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Research Article

Efficacy of Fenton Based Electrochemical Treatment in Rotating Disc Electrode Reactor for the Removal of Total Organic Carbon (TOC) from Pharmaceutical Wastewater through Different Modes

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ABSTRACT

The pharmaceutical effluent was remediated by employing batch and Batch Recirculation (BR) of fenton, Electro Oxidation (EO) and Electro Fenton (EF) processes to detach the organic compounds from the pharmaceutical wastewater using rotating disc reactor. Synthetic wastewater was modelled with Total Organic Carbon (TOC) of 298 mg/L. EF process showed enhanced results which could be attributed to the generation of large amount of hydroxyl radicals by which the generation of ferrous ions by the reduction of ferric ions reacted with hydrogen peroxide along with the anode. The optimum conditions for EF process were Fe^{2+}=0.2 g/L, H_2O_2=0.9 mM, Current Density (CD)=15 mA/cm^2, rpm=500 rpm, pH=3.5 and Fe^{2+}=0.2 g/L, H_2O_2=0.9 mM, CD=10 mM/cm^2, pH=3.5, rpm=500, flow rate=60 L/h for batch and for BR mode. This study shows outstanding results for EF process than Electro Oxidation (EO) and fenton process for the pharmaceutical effluent treatment.

Keywords: Fenton; Electrofenton; Electro oxidation; Pharmaceutical wastewater; Total organic carbon; Batch recirculation

INTRODUCTION

The wastewater generated from pharmaceutical industries has strenuous color and bad odour which is harmful and poisonous to the living beings. Pharmaceutical chemicals make adverse impact on the human kind and ecosystem [1]. The conventional methods like biological and chemical methods are well appropriated only for low molecular weight organic pollutants. Furthermore, these conventional methods become unproductive for wastewater containing high molecular refractory compounds (resistant for biological treatment) and organic pollutants. Advanced Oxidation Process (AOP) has been considered to overcome this problem [2]. In this scenario, fenton process is highly promising due to its high organic removal percentage when compared to other process. The enhanced efficiency could be due to the generation of highly reactive hydroxyl radicals (*OH) [3]. Hydroxyl radicals (*OH) are generated on the anode surface and represented in the equations 1 to 4 [4].

$$Fe^{2+} + H_2O_2 \ldots\ldots\ldots > Fe^{3+} + OH^- + {}^*OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \ldots\ldots\ldots > Fe^{2+} + OOH^- + H^+ \quad (2)$$

The two major limitations of conventional Fenton processes are the transportation risk associated with H_2O_2 that leads to the reactive activity loss and production of sludge. This can be knobbed by a tailored process called the electro fenton process [5]. EF has several advantages such as high hydroxyl generation rate and low time consumption when compared to fenton and electro oxidation process.

$$RuO_x - TiO_x + H_2O \ldots\ldots\ldots > RuO_x - TiO_x({}^*OH) + H^+ + e^- \quad (3)$$

$$RuO_x - TiO_x({}^*OH) + Cl^- \ldots\ldots\ldots > RuO_x - TiO_x({}^*OCl) + H^+ + 2e^- \quad (4)$$

Electrochemical science plays a significant role in offering eco-friendly technology for chemical synthesis, separations, fuel cells etc. The uniqueness of electrochemical technology is adaptability, ecofriendly, higher energy efficiency and low cost

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[6]. Electrochemical technology has been contributing towards zero discharge in chemical process industries by means of providing advanced treatment process such as electro coagulation, EO, electro deposition etc. [7].

Different electrochemical reactors are used in the chemical process industries for various applications from small scale to large scale commercial reactors. In general, electrochemical reactors are classified based on their electrode configuration and geometry. The selection and design of an appropriate reactor is the foremost criteria in electrochemical process with which the geometry of the reactor plays a vital role in the selectivity and yield of the process. Further, electrochemical reactors are classified based on flow pattern or mode of electrical network. Rotating Disc Electrochemical reactor (RDE) has received considerable attention owing to its facile operation. Rotating motion is being imparted to the electrode rather than a separate agitation assembly. Spinning disc drags the solution and drifts away from the core of the electrode owing to the centrifugal and centripetal force. The bulk solution replenish the transfer of solution to surface of the electrode in each and every single rotation. This results in improved mass transportation which could be owing by the forced convection and angular velocity of the electrode [8].

The aim of the current research work is to remediate the pharmaceutical wastewater in order to meet the effluent standards of Tamil Nadu Pollution Control Board (TNPCB), where total organic carbon is less than 50 mg/L, by the fenton, EO and EF process in batch and batch recirculation process through a well-designed novel reactor to analyze the capability with the conventional process. The energy consumption was estimated along with the kinetic studies in order to evaluate the reactor for scale up studies.

MATERIALS AND METHODS

Synthetic wastewater was prepared from tablet waste and the characteristics are presented in Table 1. The effluent treatment was carried out in the Rotating Disc Reactor (RDR) as shown in Figure 2. The RDR mainly consists of plexiglass cylindrical reactor with the volume of 2.75 liters, diameter and height of 100 mm and 500 mm respectively as depicted in Figure 1a. The electrodes mounted in the reactor rotate with stainless steel cathode rings (5) of 2 mm thick (outer dia. 50 mm, inner dia. 8 mm) and static anode rings (5 nos.) of outer diameter 85 mm, 15 mm thickness and inner diameter of 65 mm with a gap of 5 mm which are located vertically and parallel to each other. The cathode is held and attached by a bearing and holder at the bottom and top of the vessel. The rotational speed was measured by a digital tachometer. The anode rod is mounted at the centre connected to the power supply and attached with the anode rings of 365 cm^2 surface area. The experimental setup has provisions to operate the desired mode by adjusting the valves.

Table 1: Initial characteristics of pharmaceutical effluent.

S. No	Parameters	Values
1	pH	6.9
2	Total Solids (TS)	2490 mgL^{-1}
3	Total Dissolved Solids (TDS)	2410 mgL^{-1}
4	Total Suspended Solids (TSS)	80 mgL^{-1}
5	Phenol content	25 mgL^{-1}
6	Ammonical nitrogen content	1075 mgL^{-1}
7	Chloride content	425 mgL^{-1}
8	Biological Oxygen Demand (BOD)	260 mgL^{-1}
9	Oil content	15 mgL^{-1}
10	Total Organic Carbon (TOC)	298 mgL^{-1}

The observed peaks in FTIR analysis as shown in Figure 1b at 1654 cm^{-1} and 1700 cm^{-1} are due to the CO stretching in enols and cis-cinnamic acid. These are imperative ingredients for anaesthetic and anti-allergic pharmaceutical formulations. The UV spectra shown in the inset Figure 1b inset was increased steadily with decreasing wavelength in the visible range, which reveals the influence of particles. The effluent with turbidity could be due to the presence of dissolved organic substances as inferred from the finger print at 280 mm.

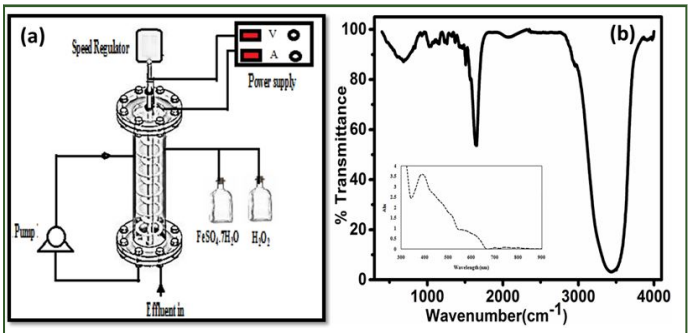

Figure 1: a) Schematic representation of rotating disc electrochemical reactor; b) FTIR analysis of raw effluent, inset shows UV analysis of raw effluent.

Analytical methods

FTIR (PerkinElmer spectrum RX11.60) and UV spectrophotometer (shimadzu) were employed to study the functional groups present in the untreated and treated wastewater. Total Organic Carbon (TOC) was analyzed by UV chemical oxidation.

RESULTS AND DISCUSSION

Fenton process in batch and recirculation mode

This method is non-selective and oxidizes the organic compounds efficiently by means of hydroxyl radicals [9]. The parameters such as rotational speed, H_2O_2, ferrous sulphate concentration and flow rate were optimized in the Fenton process as shown in Figure 2A. The rotational speed was varied between 0, 250, 500, 750 and 1000 rpm. The mixing rate enhanced with increase in the rotational speed as a result, uniform consumption of fenton reagent was achieved in order to remove the organic particles efficiently. The rotational speed of 500 rpm was found to be optimum as the maximum removal of organic compounds was achieved in 4 hours for batch and BR mode. It is inferred that there is only marginal improvement in the removal percentage with increase in the rotational speed. Similarly, H_2O_2 and ferrous sulphate was varied such as 0, 0.3, 0.6, 0.9, 1.2, 1.5 mM and 0, 0.05, 0.1, 0.15, 0.2, 0.25 gL^{-1}.The optimum conditions were observed at 0.9 mM and 0.2 gL^{-1}. The flow rate was adjusted to bring an axial and radial dispersion in the reactor in order to achieve efficient organic pollutant removal in BR mode. The optimum flow rate was 60 L/h due to its high removal efficiency and also increase in flow rate increase in energy loss. The pH was not varied because the degradation can takes place effectively in acidic pH. The results in Figure 3a shows TOC values and % TOC removal at 4 hr time period in batch and BR mode were 94% and 95% of TOC removal respectively. This implied that fenton process can consume more time like conventional process in the removal of organic compound [10].

Electro oxidation in batch and recirculation mode

The reactor was operated effectively by covering the wide range of significant parameters to find the optimum conditions in electro oxidation process. So, pH was varied as 3,5,7 and 10 for both batch and BR mode as shown in Figure 2A. The maximum organic removal was observed at pH 3.5 and 7 for batch and BR modes, this is due to the increase in chlorine evolution which leads to the degradation of pollutants by indirect oxidation. The cathode rotational speed varied from 0, 250, 500, 750 and 1000 rpm for batch and BR mode and implied that increase in rotational speed increases the turbulence which in turn increases the mass transfer coefficient. The optimum speed was observed as 500 rpm based on energy considerations. CD was varied from 5, 10, 15 and 20 mA/cm^2 and the optimum CD was found to be 15 and 10 mA/cm^2 for batch and BR mode because increase in CD increases the temperature inside the reactor.

The flow rate was adjusted for BR mode from 15, 30, 60 and 120 L/h and the organic removal was maximum at 60 L/h and 120 L/h because of increase in mass transfer rate on the surface of the anode. Although, 60 L/h was chosen as optimum for EO process due to an energy conservation. The optimized results for batch and BR modes were pH 7, cathode rotational speed 500 rpm, CD 15 and 10 mA/cm^2 and flow rate 60 L/h with the organic removal efficiency of 92.3 %. The % TOC removal for batch and BR mode in 2 hours which shows significant effect when compared to conventional Fenton process without any formation of sludge is shown in Figure 2A.

Electro fenton in batch and recirculation mode

Fenton process was integrated with electro oxidation to generate high amount of hydroxyl radicals to remove organic pollutants effectively in this study. CD was varied from 5, 10, 15 and 20 mA/cm^2. The optimized dosage of $FeSO_4.7H_2O_2$ and H_2O_2 were 200 mg/L and 0.9 mM exhibited in Figures 2B. The removal efficiency were 92% and 96% at pH 3.5, cathode rotational speed 500 rpm, CD 15 and 10 mA/cm^2, H_2O_2 0.9 mM and $FeSO_47H_2O_2$ was 200 mg/L and flow rate 60 L/h for batch and BR modes respectively in 1 hour. The attained results revealed that electro fenton process is most promising and suitable for pharmaceutical wastewater treatment in scale up process with lower energy consumption.

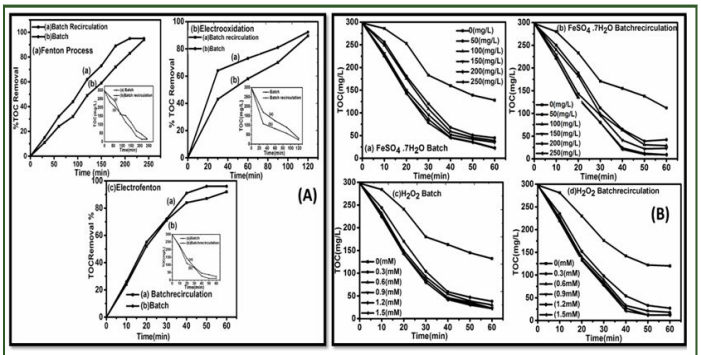

Figure 2: (A) % TOC Removal of a) Fenton process; b) Electro oxidation process and; c) Electro fenton process, inset shows TOC removal. (B) Electro fenton process optimization of a) $FeSO_4.7H_2O_2$ batch; b) $FeSO_4.7H_2O$ batch recirculation; c) H_2O_2 batch and; d) H_2O_2 batch recirculation.

Specific Energy Consumption (SEC) and cost analysis

The performance of electro oxidation is characterized by its consumption of energy in terms of TOC removed (kWh/kg). It plays a very important role as it confines the commercial applicability of the electrochemical process. It is described as

$$\text{Power consumption } (E_1, \text{kWh/kg COD}) = \frac{VIt}{3600 \times 10^3} \times \frac{1000}{\Delta C \times V_e \times 10^{-6}} \quad (5)$$

Where 'V' the applied voltage in volts, 'I' the current in milliampere,'t' the electrolysis time in hours. 'ΔC' the difference in TOC expressed in mg/L, 'Ve' the volume of effluent treated in liters. Table 2 shows energy consumption and energy cost of EO and EF process. The energy consumption EF is very low compared to EO for the removal of organics because it requires very shorter time. The energy cost (kWh m^{-3}) for the removal of TOC for each process was estimated by applying the below equation

$$\text{Energy Cost} = \frac{V\ I\ t\ TOC_{in}}{Vol * \Delta TOC} \quad (6)$$

Where 'V' Voltage (V), 'I' applied current (A), 't' electrolysis time (h) and 'Vol' volume of solution (L).

SEC and energy cost for electro fenton BR mode was 50 % lesser than electro oxidation BR mode which was due to the integrated and lesser time taken for electrolysis as shown in Figure 3b. The energy consumption was less when compared to some integrated Fenton process as UV illumination consumes more energy when compared to EO. The cost is considerably less when related with other Fenton based research works and is depicted in Table 2. Therefore, EO integrated Fenton process is feasible for all type of effluent treatment with high organic loading and is appropriate for scale up studies as well.

Table 2: Specific energy consumption and cost analysis.

S. No	Process and modes	SEC (KWh/Kg TOC)	Energy cost (kWh/m^3)
1	**Electro oxidation**		
	Batch	41	12.23
	Batch recirculation	22	6.48
2	**Electro fenton**		
	Batch	20	6
	Batch recirculation	11	3.099

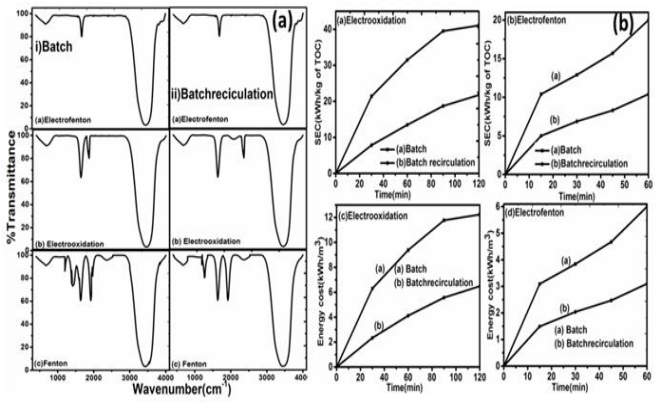

Figure 3: FTIR analysis of (A) Batch process and; a) Electro fenton; b) Electro oxidation and; c) Fenton; b) Specific energy consumption of (B) Batch recirculation process for; a) Electro oxidation; b) Electro fenton energy cost of; c) Electro oxidation and; d) Electro fenton process.

Instrumental analysis

The presence of alkyne groups at 2070 cm-1, alkenes at 1653 cm-1, ketone groups at 1508 cm-1 and amine groups at 3976 cm-1 in Figure 1b. The bands that are produced by several contaminants, existing enols, alkynes and alcohol functional groups have been found to disappear after treatment and further, confirm that the degradation was by oxidation. Thetreated water in batch and BR mode by fenton, EO and EF for one hour operating time is shown in Figures 3A.

UV fingerprints of treated and untreated water by fenton, EO and EF process in batch and BR mode is shown in Figures 4 A. The decrease in absorbance at 380 nm shows that the organics were effectively removed by AOP. EF process successfully removed the maximum amount of pollutants in both modes within one hour. The slight decrease in the peak intensity signify the decolourization and TOC decrease. The attained results were in good agreement with the FT-IR spectral results.

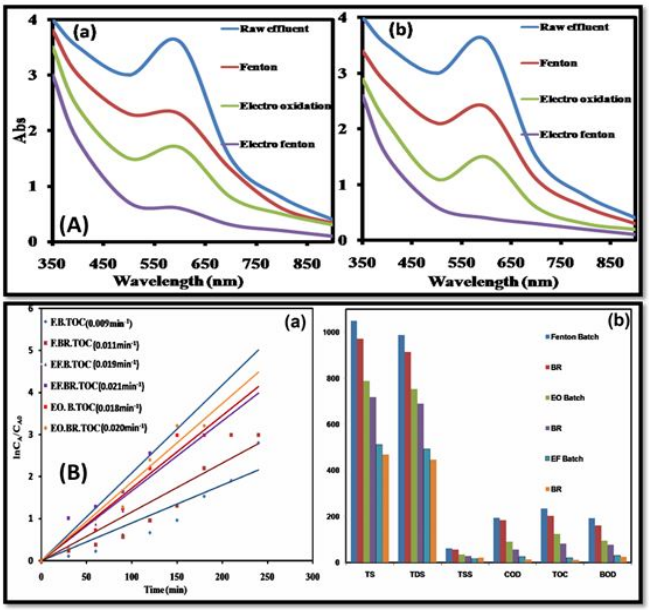

Figure 4: (A) UV analysis of all the three process in a) Batch and; b) Batch recirculation. (B) a) Kinetics and; b) Performance analysis of all the three process in batch and recirculation mode for one hour treatment.

Kinetics and performance analysis

Kinetics of all the three processes of fenton, EO and EF in batch and BR mode with rate constants of 0.009, 0.0011, 0.018.0.20, 0.019 and 0.021 min^{-1}. The rate constant for EF batch recirculation was high which assures the higher organic removal. The kinetics also revealed that integration of both EO and fenton process elevated the reaction rate constant higher as compared to the individual process. The performance of all the three process were determined under the best operating condition for one hour treatment time period. It was observed from Figure 4B that at one hour treatment time electro fenton shows maximum organic removal and the pH was shifted from acidic condition to slightly neutral condition. This could be due to the complete mineralization of organics whereas in electro oxidation, there is no significant change as the process was carried out at neutral pH. Perhaps, it needs extra electrolysis time for the removal of organics. The performance of the fenton process is determined and it shows longer time period for complete mineralization of organics.

BR mode was found to be better when compared to batch mode in terms of TOC removal at various operating parameters for all the three processes is shown in Figure 4B. The pollutant removal increased significantly with increase in the recirculation at an optimum condition of 60 lph. The reduction in flow rate limits the process by the reduction in transfer coefficients and an increase in the reactor volume causes greater capital investment. Thus, the recycle system of operation can be concluded as better performance among the conventional reactor configurations studied. The percentage TOC, COD and BOD removal for batch and batch recirculation mode in optimum operating conditions for all three processes as shown in Figure 4. It is concluded from the results that EF process showed maximum removal of pollutants at a period of one hour treatment time.

CONCLUSION

EF process using RDR was significantly effective for a shorter period of treatment time when compared to the conventional Fenton process. The % TOC removal efficiency for fenton, EO and EF processes in batch and BR modes were 94, 90, 92 and 95, 92 and 96% in 4, 2 and 1 hour respectively. EO and EF process have appreciable advantages such as shorter operating time, higher removal efficiency of organics which was ascertained by UV, FT-IR analysis and kinetic studies. Thus, EF is more feasible as Fe^{2+} ions prevent the peroxide overflow by means of continuous generation of hydroxyl radicals and remarkable advantage of shorter reaction time with high removal efficiency that satisfy the effluent standards of TOC despite high cost of EF when compared with conventional fenton method.

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