Using Electroreduction to Treat Wastewater

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ABSTRACT. The chemical principles and real-world issues associated with wastewater treatment are explored.

KEYWORDS. Electroreduction, Wastewater Treatment, Water Pollution

Maintaining the cleanliness of water continues to be imperative to maintaining the environment and the health of living organisms. Through industrial and municipal use, water becomes polluted with heavy metals and various chemicals that harm the environment and are health hazards to humans if left untreated. For example, the pollution of water in the environment with antibiotics from sewage and pharmaceutical waste can result in an increase in the number of antibiotic resistant bacteria due to the ability of bacteria to mutate when it is exposed to a nonlethal dose of antibiotics *(2)*. This development of antibiotic resistant bacteria and their spread to humans can cause an increase in the contraction of bacterial infections that are unresponsive to treatments which results in the overall decline of human health *(2)*. Due to this, wastewater must be treated to prevent high concentrations of pollutants from adverse effects to environmental equilibrium and the health of living creatures.

Typically, wastewater is treated through a two-step process. During the first step, large chunks of debris and solids are removed from the water through a filtration system, and during the second step, the wastewater is purified through biological processes *(4)*. In addition to biological processes, the use of physical-chemical separation techniques is also used to purify wastewater with methods such as carbon absorption and reverse osmosis *(4)*. Another way that wastewater is treated is using electrochemical processes including electrochemical oxidation, electrochemical reduction, electrocoagulation, and electrodialysis *(1)*. There are three types of electroreduction used to purify wastewater: electrodeposition is used to purify heavy metals, cathodic electrical dichlorination is used to remove chlorinated organic compounds (COCs), and cathodic electrochemical denitrification is used to reduce nitrate and nitrite *(1)*. **This research essay will highlight wastewater treatment, more specifically the use of electroreduction to treat nitrates and nitrites present in wastewater. This is relevant to readers since water containing high concentrations of nitrate and nitrate can cause adverse environmental effects, such as eutrophication, and adverse human health effects.**

Through electrochemical reduction, chemicals present in wastewater that can cause environmental deficits and pose health effects are either removed or converted into products that are not harmful. A chemical is reduced when it has gained electrons and its oxidation state has become more negative, and a chemical is oxidized when it has lost electrons and its oxidation state has become more positive. A chemical's oxidation state is the number of electrons it has gained or lost (if a neutral chemical were to lose an electron it would have an oxidation state of +1 and if it were to gain an electron it would have an oxidation state of -1).

Oxidation of a chemical:
$\text{Chemical}^{(\text{oxidation state})} \rightarrow \text{Chemical}^{(\text{previous oxidation state } +x)} + xe^-$

Reduction of a chemical:
$\text{Chemical}^{(\text{oxidation state})} + xe^- \rightarrow \text{Chemical}^{(\text{previous oxidation state } -x)}$

"x" = the coefficient attached to the electron

Although nitrates and nitrites are naturally found in the environment, the use of nitrates and nitrites for industrial purposes and use in agriculture has resulted in an increase in the concentration of these chemicals in water. It is necessary to treat wastewater of nitrates and nitrites before returning the water to the environment because the consumption of these chemicals in high concentrations results in adverse health effects such as the development of methemoglobinemia in infants, which is a mutation to hemoglobin that results in a decreased ability to transport oxygen *(3)*. Additionally, among some individuals, the consumption of high levels of nitrates also correlates with "decreased blood pressure, increased heart rate, reduced ability of the blood to carry oxygen to tissues, headaches, abdominal cramps, vomiting, and even death" *(3)*.

In a research study conducted by Qing Wang, Hui Huang, Laichun Wang, and Yinguang Chen on the electroreduction of nitrate, the electroreduction of nitrate was performed using six different types of titanium (Ti) cathodes under different conditions (different pHs, different electrodeposit times of copper (Cu), and addition of activated carbon (AC) and copper-modified activated carbon(Cu/AC)) and compared to a control (which was the individual cathodes used with a low current density) (*5*). The purpose of the study was to reduce the costs of nitrate removal while optimizing the efficiency, and the conducted experiment found that the best conditions were when the Cu/Ti cathode was used in a neutral pH with a copper electrodeposited time of 30 minutes and the addition of the AC and Cu/AC *(5)*.

Figure 1 shows, oxidation (the loss of electrons) occurring at the anode and reduction (the gain of electrons) occurring at the cathode. The electrons flow from the anode to the cathode. For the electroreduction of nitrate within the conducted study, the system in Figure 1 is used in which the metal of the cathode is oxidized and releases electrons that reduce nitrate within the solution the electrodes are submerged in and then the metal ion that was previously oxidized is reduced by the flow of electrons that runs from the anode to the cathode.

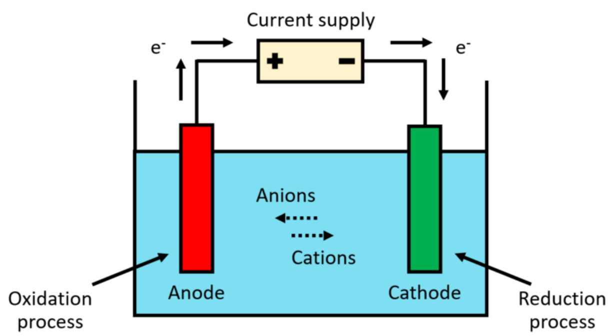

Figure 1. *Diagram of electrochemistry using electrodes. Image (Electro-oxidation apparatus) is used under the Creative Commons License [CC BY-SA 4.0]*

In the research study, the trial that most efficiently reduced the nitrate used a Cu/Ti (Copper and Titanium) cathode and a Ru/Ir/Ti (Rubidium, Iridium, and Titanium) anode *(5)*. The electroreduction was performed with a constant current of 5 Volts that was supplied by a DC Power Supply, and the electrolyte solution was bubbled by an argon gas tube that was connected between the two electrodes *(5)*. The Copper (Cu) in the cathode was oxidized into Copper(I) and the electron released in this process was used to reduce nitrate *(5)*. The applied voltage that was supplied allowed for Copper(I) to be reduced back into Copper *(5)*. From this process, there was a constant interchange between the presence of Cu and Cu(I) which allowed for the reduction of nitrate to continue occurring *(5)*. The nitrate went through several reduction reactions until the final product of diatomic nitrogen or ammonium was produced *(5)*. First, the nitrate was reduced into nitrite with hydroxide as a byproduct *(5)*. Second, the nitrite was reduced into nitrous oxide with hydroxide as a byproduct *(5)*. Finally, the nitrous oxide was reduced to produce either diatomic nitrogen or ammonium with hydroxide as a byproduct *(5)*. Nitrite and nitrous oxide are considered intermediate products that are produced, but then used as the reaction persists towards the final products *(5)*. Additionally, when the activated carbon is used in the electroreduction of nitrate, it also participates in the process by increasing the removal rate of nitrate which further optimized the process *(5)*.

Oxidation of Copper:
$Cu \rightarrow Cu^{+} + e^{-}$

Reduction of Copper (I):
$Cu^{+} + e^{-} \rightarrow Cu$

Overall reduction of Nitrate:
$2NO_3^{-} + 6H_2O + 10e^{-} \rightarrow N_2 + 12OH^{-}$
$NO_3^{-} + 7H_2O + 8e^{-} \rightarrow NH_4^{+} + 10OH^{-}$

One issue that the study works to resolve is reducing the costs of using electroreduction to remove nitrates and nitrates from wastewater. Since reducing nitrates and nitrites from wastewater requires that the electrochemical process be performed on a large scale, and the issue that arises with this is that obtaining enough metal electrodes for this purpose can become expensive. By experimenting with the type of cathode being used and the conditions the electroreduction was performed under, the study was able to conclude the conditions, among those that were tested, that most efficiently reduced nitrate (i.e., the greatest amount of nitrate was reduced under these conditions). Through finding the materials that optimize the reduction of nitrate, the study has helped work towards resolving cost issues by determining which materials would be most cost-effective (i.e., how effective the electroreduction process is relative to the cost of the materials).

To conclude, wastewater treatment continues to be a necessity within society due to the detrimental effects, for both the environment and living organisms, of pollutants that are present within wastewater (heavy metals, toxic chemicals, antibiotics, etc.). The use of electroreduction to treat wastewater, in which harmful chemicals are either reduced out of the water or into products that are not harmful, continues to show promise. One step that need to be taken for this process to become more effective is being able to reduce costs for these different processes, which the experimental study conducted by Qing Wang, Hui Huang, Laichun Wang, and Yinguang Chen worked towards. Additionally, it must also be determined if this method of wastewater treatment is the more effective in comparison to other methods of treatment. To determine this, some factors that should be compared are how long each method takes to treat wastewater and the cost effectiveness of the different methods.

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