NaCl} = 2.5 g/L.

tion products and the process follows nearly pseudo zeroth order reaction kinetics [13,23]. In Fig. 7 the relative COD degradation for the case where a higher initial phenol concentration was used, the degradation is nearly linear, which implies this shift from pseudo first order to pseudo zeroth order reaction kinetics.

3.7. Energetic evaluation

To evaluate the energy consumption for the phenol degradation, an energetic response parameter was chosen, i.e., the specific energy consumption (SEC) [22]. This parameter represents the amount of energy (in kWh) that is required to remove 1 g of COD from the wastewater (Eq. (13)).

$$SEC = UI\Delta T/(3600\Delta COD) \tag{13}$$

with U (V) the voltage between the anode and cathode, I (A) the current and ΔCOD (g O_2/L) the amount of organic load that is removed in a chosen time interval Δ*t* (s). To make a relevant comparison based on the SEC for different experimental conditions, $SEC_{90\%}$ was defined. This value represents the SEC, calculated for the point in time where 90% of the initial COD is removed ($t_{90\%}$). Fig. 8 shows the evolution of the $SEC_{90\%}$ for different experimental conditions. On the secondary axis, also $t_{90\%}$ is displayed. In some cases, not only the energetic feasibility is important, but also the treatment time. Therefore, the $SEC_{90\%}$ must always be evaluated in combination with $t_{90\%}$ if there is a time limit for the degradation.

The most important parameter that influences the specific energy consumption is the concentration of chlorides in the water, since a lower concentration not only affects the oxidation rate as discussed above, but also results in an increase in consumed electrical power due to a lower conductivity. A low concentration of 0.5 g/L results in an $SEC_{90\%}$ of 0.211 kWh/gCOD. The higher the concentration of NaCl in the wastewater, the lower the $SEC_{90\%}$ (0.272 kWh/gCOD for 1.5 g/L and 0.216 kWh/gCOD for 2.5 g/L).

Furthermore, the applied current density is observed to be important for the SEC: at high current densities, the degradation of organic matter is initially high, but decreases as a function of time (pseudo first order kinetics). At low current densities, the total amount of removed COD per unit of time is nearly constant due to the shift from pseudo first to pseudo zeroth order kinetics. This results in an approximately constant specific energy consumption as a function of reaction time. However, the time for 90% COD removal is much lower when using a higher current density.

The variation in pH has only a small effect on the $SEC_{90\%}$. The difference in $SEC_{90\%}$ between pH 3 and 6 was higher than the difference between pH 6 and 9. This is explained by the larger difference in oxidative power between Cl_2 and HClO than between HClO and ClO^-. A similar trend was observed for the response parameter $t_{90\%}$.

For the experiments with different initial phenol concentration, it was seen that a higher initial concentration had a lower $SEC_{90\%}$ value since the initial concentration also affects the reaction order kinetics. The value for $SEC_{90\%}$ is the highest for the intermediate initial concentration of organics (0.0531 kWh/gCOD for COD_0 = 250 mg O_2/L). A lower initial concentration (COD_0 = 150 mg O_2/L) implies a faster degradation due to the higher reaction rate constant for the same required energy (0.0382 kWh/gCOD). When using a higher initial concentration of phenol (COD_0 = 500 mg O_2/L), the $SEC_{90\%}$ also decreases (0.0456 kWh/gCOD). This can be explained by the higher absolute COD removal whenever the initial COD is higher (as already discussed in section 3.6.).

Based on the above-mentioned observations, it depends on several criteria such as maximum treatment time, availability to adjust pH and NaCl concentrations or other parameters, to select optimal reaction conditions.

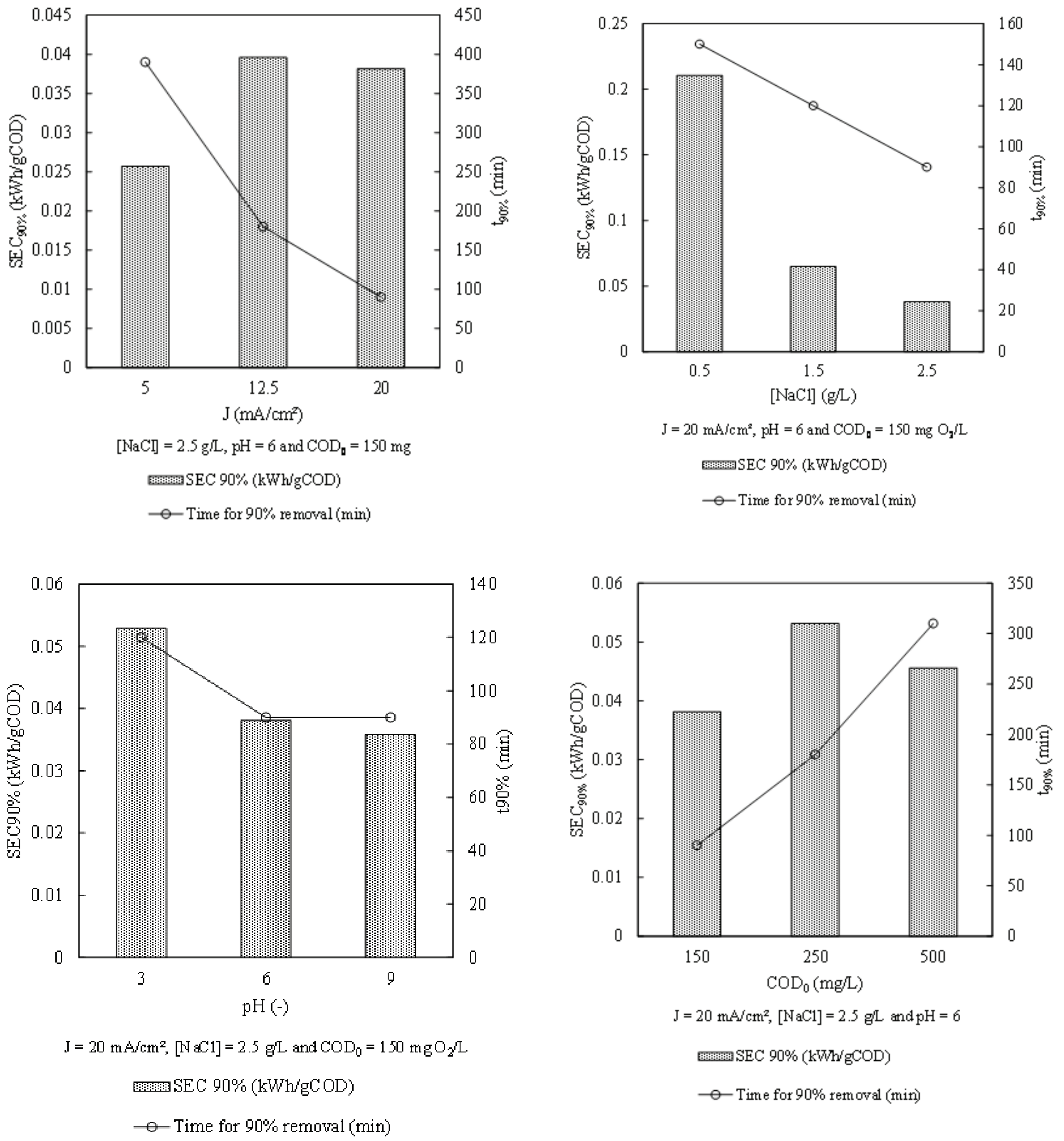

Fig. 8. Influence of some operational parameters on $SEC_{90\%}$ and $t_{90\%}$.

4. Conclusions

The electrochemical oxidation of phenol by a relatively low cost and commercially available Ti/RuO_2-IrO_2 anode in the presence of chlorides showed a fast degradation profile. In a lab-scale batch reactor with an initial phenol concentration of 63 ppm, 90 % was removed after a reaction time of 90 min (with an applied current density of 20 mA/cm² and 2.5 g/L NaCl as supporting electrolyte). The use of sulphate as supporting electrolyte or the use of an uncoated Ti anode appeared to be inefficient due to a lack of mediators and the formation of an insulating TiO_2 layer, respectively. A design of experiments was carried out to highlight the main influencing parameters on the degradation process. Five important process parameters (i.e., applied current density, initial pH of the solution, concentration of chlorides, temperature of the solution and stirring rate) were ranked according to their contribution in COD and phenol removal after 1h of treatment. Resulting from this design of experiments, it was concluded that the applied current density, initial pH of the solution and concentration of chlorides were the main parameters influencing the degradation process. The subsequent kinetic and energetic study showed that the fastest degradation is carried out in a chloride-rich and alkaline wastewater with a high applied current density. Based on the specific energetic consumption of the treatment, a low value for the applied current density in combination with a high chloride concentration and a high initial pH of the wastewater, is advised.

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Symbols

d[COD]/dt — The change of chemical oxygen demand as a function of time (differential)
k, k′ and k″ — Reaction rate constants
[COD] — Concentration of chemical oxygen demand
[mediator] — Concentration of a mediator
COD/COD$_0$ — Concentration of chemical oxygen demand, relative to its starting value at time 0
J — Applied current density
pH — pH-value of the solution
[NaCl] — Concentration of NaCl
SEC — Specific energy consumption
U — Applied voltage
I — Applied current
ΔT — Difference between two temperature values
ΔCOD — Difference between two chemical oxygen demand values

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