COD REDUCTION OF PHARMACEUTICAL INDUSTRY WASTE WATER BY ELECTRO OXIDATION PROCESS BY GENERATION OF IN SITU HYPOCHLOROUS ACID

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ABSTRACT

In this present work, to reduction of Chemical Oxygen Demand (COD) is measured by electrochemical oxidation treatment of pharmaceutical waste water which was collect after primary treatment. The influence of the critical parameters of electro-oxidation such as pH (7 to 8.5), Time period (0min to 90 min), Salt concentration (5gm/L to 20 gm/L) and Current voltage (3V to 12V) on the reduction of COD was studied using different electrode. In this treatment process, in-situ production of hypochlorous acid was achieved by the use of sodium chloride solution for chlorine production. The hypochlorous acid was utilized for the oxidation of organic matter present in the wastewater. It was used graphite, iron and copper electrodes with dimension of (5cm x 20cm x 1mm) using a glass reactor with an optimum capacity of 7 L. The electrodes were arranged parallel to each other. The distance between the two electrodes kept 3cm. The maximum reduction of chemical oxygen demand was carried out at high current voltage, high salt concentration of Nacl. The maximum COD was 68.26% at 7 pH , 30 mg/L Nacl concentration, 12V applied voltage and an electrolysis time period of 90 min.

Keyword : - *Pharmaceutical wastewater, Electrode, Nacl, Electro oxidation, Chemical oxidation demand*

1. INTRODUCTION

The Indian pharmaceutical industries are currently top of the India's industries with wide range capabilities in the complex field of drug manufacturing and technology. India's pharmaceutical industry has consisted of 250 to 300 companies. The Indian pharmaceutical sector is high fragmenting with more than 20,000 registrated units. The pharmaceutical industry in India provides around 70% of country demand for drug intermediates, pharmaceutical formations, chemicals, tablets and capsules. A pharmaceutical or drug company is a commercial business whose focus is to research, developing, marketing and distributing of drugs in the contexts of healthcare. India's pharmaceutical industry is the 3rd largest in the world in term of volume and stands 14th in the term of value. According to Department of pharmaceuticals, Ministry of chemicals and fertilizers, the total turnover of India's pharmaceutical industry was US$ 21.40 Billion. According to the "Directors of Pharmaceutical Manufacturing Units in India", there are 10,563 pharmaceutical manufacturing units in the country.

The wastewaters are produced in different procedure in the production of pharmaceuticals and various medicines are called as Pharmaceutical wastewater. The treatments of effluents of pharmaceutical are a serious problem. This type of wastewater does not discharge directly on surface or in the water media. So that the large amount of effluent to be treated before their disposal. The effects of pharmaceutical chemicals on human and environment is very dangerous because of their high toxicity impacts. If the effluents are not treated with properly method, there may be chances of dangerous impact on human and environment. There are divided in main three categories of primary, secondary and tertiary treatments in the processes for the treatments.

Recently, graphite electrode has been widely used for the decomposition of organic matter because it is economical. Graphite has a large surface area; this feature enables it to increase the rate of organic matter removal through electro-oxidation.[12]

2. ELECTRO-OXIDATION

There are various electrochemical treatments for removal of organic and inorganic impurities of wastewater. It is most usual method like electro coagulation, electro floatation, electro oxidation etc. Electro oxidation means the oxidation of organics which are present in wastewater to carbon dioxide and water or other oxides. The EO is used for degradation of pesticides, paints, industrial pollutants, pharmaceutical waste and other organic. The advantage of EO is that finally products are CO_2 and H_2O and also chlorine is not the problem because of it is converted in the form of Hypochlorite or chloride ion.

In the electrochemical oxidation, organic pollutants are removed by electro-generated oxidizing agents like chlorine and hypochlorite. In general, the following reaction takes place during electro-oxidation using graphite electrodes in the presence of sodium chloride.

At the anode:

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad (1)$$

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \quad (2)$$

At the cathode:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad (3)$$

In the undivided cell, chlorine formed at the anode and hydroxides formed at the cathode react to form chloride and hypochlorite. Both the hypochlorite and free chlorine are chemically reactive and oxidize the organic pollutants in the effluent to carbon dioxide and water.

HOCl is then formed.

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (4)$$

The HOCl further dissociates into OCl^- and H^+ ions.

$$HOCl \_ H^+ + OCl^- \quad (5)$$

This hypochlorite ions act as a main oxidizing agent in the organic degradation. The overall desired reaction of electrolysis is:

$$\text{Organicmatter} + OCl^- \longrightarrow \text{intermediates} \rightarrow CO_2 + Cl^- + H_2O \quad (6)$$

The objective of the present work is to study the electro oxidation of wastewater using graphite electrode. The parameters of electrochemical oxidation such as pH, period of oxidation, concentration of sodium chloride and current density were varied. Scope of the present work also includes the study of reusability of treated wastewater.

3. WASTE WATER SAMPLING

The wastewater samples were collected from the pharmaceutical intermediate products manufacturing industry located at Vapi, (Gujarat) India. First the sampling bottle was cleaned and rinsed with using of distilled water. The sample was filled in bottle and seal air tightly. About 4 to 5 cm air space is left in the bottle for proper mixing by shaking. The sample was stored at room temperature in the laboratory.

4. MATERIALS AND METHODS

Various methods and devices were used to both characterize and monitor the EO process. Some of these methods and devices are briefly described. The electrodes used were Graphite, Iron and Copper of size 5 cm x 20 cm x 1 mm .Various devices were used like pH meter, DC power supply. Nacl was added for increasing the conductivity

.4.1 Experimental Set-Up

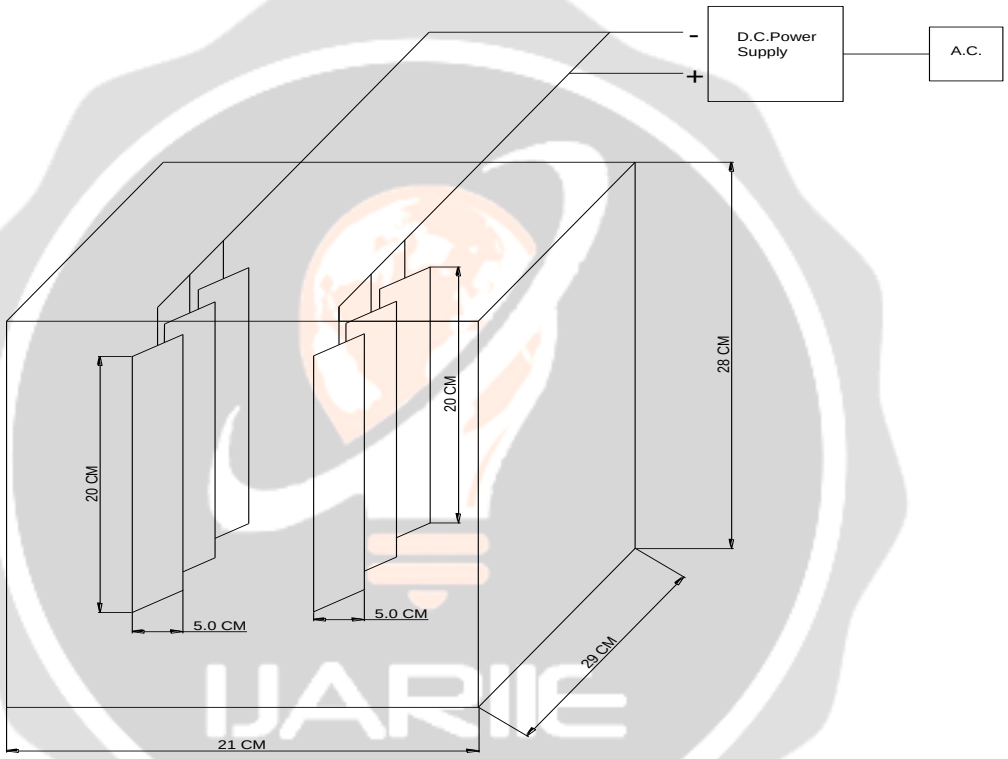

Figure 1: Schematic diagram of electro-oxidation cell

The treatment of wastewater is carryout as above shown in figure in a cubic rectangular batch electrolytic cell made of glass with an optimum capacity of 7 L with the dimensions of (21cm x29cm x28 cm). There are iron and copper electrode with dimension of (5cm x 20cm x 1mm) and also graphite electrode with 5cm in diameter and 20cm in length used as anode and cathode and Nacl is used as electrolyte. The electrodes are arranging parallel to each other. The distance between the two electrodes keep 3 cm. electrodes are connected with wire and connected to direct current supplied by AC/DC convertor. COD is measured with different condition like pH, concentration of Nacl, different current density.

4.2 Experimental Procedure

Sample was taken in the reactor. Electrodes were connect parallel to each other. Regulated current was passed through the electrode with the help DC power supply. Constant stirring of the sample is achieved by the manually. Samples were taken at 30, 60, 90, min respectively. Samples were taken from 5 cm height from bottom.

Sample was collected after the treatment and allows it to cool down and also allow the flocs to settle. After that sample was filter through a filter paper.

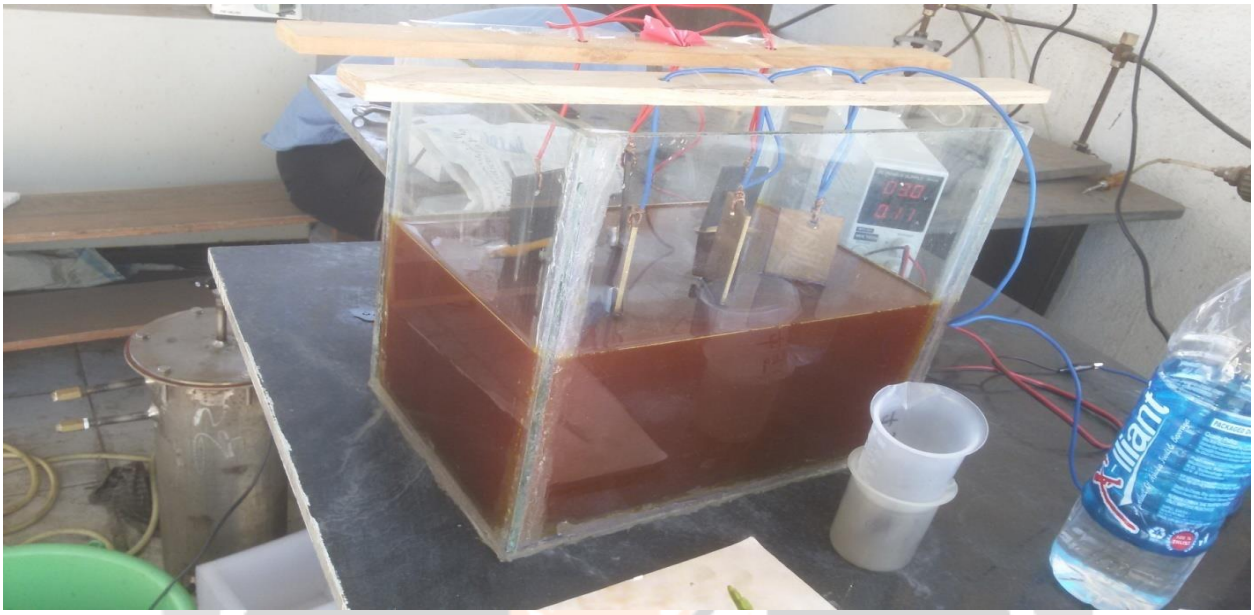

Figure 2: Experimental model

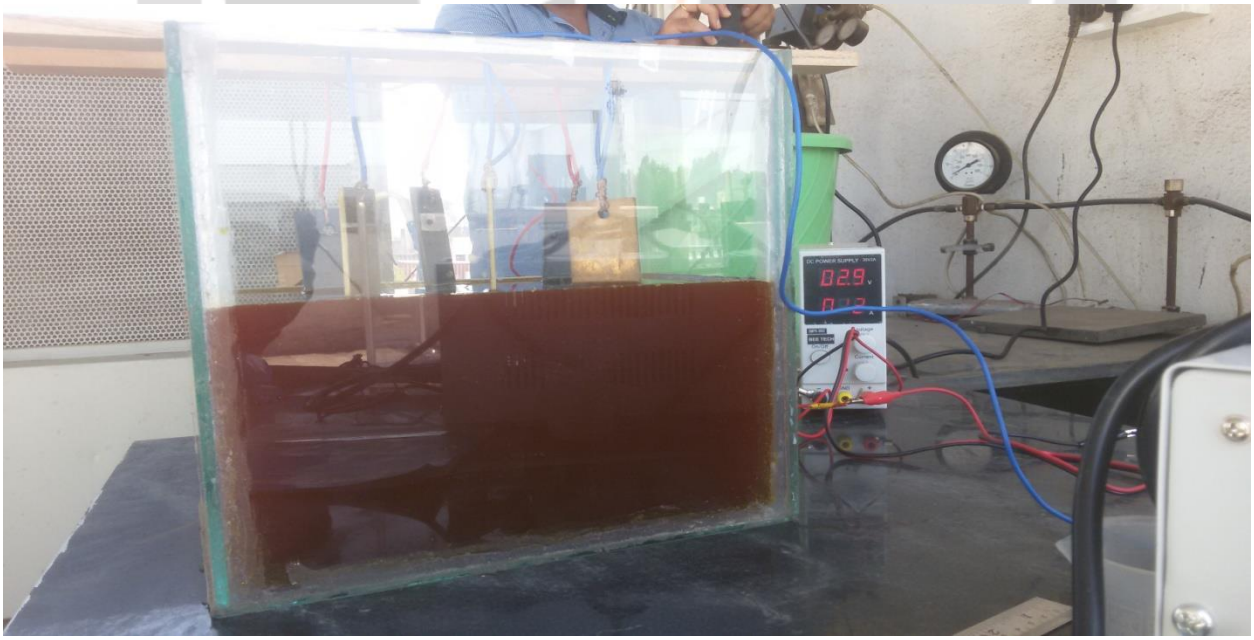

Figure 3: Experimental model

4.3 Characterization of Wastewater

Table 1: Characterization of wastewater

Parameters	Results	Test method
pH	6.5-8.5	IS 3025 (PART 11) 1983, APHA 22nd Ed.2012,4500-H+,B
COD	3000 – 6000	IS 3025 (PART 58) 2006, APHA 22nd Ed.2012,5220-B
TDS	1000 – 1400	IS 3025 (PART 16) 1984, APHA 22nd Ed.2012,2540-C

5. RESULTS

Table 2: Reduction of COD at 12V (2A) current, 20cm x 5cm x 1mm electrode, 27^0C temperature, 30 gm/L Nacl, 7 pH.

Sr. No	Time (min)	Anode- Copper, Cathode- Graphite	
		COD reduction Mg/L	In %
1	0	4551.2	0%
2	30	3037.1	33.26%
3	60	2375.7	47.80%
4	90	1770.8	61.09%

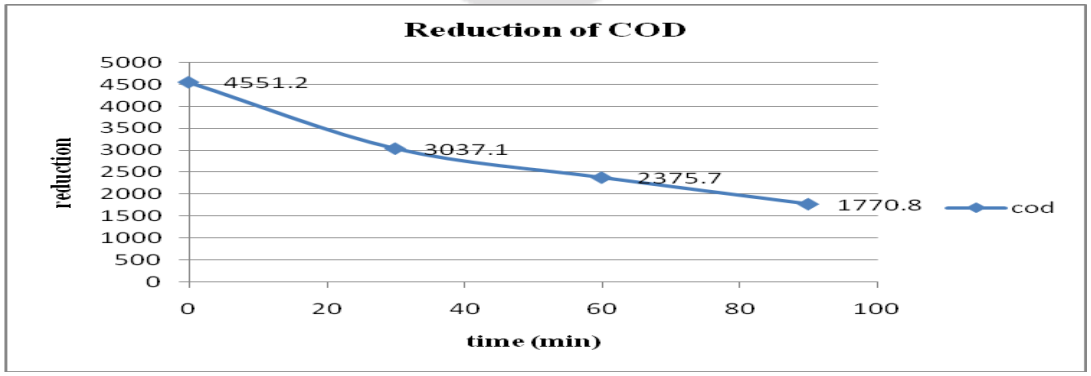

Chart 1: COD reduction at 12V (2A) current, 27^0C temperature, 30 gm/L Nacl, 7 pH.

Table 3: Reduction of COD at 12V (2A) current, 20cm x 5cm x 1mm electrode, 27^0C temperature, 30 gm/L Nacl, 7 pH.

Sr. No	Time (min)	Anode- Iron, Cathode- Graphite	
		COD reduction Mg/L	In %
1	0	3175.04	0%
2	30	2512.8	20.8%
3	60	1331.03	58.07%
4	90	1007.50	68.26%

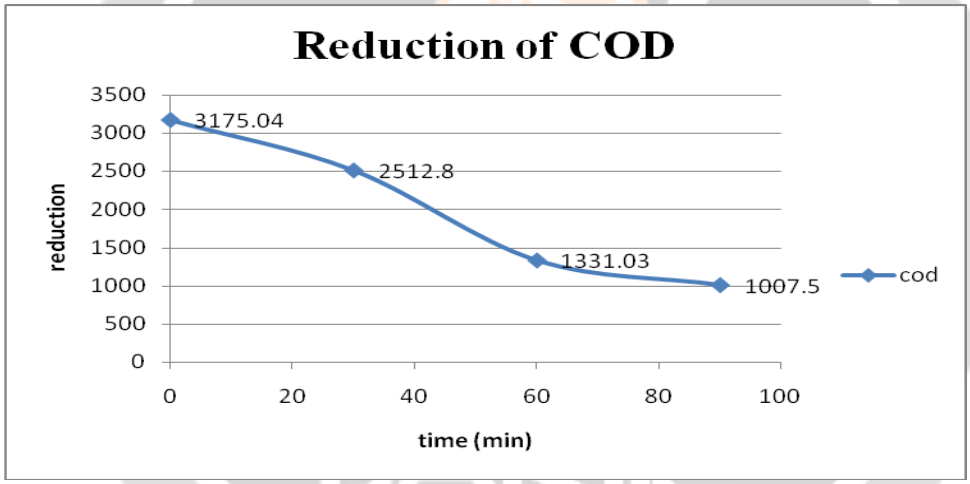

Chart 2: COD reduction at 12V (2A) current, 27^0C temperature, 30 gm/L Nacl, 7 pH.

In this study, the maximum reduction of COD was carried out 61.09% and 68.26% using copper and iron electrode as anode respectively.

6. CONCLUSIONS

This study confirmed that the reduction of COD was achieved by the increase in salt concentration and increases the appied voltage. The maximum removal was achieved at 12V current voltage and 30 gm/L Nacl concentration. Also concluded that the reduction of COD was found to be directly proportional to salt concentration. The increased rate of generation of hypochlorite ion with increase in current voltage. The generated hypochlorous acid was very effective in oxidizing organic matter. The maximum reduction was measured 61.06% and 68.26% using copper and iron electrode respectively. Its shows that iron is more effective with compare to copper. In Electro oxidation surface area is to kept more and space between the electrodes must be as less as possible for better results.

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