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Fabrication and characterization of a Cu-Pd-TNPs polymetallic nanoelectrode for electrochemically removing nitrate from groundwater

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HIGHLIGHTS

- A novel Cu-Pd-TNPs polymetallic nanoelectrode was fabricated.
- The novel nanoelectrode was used for electrochemical denitrification.
- The novel nanoelectrode has high reduction efficiency for nitrate.
- Very few by-products produced when added appropriate sodium chloride.

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ABSTRACT

A novel Cu-Pd-TNPs (Copper-Palladium-TiO_2 Nanopores) polymetallic nanoelectrode was fabricated, and then used to catalytically reduce dissolved nitrate in groundwater. The aim was to develop a high efficient nanoelectrode for removing nitrate from groundwater. The Cu-Pd-TNPs polymetallic nanoelectrode was fabricated by plating Pd onto a TiO_2 nanoporous matrix and then plating Cu onto the layer which is previous coating. TiO_2 nanopores on the Cu-Pd-TNPs electrode surface gave the electrode a large specific surface area, and the Pd and Cu nanoparticles gave the electrode a high nitrogen to hydrogen ratio and a high nitrate reduction activity. Scanning electron microscopy images indicated that the Cu-Pd-TNPs polymetallic nanoelectrode was porous with lamellar deposits. The elements on the Cu-Pd-TNPs electrode surface, identified by energy-dispersive X-ray spectroscopy, were Ti, Pd, Cu, and O. The Cu-Pd-TNPs electrode gave a high nitrate reduction rate, removing 287.3% nitrate more than that was removed by a Ti nanoelectrode under the same conditions. The optimal NaCl concentration, at which the electrode effectively removed nitrate and produced as few byproducts as possible, was determined. Nitrate was completely removed using the Cu-Pd-TNPs electrode with a Pt anode at a NaCl concentration of 0.5 g L^{-1}, little ammonia and almost no nitrite were detected in the treated solution. Using a constant current density, temperature strongly affected nitrate removal, but the initial nitrate concentration affected the removal rate little. Maximum nitrate was removed at pH 3 when the other conditions were constant.

1. Introduction

Improvements in living standards and rapid economic development are causing water scarcity to become an increasingly serious problem. Groundwater is an important source of drinking water, but polluted groundwater cannot be used as drinking water when seeking to alleviate water shortages. There are numerous groundwater pollutants, but nitrate is of particular concern because nitrate pollution is becoming more serious and widespread (EPA, 2000; Wang et al., 2017). Nitrate contamination of groundwater is a problem around the world, and affects 24 × 10^6 people in the USA alone. The removal of nitrate from groundwater has therefore attracted attention (Liu et al., 2016a; b). Nitrate in groundwater is mainly derived from sewage, manure, fertilizers, industrial

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wastewater, and atmospheric nitrogen and oxygen (through both dry and wet deposition). The US Environmental Protection Agency has set a maximum nitrate concentration in groundwater of 10 mg L^{-1} (EEC, 1987; EEC, 1998; Li et al., 2009a; b; Liu et al., 2016a; b). In the European Union, the maximum nitrate concentration allowed in potable water is 50 mg L^{-1}, but it is 15 mg L^{-1} for water consumed by infants (EEC, 1987; EEC, 1998; Liu et al., 2016a; b). The most recent Chinese groundwater quality standard maximum nitrate concentration is 20 mg L^{-1}. Drinking water containing a high nitrate concentration can be toxic. Nitrate does not pose a direct hazard to humans but can be converted to nitrite in a hypoxic environment. Nitrite can oxidize low hemoglobin into high hemoglobin, decreasing the oxygen carrying capacity of the blood. Nitrite can also react with secondary amines to generate carcinogenic nitrosamines. The main effect of nitrate exposure is “blue baby syndrome” (EPA, 2000; Wang et al., 2017).

Attention has therefore been paid to removing nitrate from groundwater. Numerous chemical, biological, physicochemical, and electrochemical methods for removing nitrate from groundwater have been proposed (Polatides and Kyriacou, 2005; An et al., 2017; Beltrame et al., 2017; Chen et al., 2017; El-Nagar et al., 2017; Niu et al., 2017; Ye et al., 2017) Chemical methods produce toxic byproducts such as nitrite (Beltrame et al., 2017). Biological methods have various disadvantages, such as needing to be continually monitored to ensure the desired microorganisms grow, being difficult to control, giving incomplete reactions, generating large amounts of biological sludge, and requiring a constant supply of organic substrate (Polatides and Kyriacou, 2005; Chen et al., 2017; Beltrame et al., 2017). Physicochemical processes. Such as distillation, reverse osmosis, electrodialysis, and ion exchange (An et al., 2017; Chen et al., 2017; Niu et al., 2017), produce secondary waste because these processes separate but do not destroy nitrates.

Attention has recently been focused on electrochemical methods of removing nitrate from groundwater. The reaction rate at an electrode can be changed by adjusting the electrode potential. Changing the overpotential by 1 V will decrease the activation energy by 40 kJ, which will increase the reaction rate by a factor of 107 times (Ma, 2015). It is easy to control the direction of the reaction at an electrode by selecting an appropriate electrode and applying an appropriate potential. Electrochemical methods also cause little environmental pollution because electrons act as the oxidant or reductant. Electrochemical processes can easily be automated and can be performed continually, and the reaction can be terminated at any time. Very little waste is therefore emitted to the environment.

The electrode material directly affects the nitrate removal rate during electrochemical methods. The electrode is a heterogeneous catalyst, and acts as the reaction field and an electron donor or acceptor site (i.e., the electrode functions as a catalyst for the chemical reaction and is simultaneously involved in electron transfer). During a catalytic reaction the electrode activates an electrochemical reaction involving molecules or ions, strongly decreasing the activation energy for the catalytic reaction. It is therefore very important that suitable electrode materials are developed for specific reactions. Electrochemical nitrate reduction requires an electrode material that is extremely chemically stable and has an appropriate electrocatalytic activity and an appropriate selectivity (Dima et al., 2003). Nitrate removal performances of electrodes made from various materials, including alloys, diamonds, metals, and metallic compounds, have been studied (Szpyrkowicz et al., 2006; Dima et al., 2003; Stortinia et al., 2015). Many metal electrodes, including Cu, Pd, Pt, and Ti electrodes, have been studied. Ti has often been used in electrodes for environmental applications because it is relatively resistant to corrosion. Pt has a poor nitrate reduction activity, Cu and Pd have much higher activities (Chen et al., 2017; Niu et al., 2017). Cu is a good promoter of the electroreduction of nitrate (Prasad et al., 2005; Lima et al., 2012) found that 70% of the nitrate in effluent containing 190 mg L^{-1} nitrate could be removed in 6 h using a Cu electrode with a current density of 0.89 mA cm^{-2} at pH 8. Electrodes made of two metals often have higher catalytic activities than those made of one metal. According to a study of the catalytic reduction of nitrate, Cu active sites reduced NO_3^- to NO and N_2O and Pd active sites reduced the NO and N_2O to N_2. Vorlop and Tacke (1989) found that nitrate could be efficiently reduced to nitrogen gas using an appropriate polymetallic supported catalyst and mild reaction conditions. Various polymetallic materials have been investigated since then, and Cu—Pd has been widely accepted as one of the most promising combinations for catalytically reducing nitrate to nitrogen.

Materials containing nanostructures are generally called nanomaterials. Developments in the nanoscience field have allowed various nanomaterials to be synthesized and used in different applications. It has been shown that nanostructures on metal nanoelectrode surfaces can improve the electrochemical reduction performance by giving the nanoelectrode a large specific surface area (MaCova and Bouzek, 2005; Li et al., 2009a; b; Lima et al., 2012; Chen et al., 2015). Although good results have been obtained using such nanoelectrodes, the use of nanoelectrodes has been limited by poor reproducibility of the activated surfaces that can be prepared and the poor nitrate removal efficiency over the short period such nanoelectrodes can be used. There is an urgent need for an efficient method for fabricating polymetallic nanoelectrodes that can efficiently remove nitrate. To the best of our knowledge, Cu—Pd—TNPs polymetallic nanoelectrodes have not previously be used to electrochemically reduce nitrate.

The aim of this study was to develop a new and efficient nanoelectrode for removing nitrate from groundwater. We fabricated a Cu—Pd—TNPs polymetallic nanoelectrode and then determined its nitrate reduction performance. We developed a fabrication method to give the best possible nitrate removal efficiency. We also investigated the nitrate removal mechanism and the effects of changing the experimental conditions. The results provide insights into the effects of the electrode material on the denitrification process. The nanoelectrode we produced has great potential for application removing nitrate during water treatment processes. The fabrication strategy may allow the catalytic reduction performances of various electrodes to be improved.

2. Materials and methods

2.1. Materials and chemicals

Two cylindrical electrolytic cells were prepared for use in electrochemical reaction devices. Each electrolytic cell was made from an acrylic sheet. Each cell was 100 mm high and had a 40 mm inner diameter at the bottom, walls 5 mm thick, and a volume of 100 mL. There were two small slivers of acrylic 8 mm apart 5 mm from the top of the cell, and each sliver had a groove to which an electrode was fixed. The electrode gap was therefore also 8 mm.

Acetic acid, amino sulfonic acid, ammonia, ammonium phosphate chromogenic agent, copper sulfate, hydrofluoric acid, palladium chloride, sodium nitrate, sodium sulfate, and sulfuric acid were provided from Xilong Scientific Co., Ltd., whereas ammonium chloride, hydrochloric acid, potassium sodium tartrate, from Sinopharm Chemical Reagent Co., Ltd. The acetic acid and hydrochloric acid were guaranteed reagent grade, and the other chemicals were analytical grade.

When fabricating the nanoelectrode, a Ti plate was used as the anode and a graphite plate was used as the cathode. When