Treatment of Wastewater by Electrochemical Oxidation Process

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Abstract— In recent years, there has been increasing interest in finding innovative solutions for the efficient removal of a wide range of pollutants exist in various types of wastewaters, e.g., refractory organic matter, nitrogen species, microorganisms, etc. this research paper focuses on the fundamental mechanisms of electrochemical oxidation process and provides discussions on the possible applications in wastewater treatment. Also, operational and capital cost for the treatment facilities have become more important when sustainability is considered in relation to domestic wastewater treatment in developing countries. The electrochemical processes are one of the sustainable process. In this study, the removal of chemical oxygen demand (COD: 5580 mg/L), suspended solids (SS: 245 mg/L), total phosphorus (4.9 mg/L), nitrate nitrogen (1.3 mg/L) and nitrite nitrogen (0.31 mg/L) from domestic wastewater by electrochemical processes using Iron (Fe-Fe) Electrodes, were experimentally investigated at 5V, 10V and 15V voltage and different processing times (15-30-60-120 min.).

Keywords: COD: Chemical Oxygen Demand; SS: Suspended Solids; TP: Total Phosphorus EO: Electro-Oxidation Process

I. INTRODUCTION

Wastewater treatment can be generally categorized by the character of the treatment process operation being used such as biological, chemical or physical methods. Wastewater treatment via biological technology is the most economical means of treatment and normally utilizes for the removal of biodegradable organic pollutants presented in the wastewater. Nevertheless, the presence of toxic and refractory substrates in the wastewater would virtually foil the biological treatment process as these substrates are potentially inhibiting the bioactivity of microorganism. Among the various techniques, the use of electro-chemical oxidation process in the wastewater treatment has engrossed many researchers attention, particularly in remediating industrial wastewater. To date, electrochemical oxidation processes have been shown to be a valuable option for the elimination of refractory organic compounds from various types of wastewaters. Electrochemical oxidation is highly capable and efficient in reducing the organic compounds from various types of wastewater as compared with other types of physio-chemical technologies which only bring about phase transfer of the contaminants in question with no chemical destruction is taking place.

II. ELECTROCHEMICAL OXIDATION PROCESS

Electro-oxidation (EO), also known as anodic oxidation or electrochemical oxidation, is a technique used for wastewater treatment, mainly for industrial effluents, and is a type of advanced oxidation process (AOP). The most general layout comprises two electrodes, operating as anode and cathode, connected to a power source. When an energy input and sufficient supporting electrolyte are provided to the system, strong oxidizing species are formed, which interact with the contaminants and degrade them. The refractory compounds are thus converted into reaction intermediates and, ultimately, into water and CO_2 by complete mineralization.

The set-up for performing an electro-oxidation treatment consists of an electrochemical cell. An external electric potential difference (aka voltage) is applied to the electrodes, resulting in the formation of reactive species, namely hydroxyl radicals, in the proximity of the electrode surface. To assure a reasonable rate of generation of radicals, voltage is adjusted to provide current density of 10-100 mA/cm^2. While the cathodes materials are mostly the same in all cases, the anodes can vary greatly according to the application, as the reaction mechanism is strongly influenced by the material selection. Cathodes are mostly made up by stainless steel plates, Platinum mesh or carbon felt electrodes.

The electrochemical reactor in the laboratory experiments is shown in Figure 1. Figure 2 shows the conceptual diagram of electrochemical reactor for wastewater treatment, which includes a direct current (DC) power supply, a cathode, an anode, and the electrolyte (a medium that provides the ion transport mechanism between the anode and the cathode necessary to maintain the electrochemical process).

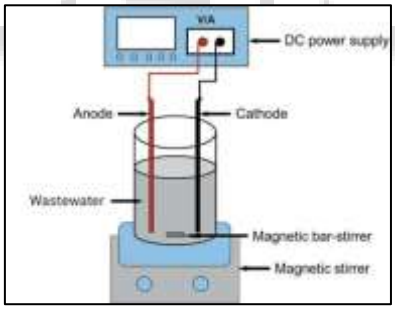

Fig. 1: The electrochemical reactor in the laboratory experiments

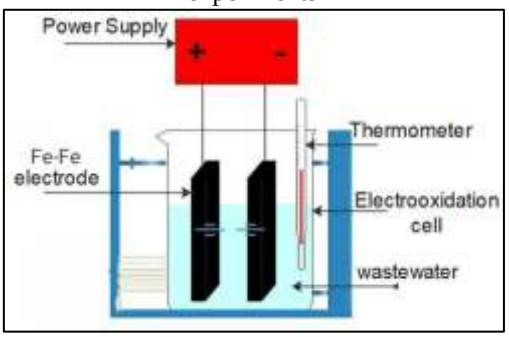

Fig. 2: Conceptual diagram of an electrochemical reactor.

Electrochemical oxidation of impurities in wastewater is accomplished through two different mechanisms as demonstrated in Figure 3: (1) direct anodic oxidation, where the pollutants are destroyed at the anode surface and (2) indirect oxidation where mediators (NaCL,

HClO, H2S2O8, etc) are electrochemically produced to achieve the oxidation. It should be clear that during electro-oxidation of aqueous effluents, both oxidation mechanisms may coexist. Generally, the mechanism of electrochemical degradation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step.

A. Direct oxidation

Direct oxidation of pollutants takes place in two steps: (i) diffusion of pollutants from the bulk solution to the anode surface and (ii) oxidation of pollutants at the anode surface. As a result, the effectiveness of the electrochemical oxidation will depend on the correlation between mass transfer of the substrate and electron transfer at the electrode surface. The rate of electron transfer is determined by the electrode activity and current density. In general, there are two different pathways of anodic oxidation of organic substances as shown hence forth:

– Electrochemical conversion. Organic substances (R) are partially oxidized as presented in Eq. 1. Thus, a following treatment is needed to completely destroy the oxidized substrates.

$$R \rightarrow RO + e- \quad (1)$$

– Electrochemical incineration (combustion). Organic substances are transformed into water, carbon dioxide and other inorganic constituents as presented in Eq. 2.

$$R \rightarrow CO2 + H2O + Salts + e- \quad (2)$$

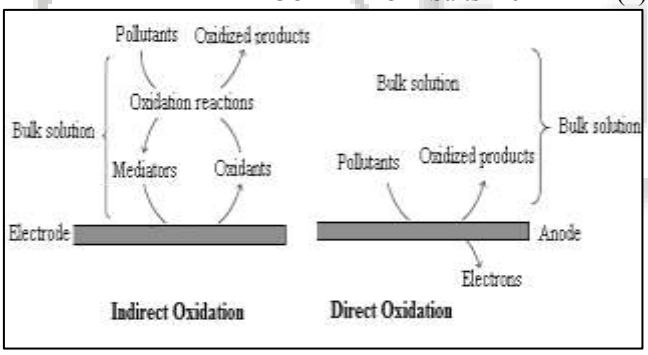

Fig. 3: Schemes for direct and indirect electrolytic treatment of pollutants.

B. Indirect oxidation

During indirect electrochemical oxidation, a strong oxidizing agent is electro-generated at the anode surface and subsequently destroys the organic compounds in the bulk solution. The most widespread electrochemical oxidant is chlorine which is produced via the oxidation of chloride at the anode. Throughout indirect oxidation, the agents produced on the anode that are responsible for oxidation of inorganic and organic matters could be chlorine and hypochlorite, hydrogen peroxide, peroxodisulfuric acid, and ozone. Accordingly, throughout the electrochemical oxidation of wastewater, the impurities removal principally occurred due to indirect oxidation, utilizing chlorine/hypochlorite produced by anodic oxidation of chlorine that existing or being added in the aqueous. A chain of reactions that involve chlorine/hypochlorite indirect oxidation are presented in Eqs. 3-10.

Reactions in a cathode environment,

$$2H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) \quad (3)$$

$$8H^+(aq) + 8\,e^- \longrightarrow 4H2(g) \quad (4)$$

Equation (3) is a cathodic reaction occurring during the electrolysis of water. As hydroxyl ions (OH_) are released during this reaction, the pH increases. In addition, the observation of vigorous bubbling on the cathode indicates hydrogen production, according to Equation (3) and (4).

Reactions in an anode environment,

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \quad (5)$$

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^- \quad (6)$$

Our study showed that if an iron rod is used as anode material, oxidation gasses, such as oxygen, carbon dioxide, and chlorine are not bubbled on the surface of the anodic electrode. Instead, there is formation of green flocks in the aquatic media, indicating its conversion to Fe(OH)2. These results show that Equation (6) forms despite Equation (5) at the anode area.

Due to OH_ ion concentrations increasing near the cathode, the pH of the medium begins rising. Meanwhile, the anode melts and dissolves ferrous ions into solution as shown in the following equation:

$$Fe^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Fe(OH)_2(s) \quad (7)$$

$$2Fe^{2+} + 1/2\,O_2 + 5H_2O(l) \longrightarrow 2Fe(OH)_3 + 4H^+(aq) \quad (8)$$

After melting of the iron in the presence of hydroxyl alkalinity, Fe (OH)2 and Fe(OH)3 flocks develop in the medium [given with Equation 7)]. Oxidation developing over time affects the formation of Fe(OH)3 flocks [given with Equation (8)]. Besides, if oxidant forms such as H2O2 add into the electrolysis cell, Fe2_ ions convert to Fe3_ ions [Equation (9)], and following brownish Fe(OH)3 flocks form [Equation (10)]. Hydroxyl radical in Equation (9) does not put forward an apparent Fenton's oxidation due to dominating high pH.

$$Fe^{2+}(aq) + H_2O_2(aq) \longrightarrow Fe^{3+}(aq) + OH + OH^-(aq) \quad (9)$$

$$Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s) \quad (10)$$

The hydroxide (OH^-) generated in bulk solution (Eqs. 9 and 10) is a strong oxidizing agent that can oxidize aqueous organic substances. In addition to the common oxidants that can be electrochemically produced, metal catalytic mediators (Ag+2, Co+3, Fe+3, etc.) are also employed for the generation of hydroxyl radicals, as seen in the electro-Fenton system. Nevertheless, the use of metal ions may result in the treated effluent to be more toxic than that its initial state. Therefore, the system of this kind needs a separation step to recover the metallic species, leading to the unfavorable intricate treatment process.

III. RESULTS AND COMPARISON

This study is mainly aimed to determine basic operation parameters of treatment of wastewaters. Therefore, COD, SS and nutrient were investigated in terms of applied voltage and retention time with same electrode material Iron (Fe-Fe), in order to determine optimum operating conditions for maximum removal efficiency of COD, SS and nutrient. For accurate results the tests were conducted for two times, as the results shown bellow in the form of graph.

Removal efficiency (RE) equation is shown below:

$$100\ RE\ \%\ A\ B\ x\ A = \quad (11)$$

Where A is initial COD and B is current result.

A. Changes in odour and colour

The order of the wastewater before the treatment was strong and nauseating but after the treatment in every time interval got better in smell.

Also the colour of the wastewater was like grey before the treatment was done but after the treatment the colour was nearly transperant as shown in the figure 5.

Fig. 4: Wastewater before treatment and the treated water

B. Changes on pH and temperature

The changes during process operation are also important as much as startup parameters. The changes in pH, temperature and electrical conductivity were measured in 15, 30, 60, 120 minutes.

The initial pH of the wastewater was 8.6. But as a result of reactions taking place in the reactor, pH values were measured for purpose of control. pH values were change between 7.5 to 7.8 as shown in Figure 6 and Figure 7. For both voltage values, pH gets lower than initial pH with respect to the time.

Although there is no negative effect of temperature, some studies about effect of temperature on electrochemical treatment methods show that amount of removal efficiency increase as the temperature increases.

Figure 5 and Figure 6 show that temperature increases electrodes as time passes.

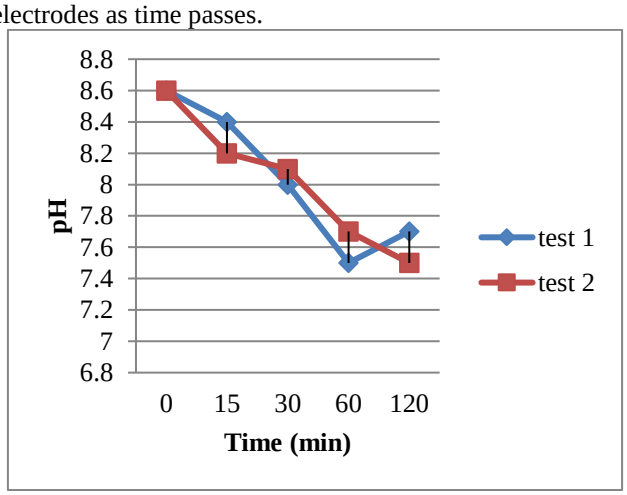

Fig. 5: Change in pH of wastewater for 7.5V

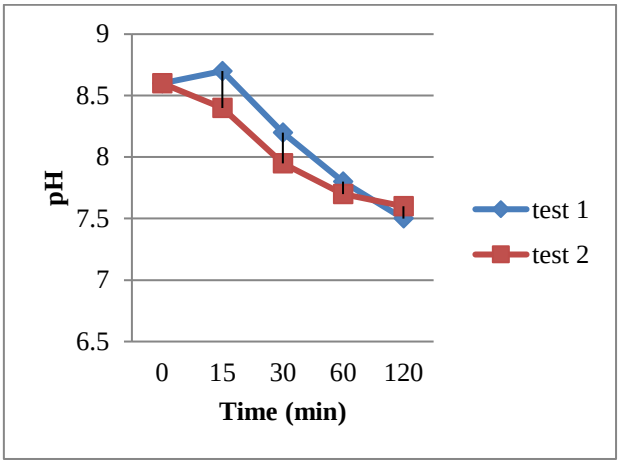

Fig. 6: Change in pH of wastewater for 15V

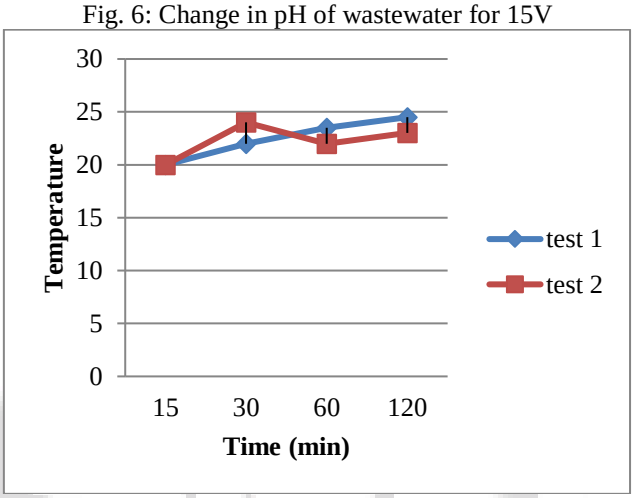

Fig. 7: Change in temperature on electrodes for 7.5V

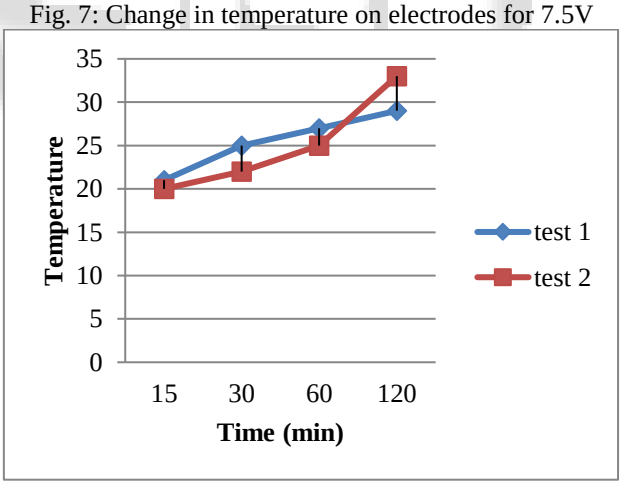

Fig. 8: Change in temperature on electrodes for 15V

C. Chemical oxygen demand removal

To optimize the electrocoagulation operating conditions, the COD was measured as a function of treatment time. The reduction of the COD as a function of treatment time under conditions of electrical conductivity 5 mS/cm pH 7.7 and reactor voltage 7.5V is shown in Figure 9.

There is a rapid increase in the COD for the first 15 min of treatment then a limiting value is reached with no further improvement.

To determine effect of voltage, reactor was operated at 15V while other parameters were the same. The results of this operation were given in Figure 10.

When we examine the literature and check other studies (Anglada *et al*. 2009), COD removal efficiencies are almost the same for domestic wastewater if we compare about the same conditions like time intervals and iron electrode but results show us that removal efficiency gets higher enough with iron electrode when the reaction time is increased 60 to 120 minutes.

The removal efficiency was highly desired values in 15 minutes whereas removal efficiency results changes due to inorganic pollution in 30, 60 and 120 minutes retention time.

The effect of applied voltage is an important parameter for organic matter removal in EO process and also causes undesirable decomposition of the electrode. As in Figure 9 and Figure 10, 7.5 voltage is provide sufficient energy to ionize metal ions which has better removal capacity than 15 V.

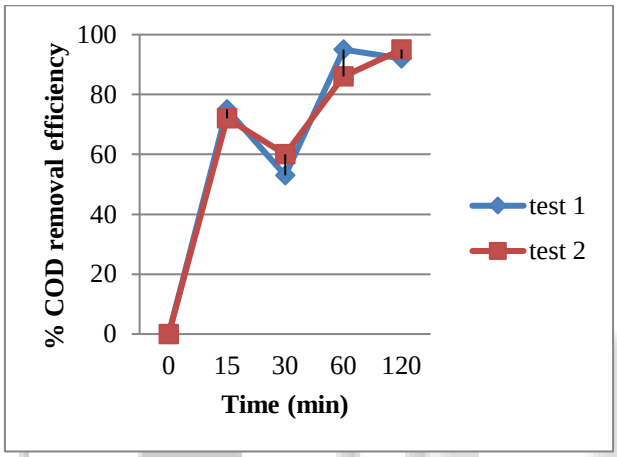

Fig. 9: COD removal efficiency at 7.5V

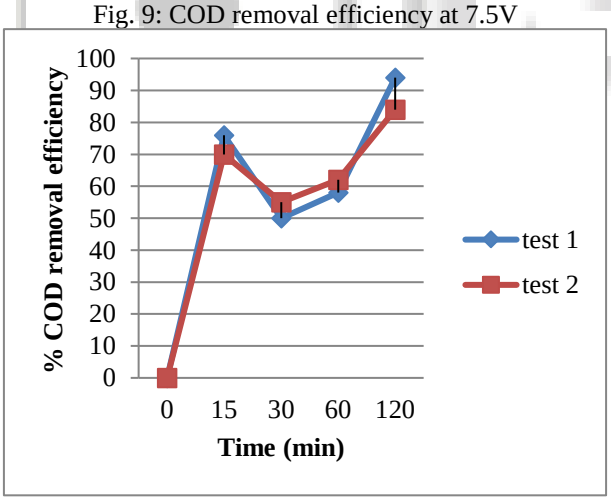

Fig. 10: COD removal efficiency at 15V

D. Suspended solids removal

The relationship between the SS removal efficiency and retention time for the electrodes used is depicted in Figure 11 and Figure 12 under 7.5V and 15 V operation voltage. The figure shows that as the contact time increased from 15 to 120 min, concentration of suspended solids varies from 40 mg/L to 2000 mg/L for both voltages of 7.5V and 15V as a function of time.

In 15 voltage operation conditions, iron ions were over dissolved in reactors and cause increase in dissolved solids amount after 60 min. These results show that the applied voltage is high enough to cause over dissolved metal ions which effect suspended solid results as seen at Figure 12. These suspended solid results were under limit of Bureau of Indian Standards (BIS).

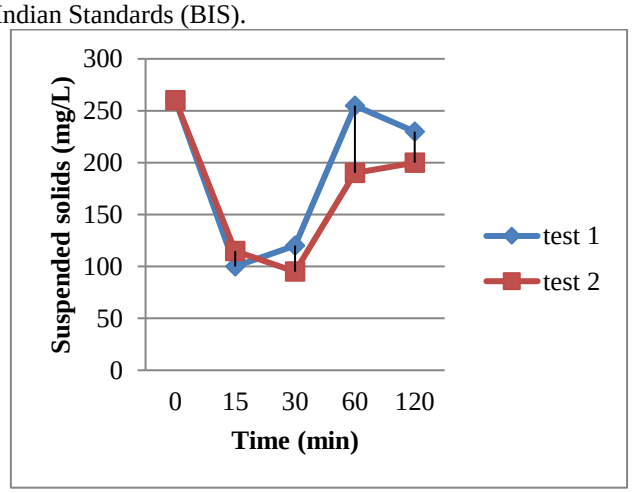

Fig. 11: Suspended solids removal at 7.5V

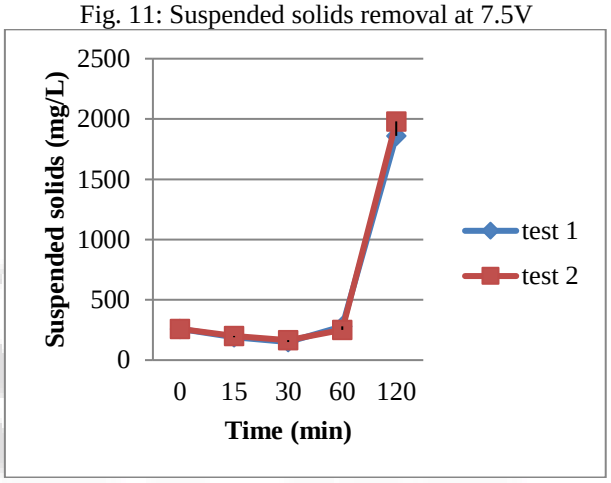

Fig. 12: Suspended solids removal at 15V

E. Nutrient removal

Nitrogen in domestic wastewater exists as ammonium or organic form, both may be solid or dissolved. Only 30% of total nitrogen is removable with conventional biological treatment methods (Chen and Hung 2007).

%90 of total phosphorus is dissolved in wastewaters. Removal of dissolved phosphorus is quite difficult with the conventional biological treatment methods (Nagata *et al.* 2006).

Due to this facts, nutrient removal efficiency was investigated during this research. Total nitrate, nitrite and phosphorus concentrations were analyzed after 120 minutes reaction time under 7.5V and 15V voltage in reactor as shown in Table 1 and Table 2.

In 15V process operation, iron electrodes over dissolved after 120 minutes reaction time and react with chemicals during analysis. These results show that 120 minutes reaction time is more than it should be.

Total phosphorus, nitrate and nitrite removal in domestic wastewater after 120 minutes,for 7.5V and 15V electrochemical process shown in table 1 and table 2 respectively.

Sample	Total P (mg/l)	NO3 (mg/l)	NO2 (mg/l)
Raw Wastewater	5.3	1.1	0.24
Treated water	1.65	0.3	0.67

Table 1:

Sample	Total P (mg/l)	NO3 (mg/l)	NO2 (mg/l)
Raw Wastewater	5.3	1.1	0.24
Treated water	1.42	0.23	0.56

Table 2:

IV. CONCLUSION

This study aimed determines applied voltage and reaction time for removal of colour, odour, COD, SS and nutrients in domestic wastewater. Domestic wastewater was succesfully treated by electrochemical process in a very short time (15 min.). These results show that iron was affective at removing COD and nutrients with 15 minutes reaction time however need more sedimentation time to provide desired values at suspended solids removal.

When the results are compared with the domestic wastewater discharge standards in India, It seems that COD, SS and pH are parameters which to be controlled. It is seen that the data obtained as a result of the study provide the desired conditions.

Based on these results, electrochemical treatment methods are effective method of treatability of domestic wastewater and also the results obtained from the electrode seem to be promising in terms of realizing other studies.

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