TREATMENT OF ANTIBIOTIC WASTEWATER BY ELECTROCHEMICAL PROCESS

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Abstract
The feasibility of electrochemical process for degradation of antibiotic wastewater was investigated. Amoxicillin was used as a model antibiotic and stainless steel was used as electrodes in a lab scale reactor operated in batch mode. The effects of time, applied current, pH and concentration of electrolyte were studied and their optimum conditions were found as 30 minutes, 0.4 A, 7.3 and 2500 mg/l, respectively. The antibiotic and COD removal efficiencies of the process were 29% and 14.0187%, respectively. Comparison of electrochemical process with chemical coagulation (with Alum and Ammonium Ferrous Sulphate) showed that electrochemical process is more effective in removing antibiotics than chemical coagulation. The process followed first order reaction with rate constant, k, of 0.0263. Energy consumption was 24827.5862 Wh/kg antibiotic removed. Anode efficiency was 0.725 x 10^{-3} kg A^{-1} h^{-1} m^{-2}.

Key words: Electrochemical Process, Amoxicillin, Antibiotic, Electrodes, Electrolyte, COD, Chemical Coagulation, Rate Constant, Anode Efficiency

1. Introduction

Antibiotics in natural water systems may come from manufacturing operations in pharmaceutical industries. Huge amount of antibiotics are used as growth promoters in intensive farming. 90% of antibiotics administered to humans and animals may be excreted through urine and feces into sewage. The effluents containing antibiotics have low biodegradability and high COD. Most antibiotics are toxic to aquatic life and can ultimately have adverse effects on human beings. In the receiving environment, antibiotics may sorb to the suspended particles and soil and remain in aquatic phase and enter the food chain (Kummerer, 2004). The presence of antibiotics in natural systems leads to the development of multi-resistant strains of bacteria. Hence, it is necessary to treat the effluents containing antibiotics properly before discharging into water bodies.

Antibiotic wastes cannot be treated easily by processes like sedimentation coagulation, filtration, etc. For treatment of such wastewaters, conventional biological treatments like activated sludge process and other chemical methods like wet air oxidation, wastewater incineration, ozonation and advanced oxidation processes are not economical and technically feasible. Their removal by adsorption on sludge sewage was also not found suitable. One method to deal with them would be to convert them into biodegradable form to cause their biological oxidation. In this aspect, electrochemical oxidation can be a promising method for treatment of antibiotic wastes.

In this work, the drug used was Amoxicillin. The effects of electrolysis time, current, pH and salt concentration were determined on antibiotic and COD removal efficiencis by electrolysis using stainless steel electrodes, while keeping the distance between the electrodes and the initial concentration of antibiotic constant. Also, a comparison was done between electrooxidation and chemical coagulation for removal of antibiotics from wastewater.

2. Materials and methods

2.1 Glassware and chemicals

All the glassware used for the experimentation was of borosil grade and all the chemicals used were of LR/AL grade and procured from

Qualigens fine chemicals or Merk. Deionized water was used for preparing reagents.

2.2 Antibiotic drug

The drug used in this experiment was Amoxicillin. The purified drug sample in powder form was procured directly from the manufacturer. Samples were prepared by dissolving 500 mg amoxicillin in 1000 ml distilled water.

2.3 Electrode material

Stainless steel (Austenite) was used as electrode material. The electrodes were prepared by cutting an austenite steel plate in size 5 cm x 10 cm. Then, they were washed with distilled water and dilute HCl so that any impurity remaining on the plates would get cleaned.

2.4 Experimental reactor setup

A lab scale electrochemical reactor was prepared with mono-polar stainless steel electrodes connected in parallel. A piece of rubber was used to maintain an inter-electrode distance of 1 cm. 250 ml of sample was used for the reactor, in which the electrodes were arranged in situ mode. Direct current supply was employed. Sodium chloride was added to the sample as electrolyte for proper conduction of electric current through the sample. Magnetic stirrer was employed to keep the reaction media constantly agitated. The analytical determination of amoxicillin was carried out with the standard methods for examination of water and wastewater (APHA) using a UVVIS spectrophotometer.

2.5 Preparation of antibiotic sample and analytical procedure

The sample was prepared by soaking Amoxicillin drug (Almox) in distilled water for 24 hours. A stock solution of 500 mg/l was prepared and whenever required was used for appropriate concentrations. All the operations were done in batch mode. For determining the effect of different parameters, each batch was operated at desired conditions. After each batch, the sample was withdrawn from the reactor and allowed to settle for 15 minutes and tested for further analysis. The experiments were carried out at room temperature. The calculations for percentage of antibiotic and COD removal were carried out as per equations (1) and (2) respectively.

$$R_A = [(A_0 - A) / A_0] \times 100 \quad \ldots..(1)$$

$$R_{COD} = [(COD_0 - COD) / COD_0] \times 100 \quad \ldots\ldots(2)$$

where, R_A → antibiotic removal in percentage

R_{COD} → COD removal in percentage

A_0 → initial antibiotic concentration (mg/l)

A → final antibiotic concentration (mg/l)

COD_0 → chemical oxygen demand before reaction (mg/l)

COD → chemical oxygen demand after reaction (mg/l)

2.6 Preparation of calibration graph

Samples of strengths 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/l were prepared and quantities of antibiotic present in each sample was determined using UV-spectrophotometer (272 nm was used as the best working wavelength for analysis of amoxicillin). Based on these values, a graph was plotted between the concentrations of various samples and the absorbance of the antibiotic present in those solutions. This graph was used to find out the quantities of antibiotics present in samples after each experiment. The graph is given below:

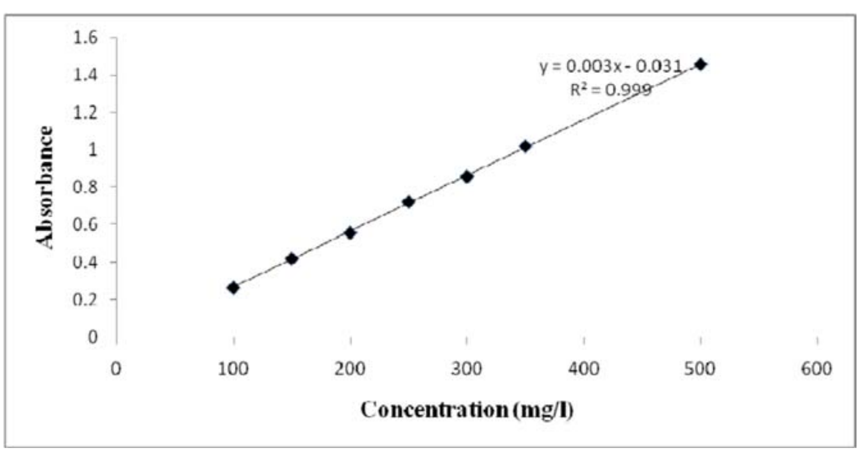

Fig. 1: Calibration curve

3. **Results and discussions**

3.1 Effect of time

Tests were performed for different time intervals, i.e. 15, 30, 45 and 60 minutes. Other parameters approximated as 0.4A current, 7.3 pH and 2500 mg/l electrolyte. Initial concentration of antibiotic was kept 500 mg/l. After each test, the treated sample was tested for absorbance of antibiotic in UV-VIS spectrophotometer. It was found that upto 30 minutes, removal of antibiotics was more than that after 30 minutes. Hence, experiments were again performed for 5, 10, 15, 20, 25 and 30 minutes. It was found that the time period of 30 minutes showed the best antibiotic removal. Thus, 30 minutes was taken as the optimum time.

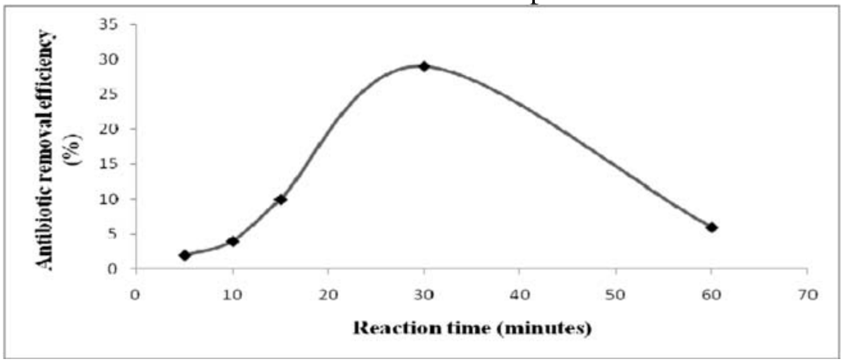

Fig. 2: Antibiotic removal efficiency with reaction time

3.2 Effect of current

The optimum time of 30 minutes, from the previous test, was taken as the electrolysis time. pH and salt concentration were maintained at 7.3 and 2500 mg/l respectively. The current for electrolysis was varied as 0.2, 0.4 and 0.6A. 0.4A showed minimum absorbance of amoxicillin and hence was taken as the optimum current needed for removal of amoxicillin from wastewater.

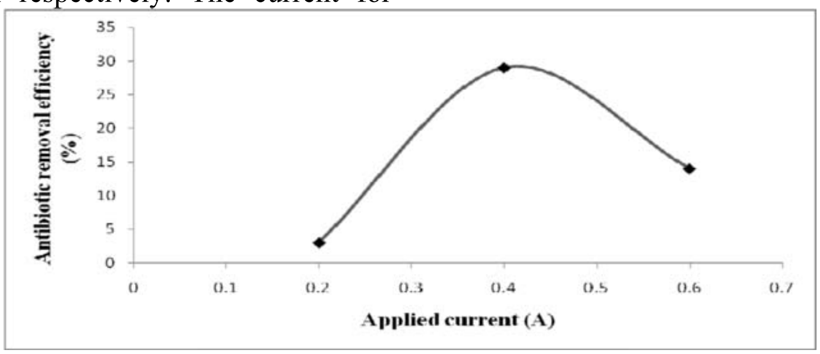

Fig. 3: Antibiotic removal efficiency with applied current

3.3 Effect of pH

Optimum time and optimum current obtained from the previous two steps were used. pH of the solution was adjusted to 5 by adding 0.4ml of 1N H_2SO_4 and to 9 by adding 0.6 ml of 1N NaOH to the sample. Electrolysis was performed on these solutions. Test was also performed for the sample at original pH of the sample, i.e. 7.3. 7.3 pH gave maximum antibiotic removal.

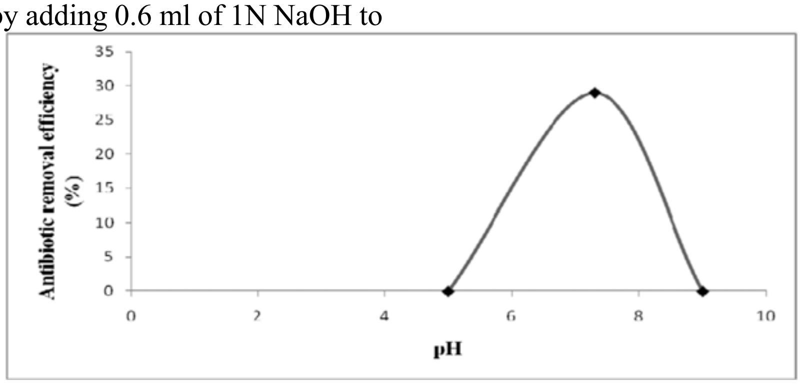

Fig. 4: Antibiotic removal efficiency with pH (Initial concentration of solution

3.4 Effect of electrolyte concentration

Optimum values of electrolysis time, applied current, pH and electrolyte concentration from above steps were used. The concentration of electrolyte was varied as 2000, 2500 and 3000 mg/l. Salt concentration of 2500 mg/l showed the minimum absorbance of amoxicillin and therefore was chosen as the optimum concentration of electrolyte.

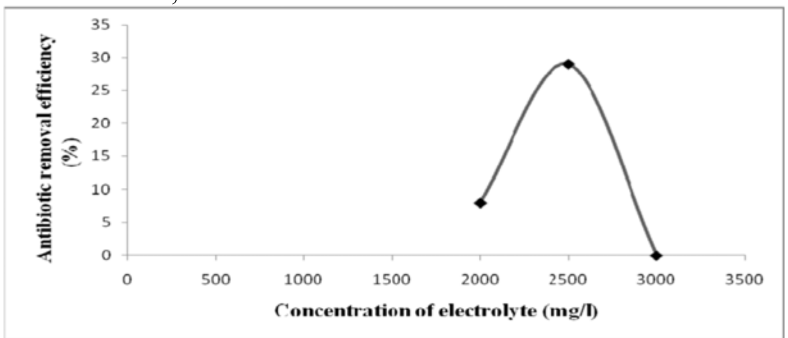

Fig. 5: Antibiotic removal efficiency with electrolyte concentration

The optimum parameters, i.e. electrolysis time: 30 minutes, applied current: 0.4A, pH: 7.3 and electrolyte concentration: 2500 mg/l, removed 29% antibiotic from the wastewater sample.

3.5 COD test

For antibiotic concentration of 500 mg/l, electrolysis time of 30 minutes, current supply of 0.4A, pH value of 7.3 and electrolyte concentration of 2500 mg/l gave maximum removal of antibiotic from the wastewater. These optimized parameters were employed for electrolysis and the treated sample, as well as the original wastewater sample were tested for COD. The original COD of sample was found to be 856 mg/l and that of the electrochemically treated sample was calculated as 736 mg/l. Thus, the percentage COD removal was found to be 14.0187%.

3.6 Chemical coagulation by jar test and determination of solids

Aluminium sulphate (alum) and ammonium ferrous sulphate were the two coagulants used. Jar test was performed for 6 samples of 250 ml having same antibiotic concentration (500 mg/l) and different coagulant doses: 10, 20, 30, 50, 80 and 100 mg/l. Coagulant doses of 50 mg/l for alum and 80 mg/l for ammonium ferrous sulphate were found to give the best antibiotic removal.

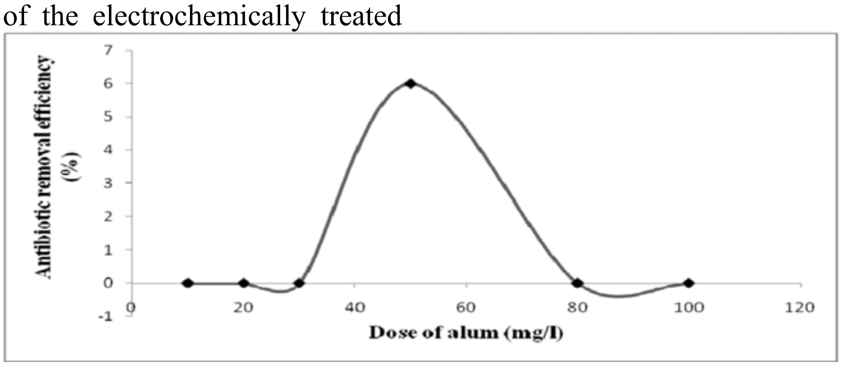

Fig. 6: Showing the percentage removal of antibiotic by chemical coagulation with aluminium sulphate (alum) used in various doses

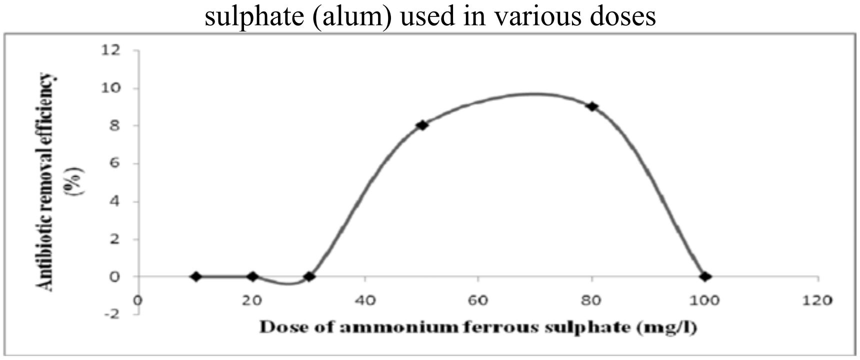

Fig. 7: Showing the percentage removal of antibiotic by chemical coagulation with ammonium ferrous sulphate used in various doses

While electrochemical process removed 29% of antibiotic from the solution, chemical coagulation could remove only 6% and 9% of the antibiotic. Hence, electrochemical process proved to be a better option for treatment of antibiotic wastewater than chemical coagulation.

4. Conclusions

1. Increasing electrolysis time from 5-30 minutes, at an interval of 5 minutes, resulted in increase in percentage of antibiotic removal from 2-29%. Further increase in time resulted in a sudden drop in this percentage. 30 minutes was taken as the optimum value of electrolysis time.
2. Increasing applied current in the range 0.2-0.6A with a difference of 0.2A increased the percentage of antibiotic removed from 3% to 29% for 0.2A to 0.4A. Applied current of 0.6A decreased this removal. Applied current of 0.4A was hence selected as optimum.
3. When pH range of 5-9 was selected, the concentration of antibiotic in the wastewater sample was found to have increased for the pH values of 5 and 9. The actual pH of the sample, i.e. 7.3 showed 29% antibiotic removal, and hence was chosen the optimum value of pH.
4. Effect of electrolyte concentration on electrochemical treatment was studied over the range 2000-3000 mg/l, which showed that the antibiotic removal percentage increased from 8% to 29% when salt concentration was increased from 2000 mg/l to 2500 mg/l. When the concentration of electrolyte was increased to 3000 mg/l, the antibiotic concentration in the sample after treatment was found to be more than that in the original sample. Hence, 2500 mg/l was taken as the optimum electrolyte concentration for maximum removal of antibiotic from wastewater.
5. Comparison of CODs of the sample before and after electrochemical treatment, using the optimum values of various parameters, showed that with the help of electrochemical process using stainless steel electrodes the COD can be reduced by 14.0187%.
6. With the help of jar test optimum doses of coagulants, alum and ammonium ferrous sulphate, were determined. 50 mg/l of alum and 80 mg/l of ammonium ferrous sulphate were found to give maximum percentage removal of antibiotic from wastewater sample, i.e. 6% in case of aluminium sulphate (alum) and 9% in case of ammonium ferrous sulphate.
7. The comparison between the results of electrochemical process and chemical coagulation process suggested that electrochemical process is a better treatment option for removal of antibiotics from wastewater than chemical coagulation process.
8. The process followed first order reaction, with a rate constant, k, of 0.0263.
9. Energy consumption per kg antibiotic removed was found to be 24827.5862 Wh.
10. For anode of 1 m^2 area, anode efficiency was calculated as 0.725 x 10^{-3} kg A^{-1} h^{-1} m^{-2}.

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