Use of Nano Zero-Valent Iron to Reduce Inorganic Species Electrogenerated during Anodic Oxidation on Boron Doped Diamond Anodes

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In this paper, the solution coming from an anodic oxidation on boron doped diamond of chloride-containing solution is treated with addition of nano zero-valent iron (nZVI) to reduce the amount of chlorinated by-products into chloride ions. The electrolyzed solutions have been obtained under galvanostatic conditions in an undivided reactor. The evolution and depletion of all the chlorinated species have been monitored by spectrophotometry and ion chromatography. The nanoscale iron particles have been synthesized in our laboratory by a fast and facile method through reaction of FeSO₄ and NaBH₄ solutions without addition of dispersants.

The effect on the conversion yield of several operative parameters has been investigated and discussed. The preliminary results indicate that a nZVI posttreatment can be considered a viable technology for the treatment of solutions containing active chlorine and chlorate. However, the reduction of perchlorate, either in mixed solutions or alone, requires too drastic conditions to be completed.

1. Introduction

Among the different types of processes and technologies applied to the environmental protection, electrochemical treatments are nowadays considered a valid alternative for decontamination of water and soil. In spite of their ease in controlling a clean process of oxidation/reduction where the main reagent is the electron, electrochemical treatments are not commonly applied on industrial scale mostly because of the expensiveness and low durability attributable to the electrode materials. For this reason, the scientific research has been focused on the development and optimization on new materials for electrochemical application. One of the most attractive material is the boron-doped diamond (BDD) thin-film electrode whose main characteristics are high stability, chemical inertness and wide potential window of water discharge. As BDD electrode exhibits high efficiency in the electrogeneration of physisorbed hydroxyl radicals by water oxidation, its use as anode, as confirmed by numerous studies, significantly improves the effectiveness of the electrochemical oxidation treatment of contaminated and drinking water.

However, in the presence of even small amounts of chloride the anodic oxidation of organic and inorganic effluents on BDD involves the electrogeneration of undesired by-products (Bergmann and Rollin, 2007), mainly active chlorine, chlorate and perchlorate (Huber et al., 2013) that have to be removed before disposal. Active chlorine production is considered helpful for the treatment of aqueous pollutant since it offers an indirect synergic support to oxidation of aqueous pollutants (Murugananthan et al., 2011) by accelerating the color removal (Montanaro and Petrucci, 2009) and in some cases also TOC decay (Petrucci et al., 2015). The electrogeneration of active chlorine occurs in solutions containing chlorides by direct oxidation to chlorine and subsequent hydrolysis to form hypochlorous acid and hypochlorite ion. The equilibrium concentration of these species is strongly influenced by pH and slightly by the temperature. Problems arise when this mixture of oxidants undergoes subsequent oxidation thus producing consistent concentration of chlorate that finally evolve to perchlorate. Perchlorate is suspected of adverse effects to humans and aquatic ecosystems and, although still unregulated, it is considered a compound of serious concern (Sijimol et al., 2015). In fact, in spite of its relatively high standard potential (1.389 V vs SHE), perchlorate exhibits an outstanding stability and only few methods have been successfully applied for its conversion to species endowed with lower oxidation...
number. So far, the most encouraging results have been achieved by electrochemical treatments at nickel (Rusanova, et al., 2006) and at rhodium electrodes (Láng et al., 2008) and biodegradation processes (Xu et al., 2015).

Recently, a new approach has been proposed for the reduction of chlorate (Westerhoff, 2003) and perchlorate (Oh et al., 2006) based on reaction with elemental iron either at micro-scale or at a nano-scale (nZVI) by using unstabilized (Cao et al., 2005) and CMC-stabilized ZVI nanoparticles (Xiong et al., 2007). Iron zero is an excellent electron donor that is being successfully used in the reduction of a wide range of pollutants (Li et al., 2006) for the remediation of contaminated waters (Yaacob et al., 2012) and soils (Gueye et al., 2015). Expectedly, the higher specific surface area of the nanostructured material accounts for the superior efficiency.

The objective of this research has been to test the treatability of a solutions containing a mixture of active chlorine, chlorate and perchlorate, that had been generated during the electrochemical treatment of chloride-containing solutions, by addition of nZVI. In particular, the proposed nZVI post-treatment was aimed at reducing the inorganic chlorinated species into chloride thus enhancing the environmental sustainability of anodic oxidations with BDD electrodes.

2. Materials and methods

2.1. Materials

Reagents were analytical grade from Sigma-Aldrich and VWR International. Sample Solutions were prepared using distilled deionized water. In tests requiring a pH adjustment, 96% H2SO4 was used.

2.2. Iron zero preparation

NZVI particles were prepared using the borohydride reduction method of iron(II) dissolved in water-ethanol solution. The synthesis method was based on previous experiences of other authors (Wang et al., 2009; Yuvakkumar et al., 2011) and it was properly optimized for this study. Before use, liquid phase reagents (i.e. distilled water and ethanol) were purged for about 30 min with nitrogen gas. The borohydride solution was prepared by dissolving 0.0531 g of NaBH4 in 12.5 mL of water. A solution of iron(II) was prepared by dissolving 0.156 g of iron(II) sulphate heptahydrate in 12.5 mL of 10%v/v water - 90%v/v ethanol in a cylindrical vial. To assure the complete solubilization, the salt was dissolved in 1.25 mL of water; the solution was vigorously stirred while 11.25 mL of ethanol was slowly added. The borohydride solution was added dropwise into iron(II) solution with hand stirring and bubbling N2 gas in order to maintain an oxygen-free atmosphere and to favor the release of H2 gas during the reaction. After the addition of the first drops of sodium borohydride solution, black solid particles immediately appeared. When the addition of borohydride was completed, the mixture was left under a N2 flow for about 5 minutes. The separation of nZVI particles from the liquid phase was obtained by means of vacuum filtration; particles were finally rinsed with about 40 mL of distilled water to remove the excess of ethanol. The final TOC deriving from the solvent presence was about <5 mgL⁻¹ in a solution containing 1 gL⁻¹ nZVI.

2.3. Electrochemical apparatus and procedure

Galvanostatic electrolyses were performed in a glass membrane-free reactor using a 2051 Amel potentiostat/galvanostat. The cell, with a working sample volume of 100 mL, was thermostated and stirred with a magnetic bar. A Boron-Doped Diamond electrode (supplied by Adamant Technologies), with a total surface area of 5 cm², was used as the anode. The cathode was a commercially available Pt wire (supplied by Amel mod. 805/SPG/12J). The electrodes were placed vertically at a distance of about 1 cm.

2.4. Analyses

pH was measured using a Crison GLP 421 pH meter.
Active chorine was determined by the EN ISO 7393/2 colorimetric method using N,N-diethyl-p-phenylenediamine (DPD) by detection at 510 nm with a PG Instruments T80+ UV/vis Spectrophotometer and quartz cells of 1 cm path length.
Anions were quantified using a Dionex 120 ion chromatograph equipped with suppressed conductivity detection. An IONPAC AS12A anionic column used with isocratic carbonate/bicarbonate eluent was adopted for the determination of chloride, chlorite and chlorate. Perchlorates were measured using a RFC 30 eluent generator and a IONPAC AS16 anionic column by adopting a gradient: from 35 to 38 mM in 8 min. The flow rate was 1.5 mLmin⁻¹. The detection limit of all the ions was 100 μgL⁻¹.
The dimension of nanoparticles was determined with a Nanoparticle Size Analyzer 90Plus (Brookhaven, Wien, Austria).

3. Results and discussion

Preliminary tests were conducted to assess the production of inorganic chlorinated species during the anodic oxidation on BDD electrodes of a solution containing an initial amount of 0.05 M chloride. As expected, the oxidation involved the formation of several intermediate species. In particular, by adopting a current density of 300 Am⁻², uncontrolled pH and T, the fast formation of active chlorine and chlorate occurred (Figure 1). These compounds achieved their maximum concentration after 3 and 6 hours, respectively, and were quantitatively converted into perchlorate after approximately 11 hours. The formation of chlorite and chlorine dioxide, verified in electrolyses conducted in a divided cell (Sánchez-Carretero et al., 2011), has not been observed here. This result, supported by a previous study (Polcaro et al., 2008), can be explained considering that in an undivided reactor the accumulation of these species is avoided either by rapid conversion to chlorates or by a concomitant reduction at the cathode (Neodo et al., 2012). Therefore, in this research, only active chlorine, chlorates and perchlorates have been monitored and quantified.

Figure 1: Evolution of chlorinated species (● chloride, ○ active chlorine, □ chlorate, ▲ perchlorate) during electrolysis of 50 mM NaCl solution in undivided cell using BDD anode. J=300 Am⁻², V= 100 mL, T=23±2 °C, natural pH. Inset of figure 1: detail of data referring to first hours of treatment expressed as mgL⁻¹.

As indicated in previous studies and confirmed by preliminary runs conducted in our laboratory, perchlorate is strongly recalcitrant to nZVI reduction even at a low concentration. For this reason, and considering also that our aim was testing the treatment on a mixed solution containing great amount of additional reducible species, we chose to work with solutions containing limited amount of perchlorate. For this reason, all the tests were conducted on solutions subjected to one-hour electrolysis. The average composition of the work solution was: 1300 mgL⁻¹ chloride, 250 mgL⁻¹ active chlorine, 400 mgL⁻¹ chlorate and 20 mgL⁻¹ perchlorate, as illustrated in the inset of Figure 1.

The addition of nZVI up to 1 gL⁻¹ also combined with an increase in the temperature up to 60 °C (data here not reported) did not enable the reduction of the chlorinated species apart from active chlorine depletion. This result can not be considered of interest since active chlorine is a species very reactive, susceptible of numerous decomposition mechanisms including spontaneous decay under particular conditions of pH and temperature.

Better performances were verified by increasing the amount of nZVI. In particular, Figure 2 shows the results of treatments conducted with 1 and 2 gL⁻¹ nZVI when the temperature was kept at 80 °C. As can be seen, the addition of 1 gL⁻¹ nZVI did not allow the perchlorate removal while a 60 % decrease in the chlorate content was verified after 30 minutes of reaction. After that time the amount of chlorate remained substantially unchanged. A two-fold amount of nZVI led to quick reduction of chlorates so that their complete conversion was achieved in less than 5 minutes. However, also under these conditions, the removal of perchlorates was negligible and hardly reached a 7% value. It is worth noting that, although the values reported in the graphics refer to the first two hours of treatment, the reaction were allowed to proceed overnight without any further
significant modification in the species values. Finally, in both the treatments, the active chlorine content was rapidly depleted and it has not been reported in the figures.

Considering the severe conditions adopted in the experiments, that is high temperature and huge amount of iron, we decided not to further increase these parameters but rather to better understand the reactions between each single species and nZVI and to evaluate a possible negative interference on the reduction due to their co-presence. To this aim, we conducted a series of tests on solutions containing chlorate and perchlorate alone at the same concentration of that adopted in the first experiments.

Figure 2: Removal of (a) chlorate and (b) perchlorate by addition of 1 gL\(^{-1}\) (full symbol) and 2 gL\(^{-1}\) (empty symbol) nZVI to solutions obtained after 1 hour electrolysis of chloride. T=80 °C, natural pH.

Figures 3 and 4 report the effect of iron concentration and temperature on the reduction of 400 mgL\(^{-1}\) chlorate in aqueous solutions. As expected, both these parameters greatly affected the reaction rate. In particular, a 1.5 gL\(^{-1}\) nZVI resulted in a rapid reduction of chlorate that was completed in less than an hour even at ambient temperature. A decrease in the added iron to 1 gL\(^{-1}\) did not imply serious delays and the reaction ended in about 70 minutes. By further reducing the iron content to 0.5 gL\(^{-1}\) a 30% maximum conversion yield was achieved after 30 minutes and this value remained unaltered also after several hours of reaction. In further experiments conducted by adding 0.5 gL\(^{-1}\) nZVI, but at a higher temperature (80 °C), we noticed that the reaction proceeded at a remarkably higher rate. In fact, after only 5 minutes of treatment a 55% reduction occurred. However, after the initial drop, no further significant depletion was observed thus indicating that such a low nZVI concentration was not quantitatively sufficient, according to the stoichiometry

\[
\text{ClO}_3^- + 3Fe^0 + 6H^+ \rightarrow Cl^- + 3Fe^{2+} + 3H_2O \quad (1)
\]

that requires a molar ratio Fe/ClO\(_3\^-\) equal to 3. Therefore, for a 400 mgL\(^{-1}\) chlorate (4.8 mM), the minimum dosage of nZVI that has to be adopted to assure complete reduction is 0.8 gL\(^{-1}\) (14.4 mM).

To assess the effect of temperature, a series of tests were then conducted by adding 1 gL\(^{-1}\) nZVI to the chlorate solution. As can be seen, the reduction of chlorate was always fast and particularly enhanced by increasing temperature. The reaction was completed in a maximum time of 70 minutes at room temperature while only 35 and 15 minutes were required at 40 and 60 °C, respectively. It is worth comparing that at 80 °C the reaction time was no longer than 5 minutes while, under the same conditions, the same content of chlorate in the electrolysis solution was only diminished but not eliminated, as described above (Figure 2). This result suggests that the treatment of the electrolyzed solution was negatively affected by the simultaneous presence of the chlorinated by-products, especially active chlorine. We also evaluated the effect of the initial pH by carrying out some tests at different initial values (pH 3 and 5) with adjustment of the natural pH with H\(_2\)SO\(_4\). After the iron addition, in tests with and without pH correction, the pH immediately increased up to 7.8-8.0 so that no effect of this parameters on the reaction rate was observed under the conditions adopted. Although it is reported that a slightly more acidic pH promotes the kinetic of reduction by nZVI (Xiong et al. 2007), this aspect was not further investigated to avoid the use of a buffer solution that would introduce additional possible interferences.

Perchlorates have proven to be particularly reluctant to nZVI reduction and no reaction was observed unless a 80 °C temperature was provided to the reactor (Figure 5). In spite of these conditions, no total conversion was verified in the investigated range of nZVI concentrations. In particular, in the treatment of a solution containing
20 mgL⁻¹ perchlorate, the depletion started to be appreciable only by dosing 4 gL⁻¹ nZVI. However, this large amount of iron was able to reduce only 30% of the initial perchlorate concentration after 6 hours thus confirming that an overdosage of iron together with high temperature conditions are mandatory to overcome the activation energy of this reaction.

**Figure 3**: Effect of nZVI concentration (○ 0.5 gL⁻¹, ■ 1 gL⁻¹, □ 1.5 gL⁻¹) at room temperature and ▲ 0.5 gL⁻¹ at 80 °C on 400 mgL⁻¹ chlorate removal at pH 6.8.

**Figure 4**: Effect of temperature (● 25 °C, ○ 40 °C, ■ 60 °C, □ 80 °C) on 400 mgL⁻¹ chlorate removal at pH 6.8 with nZVI 1 gL⁻¹.

**Figure 5**: Effect of nZVI concentration (▲ 1 gL⁻¹, ○ 2 gL⁻¹, □ 4 gL⁻¹) on 20 mgL⁻¹ perchlorate removal at pH 6.8 and 80 °C.
4. Conclusions

In this paper, we proposed a reduction treatment by nZVI prepared without dispersing agent of a solution containing a mixture of chlorinated species electrogenerated during the anodic oxidation of a chloride-containing solution on BDD anodes. The preliminary results indicate that stoichiometric amount of iron are sufficient to convert active chlorine and chlorate to chloride while an overdosage of iron and severe temperature conditions are necessary to reduce perchlorate. Therefore, a nZVI post-treatment can be considered a viable technology to enhance the environmental sustainability of electrochemical treatment using anodes with reduced ability of oxidation of chlorinated compounds such as DSA electrodes that in the oxidation of chloride only electrogenerate active chlorine and chlorate.

References


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