Performance Evaluation of Electrochemical Oxidation System to Treat Domestic Sewage

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ABSTRACT—Environmental issues have become serious social concerns of a global scale. Among these issues, the impact of water pollution is getting more serious because it is closely related to the health and lives of human beings. The removal or breakdown of organic compounds from wastewater is an important and integral part of any industrial chemical process. Treatment plants intended for the purification of any industrial wastewater utilize a combination of processing techniques such as Physical treatment, Physico-chemical treatment and Biological treatment. Also, recent literature indicates the applicability of electrochemical process as an attractive alternative for application prior to biological methods. Electrochemical (EC) treatments such as electrocoagulation, electroflotation and electrochemical oxidation have been studied extensively because of their several advantages over a typical wastewater treatment plant. Electrochemical treatments generally have lower temperature requirements and require less space, and produce fewer by-products or sludge.

1. INTRODUCTION

Traditionally, waste water with organic compounds coming from chemical industries has been treated as follows: 1) By biological treatment, with or without a chemical treatment step before. 2) By incineration treatment; if the products could be picked up in solid state. 3) By the burial after a chemical pre-treatment and sometimes storage. The advantages of the biological treatments are very well known, but also their limitations either for a high COD (Chemical Oxygen Demand) value or the presence of very toxic compounds. The possible presence of inorganic compounds, such as heavy metals, may cause a drop of the bacterial count. On the other hand, the incineration of organic compounds can originate the formation of toxic products that are dragged at the same time by the combustion gases; also, the presence of corrosive agents can cause problems in the stability of the materials of the incinerator.

2. ELECTROCHEMICAL PROCESSES

Electrochemical processes for wastewater treatment are benefiting from advantages such as versatility, environmental compatibility and potential cost effectiveness among others described by other authors. Electrochemistry offers promising approaches for the prevention of pollution problems in the process industry. During the last two decades, research work has focused on the efficiency for oxidizing various pollutants at different electrodes, the improvement of the electro catalytic activity and electrochemical stability of the electrode materials and the investigation of factors affecting the process performance and kinetics of pollutant degradation.

3. LITERATURE REVIEW

3.1. WASTEWATER TREATMENT: GENERAL

Industrial wastewater contains a vast array of pollutants: insoluble, colloidal, and particulate forms, both inorganic and organic. In addition, the required effluent standards are also diverse, varying with the industrial and pollutant class. Consequently, there can be no standard design for industrial water pollution control; rather, each site requires a customized design to achieve optimum performance. However, each of the many proven processes for industrial waste treatment is able to remove more than one type of pollutant and is in general applicable to more than one industry.

It is most important to understand the temporal variations in industrial wastewater strength flow, and waste components and their effect on the performance of various treatment processes. Industry personnel, in an effort to reduce cost, often neglect laboratory and pilot studies and depend on waste characteristics from similar plants. This strategy often results in failure, delay, and increased costs. Careful studies on the actual waste at a plant site cannot be over emphasized.

3.2. ADVANCES IN WASTEWATER TREATMENT

Several effective, affordable, and environmentally sound waste disposal options are available; others are within scientific reach. Separating waste categories can go a long way in addressing waste problems. For toxic industrial and medical wastes, non-incineration technologies such as the gas phase thermo-chemical reduction process achieve virtually 100 percent efficiency in POPs destruction and capture all residues and releases. Other emerging technologies include electrochemical oxidation, molten metal technology, solvated electron process and supercritical water oxidation.
3. WHY ONLY ELECTROCHEMICAL OXIDATION?

In electrochemical oxidation (EO), an electrochemical cell, operating at 50 to 60°C (120° to 140°F) and atmospheric pressure, is used to generate an oxidizing species (a mediated metal ion) at the anode (the negative electrode) in an acidic solution. As indicated in the flow sheet, this is accomplished by supplying a voltage across two electrodes immersed in an acidic solution containing the oxidizing species in its reduced, more natural state.

4. ELECTROCHEMICAL TREATMENT

Electrochemical treatment is a technique in which the wastewater is treated by applying electric current through electrodes in a reactor. The electrodes generate the positive and negative ions which combine to form metal hydroxides flocs. These metal hydroxide flocs combine with pollutant particles and settle down. Application of electric current also generates oxidizing groups like HOCl with pollutant particles and settled down. Along with ions generation, gas bubbles are also generated from the cathode in the form of hydrogen gas. These gas bubbles stick to the pollutant particles and float them to the surface of the water. This technology is used for removal of metals, colloidal solids and particles and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species.

fig. 2.2 shows a conceptual diagram of an electrochemical reactor for waste-water electro oxidation, which includes a power supply, a cathode, an anode and the electrolyte.

4.1. ELECTROCHEMICAL TREATMENT SYSTEM

It includes a reactor where the wastewater is subjected for actual electrochemical treatment. This reactor may be preceded by a pre-treatment unit for making the wastewater compatible for electrochemical treatment. The reactor may be followed by a post treatment unit where in the pollutants after the electrochemical treatment/conversion are removed. Electrochemical treatment system demands a regulated supply of DC power to the reactor so a power system is provided for transforming AC power to DC.

4.1.1. Pre-Treatment Unit

In this unit the wastewater is pre-treated to make it compatible for electrochemical treatment. The pre-treatment units includes any process: it may be addition of electrolyte (NaCl, sodium sulphate) to maintain the conductivity, a tank for the setting of suspended solids, a screen for the removal of coarse particles or may be tank for addition of chemicals like HCl and NaOH for pH adjustment.

4.1.2. The Reactor

Reactor allows electro-oxidation, electro-coagulation and electro-flocculation of the loaded wastewater. The reactor includes electrodes (cathodes and anodes) which may be sacrificial or non-sacrificial. Iron and Aluminum are the sacrificial electrodes while stainless steel is generally a non sacrificial electrode. Electrode used (anode and cathode) may depend on electrochemical reactions desired in the reactor. For electro-coagulation and electro-flocculation to occur sacrificial electrodes (iron and Aluminum) are favoured.

Non sacrificial electrodes (graphite, stainless steel, titanium coated with oxides) are favoured when the treatment desired is mainly electro-chemical oxidation. The reactor can be considered to include three components: body of the reactor, inlet section and outlet section. Outlet section may also include provisions for foam breaking and skimming etc.

4.1.3. Post Treatment Unit

In this unit the pollutants after the electro-chemical treatment/conversion are removed. The pollutants are removed by the use of chemicals like polyelectrolyte, by filtration of treated effluent or by simple sedimentation in the sedimentation tank.

4.1.4. Power System

For supplying the needed DC power at desired voltage and amperage, the power system is needed. System converts the input alternating current into Direct current (DC) of desired voltage. A power system has many provisions to get the desired voltage and current. Power system has the facility of polarity change at desired regular intervals. Polarity reversal do not dramatically fluctuate the voltage of the delivered power. Regulation of voltage of the output DC power should be possible and it should remain constant throughout the experiment.
5. MECHANISM OF TREATMENT AND ROLE OF ELECTRODES

Electro-chemical treatment is actually a combination of many processes like; 1) Electro-coagulation and Electro-flocculation. 2) Electro-oxidation 3) Floatation and precipitation also occurs during electrochemical treatment.

An Electro-oxidation deal with the generation of the ions from the electrodes by the process of oxidation. Electro-coagulation is the process in which neutralization of charges occurs by electrochemical treatment. Electro-flocculation is the process where metal ions released from the metal electrodes combine with hydroxide to form insoluble precipitate along with which the pollutant particles are co-precipitated. In electroflocculation process, the gas bubbles (because of the generation of the hydrogen gas) are produced on the electrodes in the electrochemical reactor. The EC technology offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions.

Electrochemical treatment is also associated with one or more of the following: 1) Dissolution of the metal electrodes. 2) Electro-oxidation, electro-coagulation and electro-flocculation of the waste water. 4) Heating of the waste water. 5) Gas production and subsequent flotation. 6) Settling of the flocculated solids and 7) Deposition of the solids on the electrode surfaces.

5.1. Electro-Coagulation and Electro-Flocculation

Application of electric current to sacrificial electrodes, usually Aluminum or iron generates aluminium and ferrous ions. These ions act as coagulating agents. They neutralize the electrostatic charges on colloidal particles and facilitate coagulation and then separation from the solution. This treatment also prompts precipitation of some of the metals and salts.

According to (Mollah et al. 2001) electro-coagulation process involves three successive stages: 1) Formation of coagulants by electrolytic oxidation of the sacrificial electrode 2) Destabilization of colloidal contaminants and breaking of emulsions 3) Aggregation of destabilized particles to form flocks 4) The destabilization mechanism of the contaminants, particulate suspension and breaking of emulsions can be summarized as follows:

a) Compression of the diffuse double-layer around the charged species. b) Charge neutralization of the ionic species present in wastewater, which is caused by the counter ions, produced by the electrochemical dissolution of the sacrificial electrode. These counter ions reduce the electrostatic inter particle repulsion sufficiently so that the van-der-Walls attraction predominates, thus causing coagulation. c) Flock formation and the flock formed as a result of coagulation create a sludge blanket that entraps and bridges colloidal particles that have not been complexes. There are various ways in which the pollutant species can interact in solution: 1) Migration to oppositely charged electrode (electrophoresis) and aggregation due to charge neutralization. 1) Cations or hydroxyl ions (OH-) form precipitates with the pollutant. 2) The metallic cations interact with OH- ions to form metal hydroxides, on which adsorption of pollutants takes place. (Bridge coagulation). 3) Metal hydroxides form larger lattice-like structures that sweep through the water (Sweep coagulation). 4) Oxidation of the pollutants.

The reactions that take place on the electrode surfaces during electro-coagulation and electro-flocculation are as follows: Reactions at the aluminium electrode are:

At Anode:

\[
\begin{align*}
\text{Al}^{(aq)} & \rightarrow \text{Al}^{3+} + 3e^- \quad (1) \\
2\text{H}_2\text{O} (l) & \rightarrow \text{O}_2 (g) + 4\text{H}^+ + 4e^- \quad (2)
\end{align*}
\]

At Cathode:

\[
\begin{align*}
2\text{H}_2\text{O} (aq) + 2e^- & \rightarrow \text{H}_2 (g) \quad (3) \\
\text{Al}^{3+} + \text{H}_2\text{O} (l) & \rightarrow \text{Al}^{(OH)}_3^{3+} + \text{H}^+ \quad (4) \\
\text{Al}^{3+} + \text{H}_2\text{O} (aq) & \rightarrow \text{Al}^{(OH)}_2^{3+} + \text{H}^+ \quad (5) \\
\text{Al}^{(OH)}_2^{3+} + \text{H}_2\text{O} & \rightarrow \text{Al}^{(OH)}_3^{4+} + \text{H}^+ \quad (6) \\
\text{Al}^{(OH)}_3^{4+} + \text{H}_2\text{O} & \rightarrow \text{Al}^{(OH)}_4^{+} + \text{H}^+ \quad (7) \\
2\text{H}_2\text{O} & \rightarrow 4\text{H}^+ + 4e^- + \text{O}_2 (g) \quad (9)
\end{align*}
\]

Reaction at the iron electrodes: (Daneshwar et al. 2006) Proposed two mechanisms for production of hydroxides and iron:

At Anode:

\[
\begin{align*}
4\text{Fe}^{(aq)} & \rightarrow 4\text{Fe}^{2+} (aq) + 8e^- \quad (10) \\
2\text{H}_2\text{O} (l) & \rightarrow \text{O}_2 (g) + 4\text{H}^+ + 4e^- \quad (11)
\end{align*}
\]

The generated iron and oxygen dissolved react to form Fe(OH)₃

\[
\begin{align*}
4\text{Fe}^{2+} + 10\text{H}_2\text{O} (l) + \text{O}_2 (g) & \rightarrow 4\text{Fe} \text{(OH)}_3 (s) + 8\text{H}^+ \quad (12)
\end{align*}
\]

At Cathode:

\[
\begin{align*}
8\text{H}^+ + 8e^- & \rightarrow 4\text{H}_2 (g) \quad (13) \\
2\text{H}_2\text{O} (l) + 2e^- & \rightarrow \text{H}_2 (g) + 2\text{OH}^- \quad (14)
\end{align*}
\]

6. SPECIFIC REVIEWS

In this section, review of literature on the electrochemical treatment technology for wastewater treatment is presented. The review is presented under the following heads:

Heavy Metal Removal by Electro-Chemical Treatment

Elsayed and Saba (2009), studied the electrochemical treatment of toxic hexavalent chromium from industrial effluents using rotating cylinder electrodes cell. The effect of chromium, sulphuric acid concentration, current density, time and speed of cathode rotation on cell. The effect of chromium, sulphuric acid concentration, on current efficiency was found to be 90%. The current efficiency was achieved at current density 225mA/cm² for 80 min.

Mukhopadhyay et al. (2007) worked out some experiments on removal of hexavalent chromium to...
trivalent chromium. Iron electrodes were used in the process. Cr (VI) is first reduced to Cr (III) in acidic pH by a reducing agent which is followed by precipitation of trivalent chromium along with metal hydroxide in alkaline pH.

7. OBJECTIVES OF THE STUDY

The specific objectives of the present dissertation work are listed 1)To fix up the ranges of operating parameters based on the literature review. 2)To fabricate the bench scale experimental set-up to evaluate the performance. 3)To optimise the operating parameters/variables viz., COD, TDS, electrical conductivity, distance between electrodes, contact time, voltage and pH enabling to treat the domestic sewage.

8. MATERIALS AND METHODOLOGY

Materials and methodology adopted to carry-out the present study is discussed in depth in this chapter. The issues discussed include: 1)Wastewater considered 2)Electrodes considered 3)Parameters considered 4)Variables considered 5)Analysis of parameters 6)Experimental set-up 7)Procedure adopted 8)Compilation of result

8.1. WASTEWATER CONSIDERED

Wastewater considered for the present study is domestic sewage. The problems associated with the actual sewage are daily collection of sewage, change in the characteristics of wastewater and thereby difficult to maintain the predetermined characteristics of the sewage to carry out experimentation under varied experimental conditions. Thus to overcome these problems, synthetic sewage having the properties of interest similar to domestic sewage was prepared and used for experimentation.

The synthetic sewage was prepared by addition of organic chemicals. The chemicals used for the preparation of synthetic sewage are starch, milk powder, urea and yeast.

The stock solution of COD concentration of 1000 mg/l was prepared by adding chemicals in the concentrations listed (Ingmar Nopens, 2001) 1)Starch = 420.4 mg/l 2)Milk powder = 400.4 mg/l 3)Urea = 53.3 mg/l 4)Yeast = 120 mg/l. The COD concentrations (Co) of 200 and 350 mg/l used for experimentation were prepared from the stock solutions with proper dilutions.

8.2. ELECTRODES (E) CONSIDERED

The electrodes viz. iron-iron and aluminium-aluminium were used in this study. Iron and aluminium electrodes were prepared from iron and aluminium plates respectively. The plates were cut into required sizes [40x140x2 mm] and provisions for electrical connections were made by making holes at the top of plates. Provisions were made in the reactor for the change of electrodes. Polarity of current was reversed at regular intervals in order to minimize the deposition on electrodes (Ankit Mohla: 2007).

8.3. PARAMETERS CONSIDERED

Based on typical characteristics of waste water quoted by various researchers, the parameters viz., Chemical oxygen demand (COD), total dissolved solids (TDS), electrical conductivity (EC) and pH, were considered. The details of parameters considered include: COD: 200 mg/l and 350 mg/l, pH: 7.5 and 8.0, TDS : 489.8 mg/l and 417.7 mg/l.

8.4. VARIABLES CONSIDERED

Generally the performance of electrochemical oxidation depends on electrode type, voltage, distance between electrodes, contact time and electrolyte concentration. Thus the present experimentation was carried out under varied conditions of experimentation viz., electrode type, voltage, distance between electrodes and contact time.

The details of variables considered are listed as: Voltage: 2, 4 and 6 V, Contact time: 10, 20 and 30 minutes, Distance between electrodes (D): 3 cm and 6 cm.

8.5. ANALYSIS OF PARAMETERS

Parameters considered in this study are analysed by standard methods (APHA: 1992).

8.6. EXPERIMENTAL SET-UP

A laboratory/bench scale unit was used to conduct the experiments in the present study. The unit includes two components: the reactor and the power supply system. The experimental set-up is outlined as below: Glass beaker up is made up of borosilicate glass of 1 litre capacity is used as reactor. Two electrodes 3. Magnetic stirrer.

Regulated DC linear power supply system (make: Pragna instruments) was used to vary voltage. Line diagram of experimental set-up is shown in fig 3.1. and the plates show experimental set-up and allied infrastructure used for experimentation.

8.7. PROCEDURE ADOPTED

The experimentation was carried out for different set of variables and parameters. By keeping, COD constant, with one type of electrode and at given pH, distance and voltage, by varying time, first set of experiment was carried out. In the next set of experimentation, for another voltage and keeping the all other variables same as in the previous, experiment was carried out for varying time. Likewise for different COD concentrations, pH, voltage and time and with two electrodes experiments were carried out.
8.8. COMPILATION OF RESULTS

The findings of experimentation of the present study are tabulated in columns, represented by graphs, inferences are drawn and conditions were made.

Plate-1: View of Experimental Set-Up (Iron Electrodes)

Plate-2: Pictorial View of Experimental Set-Up (Aluminium Electrodes)

Plate-3: Plateau of TDS Analysing Instrument

Plate-4: Pictorial View of Stock Solution

9. RESULTS AND DISCUSSIONS

Results of experimentation carried out under varied conditions of experimentation are tabulated and are represented by graphs and are documented in this chapter. Based on the results inferences have been drawn. The discussions are made in further sections and subsection emphasizing variables of experimentation on COD removal efficiency.

Results of experimentation are summarized in tables 1 and 2. Accordingly the results represented in linear and bar charts (fig- 5 and 6).

9.1. EFFECT OF CONTACT TIME

Experiments were carried out to evaluate the influence of contact time on removal efficiency. Three contact times viz., 10, 20 and 30 min were considered for study. Based on the observations the following inferences have been drawn. Linear and direct relationship between the COD removal efficiency and contact time has been observed. Maximum removal efficiency for steady contact time of 30 min and minimum removal efficiency for steady contact time of 10 min has been recorded. Same trends have been observed for all conditions of experimentation carried out.

9.2. EFFECT OF ELECTRODE DISTANCE

Two electrode distances viz., 2 and 6 cm were considered for the experimentation and observe the effect of electrode distance on COD removal efficiency. From these observations the following inferences have been drawn. The maximum COD removal efficiency has been observed at electrode distance of 6 cm compare to electrode distance of 3 cm. In all conditions of experimentation, same trend have been observed. Thus the direct relationship was found to exists between electrode distance and removal efficiency.

9.3. EFFECT OF VOLTAGE

The effect of voltage on COD removal efficiency has been studied in the present experiment. 2, 4 and 6 V were considered for the study. The following inferences were made based on the observation of the experimentation
1) The linear increase in COD removal efficiency with increase in voltage has been recorded.
2) Minimum and maximum removal efficiency has been observed at voltage of 2V and 6V respectively.
3) The similar trends have been observed from the observations of all conditions of experimentation.

9.4. EFFECT OF pH

pH viz., 7.5 and 8.0 were considered for the study to evaluate the effect of pH on the COD removal efficiency. Based on the observations, the following inferences were drawn. 1) pH has the direct influence on the COD removal efficiency. 2) The removal efficiency for the pH 8.0 is significantly more than that of pH 7.5. Same trend was continued in all the conditions of experimentation.

9.5. EFFECT OF INITIAL COD CONCENTRATION ($C_0$)

The experiments were carried out to identify the influence of COD concentration on the COD removal efficiency. Two COD concentrations viz., 200 and 350
mg/l were considered for the study. Based on the observations, the following inferences have been drawn. Inverse relationship between the COD removal efficiency and COD concentration has been observed. Higher COD removal efficiency was obtained at critical COD concentration of 200 mg/l compared to COD concentration of 350 mg/l. Same trends have been observed for both the electrodes at all conditions of the experimentations.

9.6. EFFECT OF TYPE OF ELECTRODES
To evaluate the influence of type of electrodes on COD removal efficiency, the experiments were carried out using two electrodes viz. Iron and aluminium. The relationship between type of electrodes and COD removal efficiency has been studied from the observations. Based on the observation, following inference has been drawn. Iron electrodes have more significant effect on COD removal efficiency and aluminium electrodes have least effect on COD removal efficiency.

9.7. REMOVAL EFFICIENCY OF TDS
The results of experimentation carried out for synthetic wastewater using two electrodes are tabulated in the Table. Observations are summarized below 1) The TDS removal efficiency increases with increase in contact time and voltage. 2) The increase in pH increases the TDS removal efficiency and increase in concentration decreases the TDS removal efficiency. 3) An iron electrodes has least TDS removal efficiency compare to aluminium electrodes. 4) With iron electrodes the removal efficiency was found to decrease with increase in electrode distance but with aluminium electrodes increase electrode distance was found to increase the removal efficiency.

9.8. EFFECT OF VARIABLES ON ELECTRICAL CONDUCTIVITY
Results obtained for the electrical conductivity as a function of contact time, voltage and electrode distance, are tabulated in Tables. Observations made are summarized below. 1) Electrical conductivity has indirect relationship with voltage and contact time. The electrical conductivity decreases with increase in contact time and voltage. 2) Electrical conductivity has direct relation with electrode distance with iron electrodes and indirect relation with aluminium electrodes.

SET-1: E=Iron, C_o=200 mg/l, pH=8.0, D=6 cm

The findings of the electrochemical oxidation are tabulated in Table-1. Observations made were given below 1) For 10 min of contact time, for voltages 2, 4 and 6 V, the removal efficiencies of 55, 59 and 65 % respectively have been observed. 2) Accordingly, for 20 min of contact time the removal efficiencies observed varied from 60 to 72 % for voltages 2, 4 and 6 V respectively. 3) The removal efficiencies obtained for contact time of 30 min and for voltages 2, 4 and 6 V were 66, 71 and 78 % respectively. As distance increases, the increase in removal efficiency has been observed. The removal efficiency for pH-7.5 ranged from 43 to 70 % and the removal efficiency for pH-8.0 varied from 48 to 78 %. Thus it is inferred that increase in pH, increases the COD removal (fig.4.1 and 4.2).

![fig 5: Influence of Contact Time on COD Removal Efficiency](image-url)

SET-2: E=Aluminium, C_o=200 mg/l, pH=8.0, D=3 cm and 6 cm

The results for electrochemical treatment of synthetic waste water are tabulated in Table-2 and summary of observations made are discussed. For 2, 4 and 6 V of voltages, for contact of 10, 20 and 30 min, the removal efficiency ranged between 55 to 69 %, the electrode distance being 6 cm. From the above observations, the conclusion is made that the increase in electrode distance, voltage and contact time, the removal efficiency increases.
The following are the limitation of present study and these limitations are attributed to non-availability of data, lack of infrastructure facility, time shortage, not within the preview of objectives of present study etc. 1) The experiments have been carried out only for set of variables. Confined conclusions can be drawn based only on the results of wide ranges of variables. 2) Investigations to evaluate the leaching of colours into wastewaters by iron electrodes.

SCOPE FOR FURTHER STUDY

The limitations listed above can be the subject matters for further study. 1) Studies to access the leaching of metals from electrodes into wastewaters can be taken up for further study. 2) Studies to evaluate the feasibility of electrochemical oxidation and coagulation processes for treating other industrial wastewaters. 3) Studies to compare the performance of electrochemical processes and other biological systems in treating sewage and other industrial wastewaters.

11. REFERENCES