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IRON ELECTROCOAGULATION WITH ENHANCED CATHODIC REDUCTION FOR THE REMOVAL OF AQUEOUS CONTAMINANT MIXTURES

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Abstract

This study presents enhanced reduction of soluble contaminants in a modified electrocoagulation process that is capable of treating a mixture of aqueous contaminants. By incorporating an iron foam cathode, the process can remove aqueous trichloroethylene (TCE) by 99.1% and nitrate ions by 98.2%, which represents 58.1 and 20 percent higher than the removal rates achieved by iron plate cathode, respectively. pH and ORP measurements indicate the development of a reducing electrolyte condition due to the ferrous generation from an iron anode, which facilitates the reduction of soluble contaminants because the competition from O_2 reduction is eliminated in the system. Both iron foam and vitreous carbon foam electrodes are compatible with polarity reversal, without any deterioration in the efficiency of electroreduction of TCE and nitrate. The modified iron electrolysis process demonstrates versatility for the treatment of mixtures of contaminants, including a binary mixture of TCE and dichromate, a mixture of selenate and nitrate and a mixture of phosphate and nitrate. The ferrous species generated from the iron anode can reduce and (or) co-precipitate certain aqueous contaminants such as dichromate, selenate and phosphate, while the cathodic process can directly reduce contaminants like TCE and nitrate. Compared with the conventional electrocoagulation system that consists of two planar electrodes, the proposed process is not only more effective, but also suitable for the development of integrated and versatile process for the treatment of co-contaminated wastewater or groundwater.

Key words: electrochemical reduction, iron foam cathode, modified electrocoagulation, soluble contaminants

1. Introduction

As a typical physico-chemical process, iron electrocoagulation has been applied to remove a variety of aqueous contaminants, such as heavy metal ions, grease and oil, suspended particles, soluble surfactant and dyes (Al-Shannaget al., 2014; Bhatti et al., 2009; Canizares et al., 2008; Emamjomeh and Sivakumar, 2009; Kobya et al., 2011; Moussavi et al., 2011; Parsa et al., 2011; Sengil and Ozacar, 2006). The mechanisms of removal of contaminants by iron electrocoagulation usually include coagulation, flotation and redox transformation (Emamjomeh and Sivakumar, 2009; Noubactep and Schoner, 2009, 2010). The anodic iron dissolution causes the formation of ferrous hydroxides, which can co-precipitate and adsorb contaminants through neutralization of the surface charges. The hydrogen gas released from the cathodic reaction can float some contaminants, such as grease and surfactants to the surface. Some other contaminants can be transformed by the direct or indirect redox processes induced by the electrochemical reactions.

In recent years, co-contaminated wastewater appears to pose new challenges for existing water treatment methods. For example, the ash-flushing

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wastewater from coal power plants usually contains many heavy metal ions (Hg, As etc.) and concentrated nitrate (Morita et al., 2005). These contaminants should be removed before discharge or further reuse of the wastewater. The second example is the co-contaminated wastewater from some chemical and semiconductor industry processes (Yazdani, 1991), in which chlorinated solvents and suspended particles are present at the same time. Therefore, new integrated, versatile and practical methods are needed for treatment of these co-contaminated wastewaters.

In the natural environmental matrix, such as groundwater or sediments, presence of mixtures of contaminants is also frequent and needs effective and affordable remedial technologies (Fernandes et al., 2009; Katal et al., 2014; Schlicker et al., 2000; Secula et al., 2012; Weyens et al., 2010). Electrocoagulation by iron electrolysis has the potential to address some of these challenges, although enhancements, especially for the removal of some soluble contaminants, are still needed (Emamjomeh and Sivakumar, 2009).

The objective of this study is to test and validate a modified iron electrocoagulation process aiming at the enhanced reduction of soluble contaminants. In a traditional iron electrocoagulation process, two identical iron electrodes act as anode and cathode. The polarity of the electrodes is periodically changed to prevent anodic passivation or scaling of electrode (Mishra et al., 2008; Timmes et al., 2010).

However, the reduction effect of the cathode is restricted by the iron electrode (usually low cost iron material like cast iron or mild steel), and the reduction of the contaminants in the electrolysis system is limited. In this study, a vitreous carbon foam (VCF) electrode or iron foam are adopted because of their high specific area and compatibility with periodical polarity change. More importantly, the iron foam is thought to be a low-cost and environmental-friendly material that possesses superior ability for the reduction of soluble contaminants.

Therefore, constant-current electrolysis experiments are designed to evaluate the performances of foam cathodes for reduction of contaminants in the presence of iron anode, the effect of an iron anode on the electrochemical reduction of dissolved contaminants, and the effectiveness of the overall system on the removal of mixed contaminants.

To demonstrate the universal applicability of this system, nitrate ions and TCE are selected as model pollutants because of their extensive presence in wastewaters (Li et al., 2009; Pant and Pant, 2010) and low potential for precipitation or adsorption. Additionally, the performance of the modified electrocoagulation process on treating mixtures of contaminants is also evaluated.

2. Experimental

2.1. Reagents and materials

All chemical reagents (analytical grade) were purchased from JT Baker and Sigma-Aldrich. Three kinds of cathodes, cast iron plate (Macmaster-Carr, USA), vitreous carbon foam (40 PPI, ERG, USA) and iron foam (95% iron and ~5% nickel, 60 PPI, Aibixi Ltd., China) were tested. Cast iron plate and mixed metal oxide (MMO) mesh electrode (Ta-Ir oxide coating on titanium mesh, 3N International Company, USA) were used as anodes. All electrodes were round disks of 5 cm diameter. Plate and mesh electrodes thickness was 1.5 mm, while foam electrodes thickness was 3 mm. Cast iron electrode was polished with 1~ 3# emery paper prior to assembly. The foam electrode was sonicated with 2% Micro-90 cleaning solution (Cole Parmer, USA) and distilled water prior to assembly.

2.2. Electrolysis experiments

The batch electrolysis experiments were conducted in an acrylic cell with 5.1 cm distance between an anode and a cathode, as shown in Fig. 1. The electrodes were fixed on the walls of electrolytic cell, and in electrical contact with conductive bolts. A magnetic stirring bar (500 rpm) was used to mix the electrolyte during electrolysis. An expandable glass syringe (180 mL) was connected to the electrolytic cell to maintain a gas-tight condition when TCE aqueous solution was treated. In each test, 270 mL of nitrate or TCE solution was electrolyzed by a constant current of 80 mA (4 mA cm-2 current density for the planar electrode). The nitrate solution had 200 mg/L NO_3^- concentration (prepared by 274.2 mg/L $NaNO_3$) and 0.03 M sodium sulphate (Na_2SO_4) concentration. The TCE solution was prepared by injecting a certain volume of saturated solution of TCE in the electrolytic cell that was prefilled with 0.03 M Na_2SO_4 aqueous solution. The initial aqueous TCE concentration stabilized after 30 minutes of equilibrium. In this study, the expanded volumes of the headspace were all below 20 mL, therefore the impact on the aqueous TCE concentration is assumed negligible. For the aqueous solution with a mixture of contaminants, other salts including sodium selenate (Na_2SeO_4), potassium dichromate ($K_2Cr_2O_7$) and sodium phosphate (Na_3PO_4) were used to prepare the solutions.

The supporting electrolytes for the two contaminants were also 0.03 M Na_2SO_4. The same experimental conditions (80 mA electrical current and 270 mL solution) were adopted for treating the solutions. All experiments were conducted under room temperature of 21℃, and the temperature variations of the treated solutions during electrolysis were less than 3℃.

2.3. Analytical methods

Aqueous TCE concentration was determined by a SRI 8610 GC system with a Purge-Trap autosampler (Mao et al., 2011). Nitrate, selenate and phosphate concentrations were measured by Dionex 5000 ion chromatography (IC) instrument. All the samples were filtered by 0.45 pore size PVDF syringe filter prior to the IC measurement. 35 mM KOH was used as a mobile phase at a flow rate of 1.0 mL/min.
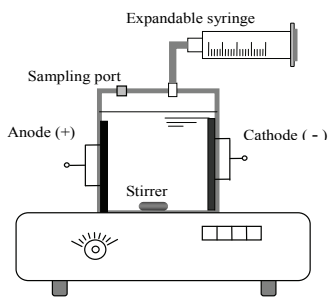

Fig. 1. Experimental setup

Dichromate was measured using Hach chroma Ver 3 reagent at 540 nm wavelength (Jasco spectrophotometer V550) (Viamajala et al., 2002), the detection limitation is 0.02 mg/L dichromate ions under the experiment condition. pH, ORP and dissolved oxygen concentration of aqueous solution were determined by pH meter (Microelectro, USA), ORP meter (Microelectro, USA) and DO meter (YSI, model 5500, USA), respectively.

3. Results and discussion

3.1. Reduction of soluble contaminants

The decay of aqueous TCE concentration in cells using different electrode configurations is presented in Fig. 2 as a function of electrolysis time. The combination of cast iron anode and cathode is what is normally adopted in a conventional electrocoagulation process. After 4 hours of electrolysis, the aqueous TCE concentration decreased from 35.3 mg/L to 20.9 mg/L in the cast iron - cast iron cell, showing inferior TCE transformation performance.

When vitreous carbon foam electrode was used as cathode (cast iron-VCF in Fig. 2a), the aqueous TCE concentration after 4 hours of electrolysis deceased to 16.5 mg/L, and the removal rate is 12% higher than that in the cast iron-cast iron cell. The most significant transformation of TCE was observed in the cell with cast iron anode and iron foam cathode. Within 3 hours, the TCE concentration was reduced lower than 1 mg/L, with aqueous TCE removal rate of 99.1%. In comparison with the VCF electrode, the iron foam electrode exhibits a significant improvement in the TCE transformation performance, which is attributed to the

electrocatalysis effect of iron on TCE reduction (Li and Ferrell, 2000; Mao et al., 2011). The performance of different electrode materials on the reduction of different chlorinated ethenes has been studied, and silver, copper and palladium-modified materials are recognized as the best materials (Roh et al., 2001; Scialdone et al., 2010; Sonoyama and Sakata, 1999), in a non-aqueous solution or in an aqueous solution. However, these materials are incompatible with an electrocoagulation system where reversing the polarity of electrodes is often needed.

The reduction of nitrate under different electrode configurations is presented in Fig. 2b. Similar to the TCE case, the combination of cast iron anode and iron foam cathode exhibits the highest nitrate reduction rate. After 4 hours of electrolysis, the nitrate concentration decreased from around 200 mg /Lto 3.7 mg/L, or a removal rate of 98.2%. Unlike the reduction of TCE, the reduction of nitrate on VCF electrode also showed fast reduction kinetics. The final nitrate concentration was 14.2 mg/L, with a removal rate of 92.9%, or about 5.3% less than the iron foam cathode.

In the presence of an iron anode, the least nitrate reduction rate is observed in the cell using cast iron cathodes. Cast iron and iron foam have the same major composition of iron, but different minor composition and surface area. For the iron foam electrode, the 5% of nickel composition does not appear to change the intrinsic affinity of metal iron on these two soluble contaminants. More importantly, the large surface area of foam electrode considerably increases the reaction rate (He et al., 2004, 2011). Compared with iron foam electrode, the VCF electrode is not suitable for the electrocoagulation process targeting enhanced TCE removal, but can be an appropriate cathode for nitrate reduction.

The effect of anode type is also presented in Fig. 2. In the presence of MMO anode, the VCF electrode show lower rate of TCE transformation (Fig. 2a). Similarly, a significant decrease in nitrate transformation is observed in Fig. 2b when the MMO anode replaces the iron anode. In an electrocoagulation process, the anodic reaction is iron dissolution, and the subsequently formed ferrous species can co-precipitate or adsorb the contaminants. While on the MMO anode, oxygen evolution replaces iron dissolution, resulting in different electrolyte condition. Fig. 3 presents the DO, ORP and pH profiles under MMO anode electrolysis and iron anode electrolysis.

The DO concentration in the cell using MMO anode increased to a steady state value around 15 mg/L. This high concentration of DO is due to the oxygen released from water electrolysis by the MMO anode. Simultaneously, the ORP of electrolyte in the MMO anode cell maintained a positive value, around 100 mV. In contrast, DO of the electrolyte in the iron anode cell decreased very fast down to below 0.1 mg/L within 10 minutes, and the ORP of the

electrolyte constantly decreased to a more negative value.

The significantly low DO concentration is believed to be the main reason of the enhanced reduction of contaminants in the presence of an iron anode, since the electron competition from oxygen is avoided. Thus, in spite of the high electrolyte pH generated because of iron anode electrolysis (Fig. 3b), which is not beneficial for the reduction process involving protons (Al-Abed, 2006), a pronounced increase in contaminants transformation is still observed. In other words, introducing foam cathode for iron electrocoagulation process does have the intrinsic advantage that a reducing electrolyte condition facilitates the reduction of contaminants on the cathode.
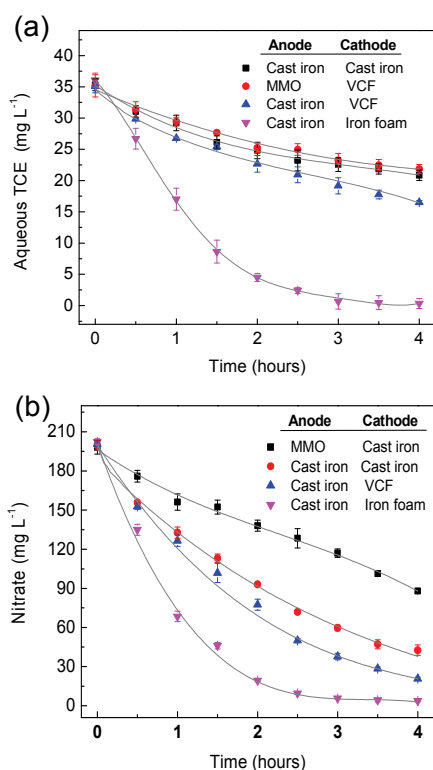

Fig. 2. Reduction of aqueous (a) TCE and (b) nitrate by different cathodes in the presence of an iron anode and an MMO anode. 80 mA current was applied in all experiments

3.2. Performance of cathode under polarity reversal

Polarity reversal is a convenient and useful method to clean the scale and fouling on the electrode and to prevent the iron anode from passivation (Emamjomeh and Sivakumar, 2009; Mishra et al., 2008; Timmes et al., 2010). At the same time, it is important to evaluate the impact of polarity reversal on the performance of cathode. Thus, sequential batch experiments were carried out for TCE and nitrate reduction. Before each trial, the foam cathode was anodically polarized for 1 minute to mimic the polarity reversal in a conventional electrocoagulation process.
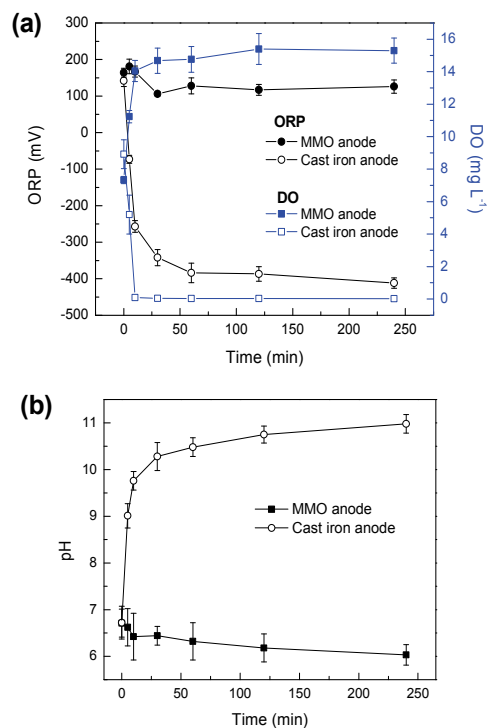

Fig. 3. ORP, dissolved oxygen concentration and pH change by an iron anode electrolysis and an MMO anode electrolysis. 80 mA current with a cast iron cathode

Fig. 4 presents the final concentration of TCE and nitrate after 3 hours of electrolysis as a function of the experiment order. The final concentration of TCE and nitrate in the cells did not show any significant changes within the period of this study, indicating that the performance of foam electrodes is not adversely affected by the polarity reversal. It is speculated that the anodic polarization may help renew the iron foam cathode since its performance for TCE dechlorination decreases under sequential batch experiments without intermittent anodic polarization. Although silver coated material or copper foam electrode exhibit superior electrocatalytic performance for dechlorination of chlorinated solvent (He et al., 2004; He et al.,, 2011; Sonoyama, 1997), they are not compatible with polarity reversal of an electrocoagulation process since these metals might release toxic heavy metal ions when they are anodically polarized.

3.3. Treatment of a mixture of contaminants

Three mixtures of contaminants were treated using conventional and modified iron electrocoagulation process. In Fig. 5, the performances of these two processes were compared. When the mixture is dichromate plus TCE (Fig. 5a), very different decay behavior is observed for these two contaminants.
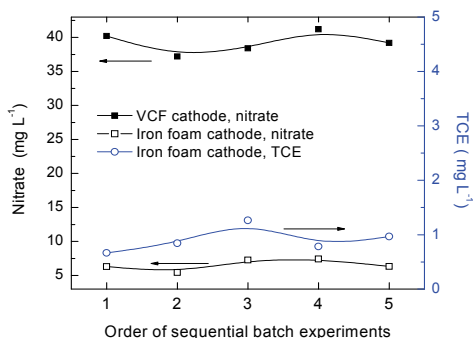
Fig. 4. Cyclic batch electrolysis experiments under polarity reversal. The foam electrode was polarized as an anode (80 mA) for 1 minute prior to being used as a cathode. After each experiment (3 hours of electrolysis), the foam electrode was only washed with distilled water
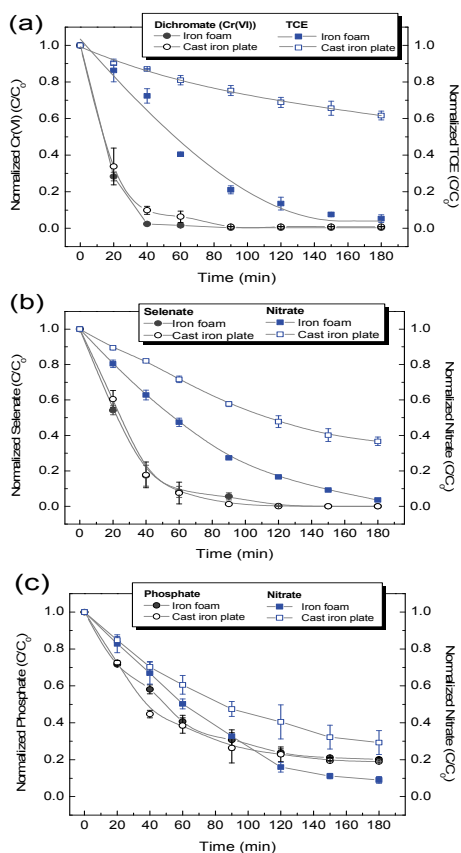

Fig. 5. Performance of the modified electrocoagulation process (with an iron foam cathode) and a conventional electrocoagulation process (with a plate cathode) for the treatment of different mixtures of contaminants.(a) 0.5 mg/L dichromate ions and 9 mg/L TCE; (b) 9.1 mg/L selenate ions and 80 mg/L nitrate; (c) 78 mg/L phosphate and 50 mg/L nitrate. 80 mA current applied for all experiments. Solutions were used as prepared and their pHs (6.4~7.2) were not regulated
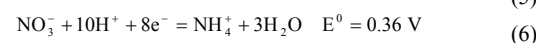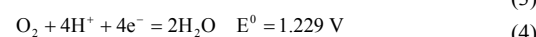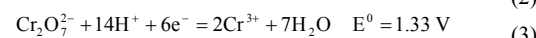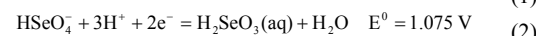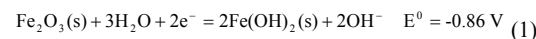
The dichromate are transformed very fast no matter what cathode is adopted for electrolysis, and the concentrations under these two conditions decrease to below detection limit after 90 minutes of electrolysis. However, for the aqueous TCE, the concentration decreases slowly in the electrolytic cell using a cast iron plate, while it decreases quickly in the one using an iron foam cathode and more than 95% aqueous TCE was transformed. This observation further confirms what is observed in Fig. 2a, suggesting that the enhancing effect of the cathode on electroreduction does not change even in a solution with dichromate. In other words, under the concentration level of this study, the dichromate did not show competitive effect on the cathodic transformation of TCE.

In Fig. 5b and Fig. 5c, the treatment of the other two mixtures (selenate plus nitrate, phosphate plus nitrate) with different cathodes is depicted. The selenate decay profiles (Fig. 5b) under the two electrode conditions are very similar, moreover, the transformation rate appears as quick as that of dichromate. The iron foam electrode still shows apparent enhancing effect on nitrate transformation under this mixed contamination condition. The final nitrate removal rate achieved by the foam electrode is 96.4%, being 32.4 percent higher than that of the cast iron plate electrode.

In case of the mixture of phosphate and nitrate, the decay of phosphate does not show a removal rate as high as that of dichromate; however, the iron foam electrode, compared with the cast iron plate, still exhibits better performance on the transformation of nitrate: the foam cathode exceeds the iron plate cathode by 20% for nitrate transformation.

It has been demonstrated that the ferrous species (Fe^{2+}, $Fe(OH)_2$, ferrous complex, etc.) can treat a series of aqueous contaminants, such as dichromate, arsenate, cyanide, hexavalent uranium and phosphate (Chen et al., 2009; Emamjomeh and Sivakumar, 2009; Noubactep, 2009; Noubactep and Schoner, 2010). Contaminants removed by electrochemically generated ferrous species concern some redox-sensitive compounds. Standard electrode potentials of the aqueous contaminants relevant to this study are, (Brimmer et al., 1987; Holliger et al., 1998; Wang et al., 2008; Zoski, 2007).

$$Fe_2O_3(s) + 3H_2O + 2e^- = 2Fe(OH)_2(s) + 2OH^- \quad E^0 = -0.86 \text{ V} \quad (1)$$

$$HSeO_4^- + 3H^+ + 2e^- = H_2SeO_3(aq) + H_2O \quad E^0 = 1.075 \text{ V} \quad (2)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O \quad E^0 = 1.33 \text{ V} \quad (3)$$

$$O_2 + 4H^+ + 4e^- = 2H_2O \quad E^0 = 1.229 \text{ V} \quad (4)$$

$$TCE + 2e^- + H^+ \rightarrow cis\text{-}DCE + Cl^- \quad E^0 = 0.45 \text{ V} \quad (5)$$

$$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O \quad E^0 = 0.36 \text{ V} \quad (6)$$

The transformation of dichromate and selenate occurs at potentials over than 1 V vs. SHE, which is much higher than the reduction potentials of TCE and nitrate. Ferrous hydroxide (Eq. 1) is a reducing species capable of reducing O_2, dichromate and selenate, producing less toxic compounds like

trivalent chromium, and elemental selenium (Chen et al., 2009; Noubactep and Schoner, 2010). In the case of TCE, although the ferrous hydroxide and ferrous ions associated with minerals can degrade TCE under very alkaline conditions and generate non-toxic products ethene, ethane and acetylene (Jeong et al., 2011; Kim et al., 2008), the rate of this reaction is much slower than that of the direct electroreduction on the cathode surface. Likewise, the transformation of nitrate to nitrogen and ammonium is due to the electroreduction on the cathode instead of the ferrous species formed in the solution (Li et al., 2009).

As a result, it is observed that the concentration profiles of dichromate and selenate are almost independent of the type of the cathode materials. Conversely, the decay of TCE and nitrate is dependent on the material type; electrolysis using iron foam cathode always achieves a better performance than using planar cast iron electrodes. For the phosphate ion, which is not a redox-sensitive species, its concentration decay is due to the formation of ferric or ferrous phosphate precipitates ((K_{sp}(FePO$_4$)=1.3×10^{-22}, K_{sp}(Fe$_3$(PO$_4$)$_2$)= 1×10^{-36}) (Girard, 2010; Zumdahl, 2009).

Therefore, the phosphate concentration profiles did not show apparent differences when the foam cathode is adopted. The results demonstrate that the modified iron electrolysis by iron foam cathode can improve the reduction rate of some reducible contaminants, which cannot be effectively treated by ferrous species in the conventional electrocoagulation process. In other words, the modified electrocoagulation process actually provides both electrolyte-based reductants (ferrous species) and electrode-based reductant (electrons) for the transformation of a wide spectrum of contaminants.

In addition, incorporating an iron foam cathode slightly decreases the energy consumption of electrolysis in comparison with the traditional process using two iron plates. Based on our observation, when an iron foam cathode was used, the average cell voltage was usually 0.2~0.3 V less than that of a traditional process: the higher surface area of cathode decreased the current density, thus causing less IR drop on the electrode/electrolyte interface. According to the recorded cell voltage data, the energy consumptions for treating the aforementioned solutions were calculated to be 2.9~3.1×10^{-3} kWh/L (within 180 minutes) when iron foam cathode was used.

4. Conclusions

A modified iron electrocoagulation process using a foam cathode is proposed for enhanced reduction of soluble, reducible contaminants in wastewater. Introducing iron foam cathode or VCF cathode does not change the production of the flocs from iron anode, but the transformation of TCE and nitrate can be considerably improved.

Furthermore, the reducing electrolyte condition caused by the dissolution of the iron anode further facilitates the reduction of contaminants on the cathode. Through the combining effects from the anode and the cathode, the modified iron electrocoagulation process shows superior performances for cleanup of a series of mixtures of aqueous contaminants. The compatibility of these two foam electrodes with polarity reversal enables this improved process to be applied to practical treatment of wastewaters or groundwater with mixed contamination.

On the other hand, it should be noted that successful application of this technology will depend on a variety of conditions, such as the chemical composition of treated water, current density, and the properties of contaminants. Research is under way to evaluate these effects and assess the practicality of this remedial strategy.

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