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Treatment of Ni-EDTA containing wastewater by electrocoagulation using iron scraps packed-bed anode

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HIGHLIGHTS

- A novel electrocoagulator with small gap between the electrodes was proposed.
- Iron scraps anode enhanced the Ni-EDTA removal comparing with iron rod anode.
- Adsorption ability of Fe(III) flocs was higher than that of Fe(II) flocs for Ni-EDTA.
- A large amount of active oligomeric ferric (Fe(O)) led to increased Ni-EDTA removal.

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ABSTRACT

The unique electrocoagulator proposed in this study is highly efficient at removing Ni-EDTA, providing a potential remediation option for wastewater containing lower concentrations of Ni-EDTA (Ni $\leq$ 10 mg L^{-1}). In the electrocoagulation (EC) system, cylindrical graphite was used as a cathode, and a packed-bed formed from iron scraps was used as an anode. The results showed that the removal of Ni-EDTA increased with the application of current and favoured acidic conditions. We also found that the iron scrap packed-bed anode was superior in its treatment ability and specific energy consumption (SECS) compared with the iron rod anode. In addition, the packed density and temperature had a large influence on the energy consumption (ECS). Over 94.3% of Ni and 95.8% of TOC were removed when conducting the EC treatment at an applied current of 0.5 A, initial pH of 3, air-purged rate 0.2 L min^{-1}, anode packed density of 400 kg m^{-3} temperature of 313 K and time of 30 min. SEM analysis of the iron scraps indicated that the specific area of the anode increased after the EC. The XRD analysis of flocs produced during EC revealed that hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) were the main by-products under aerobic and anoxic conditions, respectively. A kinetic study demonstrated that the removal of Ni-EDTA followed a first-order model with the current parameters. Moreover, the removal efficiency of real wastewater was essentially consistent with that of synthetic wastewater.

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is widely used as a powerful chelating agent in the electroplating industry to facilitate homogeneous metal deposition. (Laine and Matilainen, 2005; Seshadri et al., 2008). Nickel, a common plated metal, can be chelated with EDTA to form Ni-EDTA complexes in electrolyte solution (Salama and Berk, 2005). Due to strong chelating between EDTA and toxic nickel ions, Ni-EDTA complexes exhibit high persistence over a wide range of environments. They can easily accumulate in rivers and transfer over long distances, severely harming ecological and human health (Lan et al., 2014). At present, Ni-EDTA complexes are frequently detected in the environment (Nowack and Vanbriesen, 2005). Thus, Ni-EDTA complexes containing wastewater must be purified before discharge.

Little attention has been paid to the removal of Ni-EDTA complexes, but a number of studies have revealed that metal-EDTA

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complexes are difficult to remove completely by using microorganisms or the conventional chemical precipitation process, including hydroxide and sulphide precipitation (Sykora et al., 2001; Durante et al., 2011; Zhao et al., 2014). Indeed, the presence of chelating agents in aqueous solutions inhibits the adsorption process of heavy metal by sorbents or bio-sorbents (Wu et al., 1999). Some promising techniques, such as Fenton/Fenton-like reaction-hydroxide precipitation (FR-HP) (Fu et al., 2009; Lan et al., 2012), interior microelectrolysis (IM) (Ju and Hu, 2011; Lan et al., 2012), photocatalytic oxidation (Salama and Berk, 2005; Zhao et al., 2014) and membrane filtration (Juang et al., 1999; Di Palma et al., 2003), have also been employed to treat metal-EDTA containing wastewater on a bench scale. However, high costs, additional chemical agents, poor abatement of EDTA, and so on make these technologies impractical. Therefore, it is urgent to explore a useful and inexpensive method to improve the removal efficiency of metal-EDTA complexes.

The process of removing heavy metal or organic matter from aqueous solutions by means of electrocoagulation (EC) has been developing for over a hundred years (Chen, 2004). EC is different from simple conventional coagulation. It is an intricate successive process that includes the release of cations from a "sacrificial electrode", hydrogen evolution in the cathode and coagulants formation by the aggregation of dissolved cations in the solution. (Gomes et al., 2007). In the process, the system is accompanied by the adsorption, electrophoresis, electro-oxidation, electro-deposition, and co-precipitation of contaminants (Zhao et al., 2010; Sari and Chellam, 2015). However, only a small number of studies have involved the use of electrocoagulation for the treatment of wastewater containing metal-EDTA. In Pociecha and Lestan (2010) study, heavy metal-cheated EDTA from a soil washing solution was separated by EC with an Al anode. High removal efficiencies of 95% Pb, 68% Zn, 66% Cd and 84% EDTA were obtained when the initial concentrations were 1420 ± 200, 260 ± 30, 9 ± 1 and 18,100 ± 1600 mg L^{-1}, respectively. Kabdasli et al. (2009) investigated the treatability of chelated Zn and Ni that originated from metal plating wastewater by EC with stainless steel electrodes, and a heavy metal removal of 100% and TOC abatement of 66% were obtained at an initial TOC of 171 mg L^{-1}. All of these studies indicated that the EC process is a potential remediation option for wastewater containing Ni-EDTA due to its simple equipment, easy operation, low levels of sludge and excellent removal efficiency. Still, reports for lower concentrations ($\leq$10 mg L^{-1}) of cheated metal wastewater treatment by EC are lacking or non-existent. It is well known that most nickel (Ni ion) in electroplating wastewater can be removed by the traditional coagulation process, and that only a small portion of nickel-chelated complexes is residual (Kabdasli et al., 2009). Hence, a study of lower concentration pollution removal by EC would be indispensable and meaningful.

Despite the long history and excellent treatability of EC, large consumption of expensive sacrifice anodes, including pure Al and Fe, in the EC process has created limitations in extensive commercial applications; therefore, the production of cheaper iron-based production and exploration of iron scrap electrodes have received more attention recently (Wei et al., 2012; Tezcan Un and Aytac, 2013; Ardhan et al., 2014). Tezcan Un and Aytac (2013) reported that an electrochemical reactor with a wrapped iron wire netting anode can effectively remove COD and color in textile wastewater. Similar results were obtained with the use of a reduced-cost electrocoagulator with a machine shop turning anode. The reactor enhanced the treatability of contaminants when compared with a system with a tubular anode (Ardhan et al., 2014). It also demonstrated good removal of dye when low-cost steel wool was used as a cathode (Wei et al., 2012). This might be the consequence of the high contact area between iron scraps and the bulk solution in the EC process. However, these studies focused on the treatment of textile effluents and there remains a lack of studies on important factors in the EC process, such as the packed density and aeration rate.

The objectives of this paper were to optimize Ni-EDTA removal from synthetic wastewater by applying a novel electrocoagulator with an iron scrap packed-bed anode. We first examined the treatability of TOC and Ni as a function of the applied current, aeration mode/rate, packed density, temperature and initial pH. We also investigated the distribution of Fe(III) species at different temperatures and initial pH levels. Next, real wastewater was tested using the electrocoagulator under optimized conditions. Finally, the iron scrap after the EC process was characterized by SEM and the flocs generated were characterized by XRD to analyse the removal mechanism of Ni-EDTA.

2. Materials and methods

2.1. Chemicals and Ni-EDTA wastewater

All chemicals used in this study were of analytical grade and purchased from Sigma. The iron scrap and iron rod (purity 99%) were obtained from the XDY Environ. Prot. Co., Guangzhou, China. A stock Ni-EDTA solution (the molar ratio of Ni^{2+} and EDTA = 1:1) with an initial Ni^{2+} concentration of 1 g L^{-1} was prepared by dissolving 6.343 g of $NiCl_2 \cdot 6H_2O$ and 4.050 g of EDTA-2Na·$2H_2O$ into 1 L of distilled water and storing at 4 °C. Before the experiment, solutions of lower concentrations were prepared by through proper dilution of the stock solution. The desired pH was adjusted by using 0.1 M HCl and a 0.1 M NaOH solution. Real Ni-EDTA wastewater was obtained from the XDY Environ. Prot. Co., Guangzhou, China.

2.2. Reactor configurations

The proposed novel electrocoagulator proposed mainly consists of an iron scrap packed-bed anode, perforated graphite tube cathode, perforated electrode support and reaction cell, as shown in Fig. 1. The anode is a PVC tube packed with pretreated iron scraps from a machine shop. The PVC tube has an internal diameter of 28 mm, a length of 100 mm, a thickness of 1 mm and a volume of 50 cm^3. Holes with a diameter of 3 mm are well distributed on its surface. An iron rod with an internal diameter of 25 mm and length of 100 mm is used as the anode. The cathode is made of cylindrical graphite with an internal diameter of 35 mm, a length of 100 mm and a thickness of 2 mm; 5 mm holes are evenly distributed on its surface to allow the release of dissolved iron ion into the bulk solution. The perforated electrode support made by the PVC provides room for the air-blast-head. The electrolyti**c** **c**ell is made from plexiglass of 2 mm thickness with dimensions of 60 mm × 80 mm × 110 mm. A regulated DC power supply (DF17315D3A, 0–30 V, 0–3 A) is used to provide a steady current for the EC system. An air pump (SongbaoSB-988)/N_2 is designed to pump air/N_2 into the solution and accelerate the transformation of Fe (II) into Fe (III).

2.3. Electrocoagulation procedure

Before the trial, iron scraps were rinsed in 2% HCl for 2 h and washed with distilled water. Then, they were dried at 60 °C for 24 h in a vacuum drying oven (BZF-50, China) and stored in a drying chamber. All experiments with 450 mL EDTA-Ni solutions were conducted at ambient temperature (25 ± 0.5 °C). The same amount of sodium chloride (0.5 g L^{-1}) was added to the solution to avoid an excessive Ohmic drop. Electrocoagulation was carried out at (i) different aeration mode/rates (0–0.3 L min^{-1}), (ii) different applied