COD REMOVAL FROM SYNTHETIC WASTEWATER CONTAINING AZITHROMYCIN USING FLUIDIZED BED FENTON PROCESS

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ABSTRACT

Advanced oxidation process (AOPs) are low cost, high efficiency and ecofriendly method in the degration of toxic pollutants in waste water using hydroxyl radical for oxidation. The hydroxyl radical has a high oxidation potential and is able to react with practically all classes of organic compounds, resulting in complete mineralization of these compounds, that is, the formation of carbon dioxide, water and inorganic salts, or their conversion into less aggressive products. Some of the most popular AOPs are TiO_2 photocatalysis advanced ozonolysis, electrochemical oxidation , Fenton's reaction and Fenton/ultrasonic reaction. Among different AOPs Fenton process is found to be effective in degrading the organic and inorganic contaminants present in water. One of the main disadvantage of Fenton process is sludge formation. It requires further treatment before disposal. The Fluidized Bed Fenton(FBF) process uses carriers that reduces the production of sludge by crystalizing the pollutant onto the carrier surface. In this study, the Chemical oxygen demand (COD) removal from synthetic wastewater by FBF process has been investigated. The synthetic wastewater used for conducting the experiments in this study was produced by dissolving 0.5 g Azithromycin in 1000 ml distilled water.The chemical formula of Azithromycin antibiotic is $C_{38}H_{69}NO_{13}$.The various parameters affecting fluidized bed Fenton process are pH,H_2O_2 concentration,Fe ion concentration. Another factor affecting fluidized bed Fenton process are the carriers. Carriers are solid particles provide the surface area for the crystallization of the iron sludge, which will remain in the solid phase as iron oxide. The presence of the solid particles promotes the iron onto the carrier surface. Thus, the crystallization competes with the floccules and sludge formation of iron hydroxides. In this study Aluminium dioxide is the carrier used for fluidization. The effect of pH, H_2O_2concentration, Fe^{2+} concentration for FBF process is studied. A removal efficiency of 92% was achieved after 1hr of fluidization under optimum condition of pH = 4, $[Fe^{2+}]$=10mM, $[H_2O_2]$=20mM.

Keywords : - *AOP,Fluidized bed Fenton process , COD*

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1. INTRODUCTION

Pharmaceutical waste items are among the most intricate and lethal mechanical squanders. Immense measures of pharmaceutical are utilized every day for well being. The pharmaceutical industries frequently produces medium to high harmful wastewater which influences the quality and quantity of effluent. The grouping of metabolically dynamic and dangerous chemicals which is difficult to degrade is high. Mass pharmaceuticals are fabricated utilizing an assortment of procedures including synthetic union, maturation, extraction and other complex techniques by Elmolla et al [9]. For the most part, just a small amount of the measure of anti-infection agents is changed in the body and the rest are discharged in their local frame or as metabolites done by Elmolla and Chaudhuri [11]. All around, only a little measure of the antibiotics is changed in the body and the rest are released as metabolites. A variety of pharmaceuticals have been reported to be present in the effluent of sewage treatment plants (STPs),indicating their poor biodegradability in municipal sewage and STPs by Kulik et al [13]. They may enter the aquatic system (surface water and groundwater) or soil and can prompt to the improvement of resistance of microbial pathogens to anti-infection agents. Hence, biological treatment of waste water is insufficient in the case of antibiotics; therefore, a pretreatment process is often required prior to discharge into the sewage treatment system which is given by Elmolla and Chaudhuri, [17].

Azithromycin is an individual from the macrolide anti-infection agents. Azithromycin is a white powder which is fundamentally the same as erythromycin however is more viable in decimating Gram-negative microscopic organisms, particularly Haemophilus influenzae as by Chisholm et al., [18]. Since Azithromycin exhibits low dissolvability in water, it can be expelled utilizing some basic physical treatment forms, including coagulation and flocculation. But these processes are largely ineffective in degrading dissolved organic contaminants by Ternes et al., [19] and Westerhoff et al.,[20]. Because drugs are toxic to microbes in biological treatment and are difficult tobe degraded using biological processes, the use of new technologies to reduce pharmaceuticals in waste water is Since medications are lethal to organisms in natural treatment and are hard to be debased utilizing natural procedures, the utilization of new innovations to decrease pharmaceuticals in wastewater is fundamental.

Advanced oxidation processes (AOPs) are applied frequently for the oxidation of industrial sewage containing organic and toxic materials were given by Ahmad Reza Yazdanbakhsh et al [21]. These processes are based on the production of hydroxyl radicals which demonstrate great efficacy in breaking down organic material by Arsene et al., [25].The efficacy of the various AOPs depends both on the rate of the generation of the hydroxyl radical (•OH) and the amount of contact between the hydroxyl radical and the organic compound by Zaharia et al., [28]. The radical •OH is responsible for the destruction of organic pollutants present in water and mineralize them ultimately to CO_2 and H_2O.

Among different Advanced Oxidation Processes (AOPs), the Fenton process can be used as a alternative to treat non-biodegradable wastewater. Since this response is simple and does not create sludge, it has been broadly used to degrade toxins. The hydroxyl radical is an intense oxidant that can quickly and non-specifically oxidize natural contaminants into carbon dioxide and water so it can degrade contaminations adequately. The most effective AOP is the Fenton's process, which comprises of the reaction betweenH_2O_2 and Fe^{2+} in an acidic media for create free •OH.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe(OH)^{2+} + \bullet OH$$

Hydrogen peroxide is a green chemical that abandons O_2 and water as byproducts. It is utilized as disinfectant in medicinal and modern applications and as an oxidant in item blend and wastewater treatment. Be that as it may, the immediate treatment of wastewater with Hydrogen peroxide is constrained by its low oxidation control, since it can just assault diminished sulfur mixes, cyanides, chloride particle and certain organics, for example, aldehydes, formic corrosive and some nitro-natural and sulpho-natural mixes. Because of this reason, $H_2O_2$is enacted in acidic effluents with Fe^{2+} particle as catalyst (Fenton's reagent) to yield homogenous •OH as a solid oxidant of organics. Despite the fact that Fenton procedure has been fruitful in the degradation of the natural contaminants present in wastewater. The formation of ferric hydroxide sludge $Fe(OH)_3$ is consider to be a detriment of this procedure which requires further treatment prior to disposal. One of the contrasting options to manage this issue is the utilization of fluidized-bed Fenton reactor.

A fluidized bed is a bed of strong particles with a surge of gas or fluid going upward through the particles at a rate sufficiently incredible to set them in movement. As the fluid or gas goes through the molecule bed, it grants one of kind properties to the bed. For instance, the bed acts as a fluid. It is conceivable to spread wave movement, which makes the potential for enhanced blending. The carriers in fluidized-bed Fenton reactor can start the iron precipitation as well as crystallization process; hence, the generation of sludge is diminished.

There are several reactions occurring in fluidized-bed Fenton reactor including: Homogeneous chemical oxidation (H_2O_2/Fe^{2+}), heterogeneous chemical oxidation (H_2O_2/iron oxide), fluidized-bed crystallization, and reductive dissolution of iron oxides. The fluidized-bed Fenton process is influenced by solution pH, initial ferrous (Fe^{2+}) and hydrogen peroxide (H_2O_2) concentrations by using a single carrier. The goals of the review is to identify and set the ideal operating conditions that best suits the wastewater that are being treated to achieve high degradation efficiency.

2. METHODOLOGY

2.1.Materials and methods

The synthetic wastewater used for conducting the experiments in this study was produced by dissolving 0.5 g Azithromycin in 1000 ml distilled water.The chemical formula of Azithromycin antibiotic is $C_{38}H_{69}NO_{13}$. The COD measurements were performed by the closed reflux titrimetric method [28]. The COD of sample is found to be 300mg/L. it indicates that 500 mg/L of Azithromycin is equivalent to 300 mg/L COD which means 1mg/L of Azithromycin is equivalent to 0.6 mg/L COD. All the chemical substances used as a part of analysis,heptahydrated ferrous sulfate, and sulphuric acid were of reagent grade. Sulfuric acid (96%) and NaOH (98%) was used to adjust the initial solution pH. All of the solutions were prepared from the distilled water and the experiments were conducted at room temperature. Aluminum dioxide was the carrier used in this study. The pH measurement was performed using a pH meter.

2.2. Fluidized bed Fentonexperimental setup

The fluidized bed Fenton process is carried out in a 1.35L acrylic tube of 4.2 cm diameter and 133 cm heightas shown in fig-1. The reactor consists of inlet, outlet, and recirculation compartments. To support the carrier materialglass beads of size 2 mm are used.Aluminium dioxide(Al_2O_3) was used as carrier with diameters in the range of 0.5-2 mm.

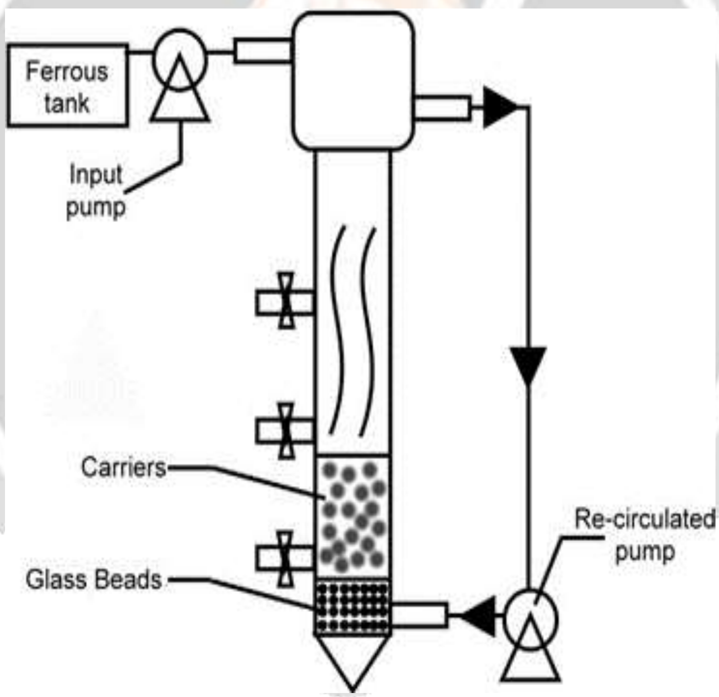

Fig-1: The fluidized bed reactor

2.3. Fluidized bed Fenton experiment

In this study, the glass beads having a diameter of 2mmare added first to the acrylic tube reactor. It is followed by the addition of 50g Al_2O_3 carriers. About 0.5 litre of the synthetic sample whose pH is adjusted by adding H_2SO_4 or NaOH is then introduced into the reactor. The pump was turned on to suspend the carriers and mix the solution properly. Carriers were suspended by adjusting the internal circulation at 50% bed expansion. The reaction began when the H_2O_2 and ferrous sulphate (Fe^{2+}) solution was added.

3. RESULTS AND DISCUSSIONS

3.1. The Effect of Time on COD Removal Rate

The effect of reaction time on COD removal rate was tested to determine an experimental condition for further research. Chart-2 depicts a typical reaction curve showing the COD removal rate of the waste water sample changes with reaction time. By keeping H_2O_2 concentration as 15mM and Fe concentration as 6mM at a pH of 3, time is varied from 30 minutes to 90minutes.The results in table1 demonstrated that organic and inorganic compounds from the sample were rapidly degraded by fluidized bed Fenton process. Most recalcitrant compounds removal occurred after 1hour of fluidization. The COD removal rate was about 85%at 60minutes. Further increase in time upto 90 minutes the COD removal was found to be 86.7%. This shows a slight increase in COD removal. So 60 minutes is kept as the optimum time required for maximum COD removal. Based on this result, the reaction time for fluidized bed Fenton process was determined to be 60minutes for further experiments.

Table- 1: Optimization of time

Time(minutes)	COD Removal(%)
30	78
60	85
90	86.7

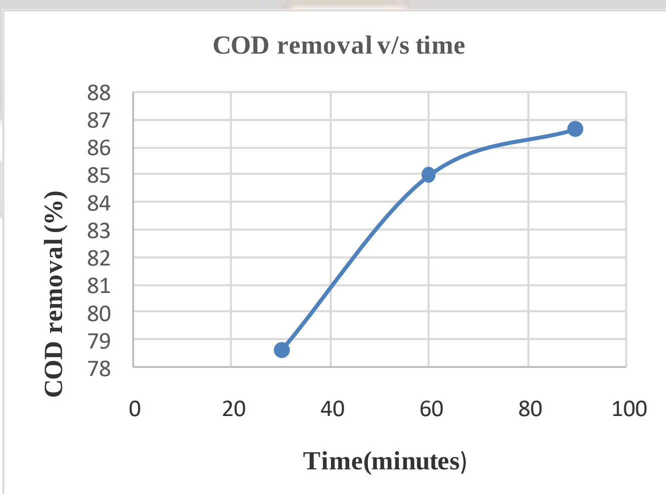

Chart- 2: Effect of Time on COD removal

3.2.The effect of solution pH

To determine the optimum pH for the Fluidized bed Fenton process, pH was varied from 2 to 12. Chart-3 shows that COD removal by the Fluidized bed Fenton process is affected by pH. As presented in chart-3, maximum COD removal was achieved at pH 4 by keeping constant H_2O_2 concentration as 30mM, Fe ion cocentration as 6mM for 1hour fluidization. When the pH is increasing substantial decrease in the efficiency of COD removal was observed shown in table 2. These phenomena could be explained by: 1- $Fe(OH)^{2+}$ is formed, which reacts more slowly with H_2O_2 and, therefore, thedegradation of H_2O_2 is slow, the scavenging effect of •OH by H^+ becomes significant at very low ranges of pH according to reaction 1 (the ions of H^+ may have inhibited the generation of hydroxyl and perhydroxyl radicals that were necessary to achieve the Fenton process) [23].

$$HO^* + H^+ + e^- \longrightarrow H_2O \quad (1)$$

At pH values higher than 7.0, a rapid decrease in COD removal was also observed. This occurs because in this pH range (alkaline solutions), Fe^{3+}ions begin to form flocs ($Fe(OH)_3$) precipitate and H_2O_2 is also unstable anddecomposes to give O_2 and H_2O and consequently loses its oxidizing properties [24].

Table- 2: Optimization of pH

pH	COD Removal (%)
2	86.6
4	94.6
5	93.4
7	88
12	84

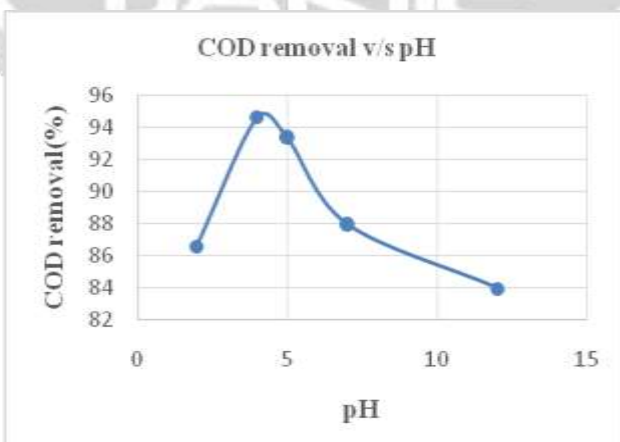

Chart -2: Effect of pH on COD removal

3.3. The effect of solution H_2O_2

The cost of H_2O_2 accounts for most of the cost of AOP processes, so the determination of optimum H_2O_2 amount is quite important in the AOP processes. The results of COD removal for the determination of optimum H_2O_2 concentration are presented in chart-3. To determine optimum H_2O_2 concentration, experiments were conducted by varying the amount of H_2O_2 from 10mM to 25mM(pH was fixed at 4 and the Fe dosage was 6mM). The result obtained is given in table.3.COD removal was high at a concentration of 20mM of H_2O_2. An increase in the concentration of H_2O_2 decreases the COD removal. Because at excessive amounts H_2O_2 acts as a scavenger of the •OH to produce the perhydroxyl radical (HO_2•) according to reaction 2 (HO_2• has much lower oxidation capacities than •OH) by Zhihui etal., [27].

$$H_2O_2 + HO^* \longrightarrow H_2O + HO_2^* \qquad (2)$$

In the optimum concentration of H_2O_2, ferrous ions completely oxidized; consequently, the generation of hydroxyl radicals increased by Elmolla and Chaudhuri [11]. Therefore, anH_2O_2 dosage of 20mM with a COD removal efficiency of 82.6%was chosen as the optimum dosage. The excess H_2O_2interferes with the measurement of COD, because theresidual amounts of H_2O_2consume $K_2Cr_2O_7$,according to reaction 3, leading to an increase in COD levels.

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \longrightarrow 2Cr^+ + 3O_2 + 7\,H_2O \qquad (3)$$

Table- 3: Optimization of H_2O_2

H_2O_2 concentration (mM)	CODRemoval (%)
10	65.3
15	52
20	82.6
25	54.6

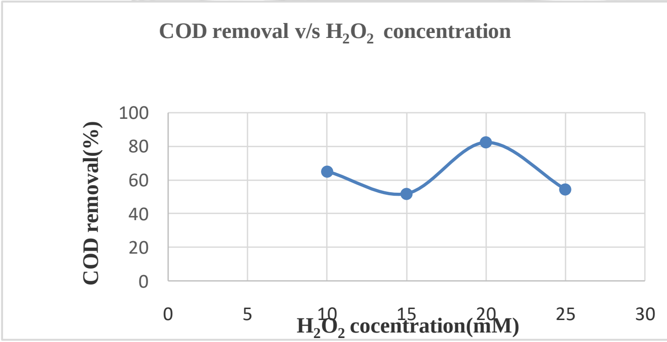

Chart- 3: Effect of H_2O_2 concentration on COD removal

3.4.The effect of [Fe^{2+}] on COD removal rate

Chart-4 presents the effect of Fe^{2+} concentrationon on COD removal efficiency for Azithromycin. During this stage, the concentration of Fe^{2+} was changed from 2mM to 16mM at a constantH_2O_2 dosage of 20mM and pH of 4.0 shown in table 4. At the Fe^{2+}dosage of 2mM to 16mM, the COD removal efficiency was increases from 17% to 91.7%.It is obvious that increasing Fe^{2+} from 2 to10mM has a great effect on the efficiency of the fluidized Fenton process. Increasing the Fe^{2+} concentration resulted in increase in COD removal, and a decrease in COD removal was observed. This can be explained by the scavenging effect of overdoses of Fe^{2+}on OH radicals. Because in higher dosages of Fe^{2+}, OH radicals may be scavenged by participating in reactions with Fe^{2+} as in reaction 4 (the formation of orange-brown iron precipitate ($Fe(OH)_3$flocs), consequently, the COD removal could decrease by Elmolla and Chaudhuri [9].

$$Fe^{2+} + HO^{*} \longrightarrow HO^{-} + Fe^{3+} \quad (4)$$

Of course, it must be noted that the formed Fe^{3+} again enters a reaction with hydrogen peroxide and produces Fe^{2+} in the solution and this leads to an increase in the removal efficiency. Therefore, as the optimum COD removal (90%) occurs at Fe^{2+} = 10mM and given that a slight increase in COD removal was obtained by increasing the iron concentration more than the optimum amount .Considering the above-mentioned results, a Fe concentration of 10mM was selected as the optimum concentration for the removal of Azithromycin COD.

Table- 4: Optimization of Fe ion

Fe ion concentration(mM)	COD removal (%)
2	17
4	50.8
6	82.6
10	90
16	91.7

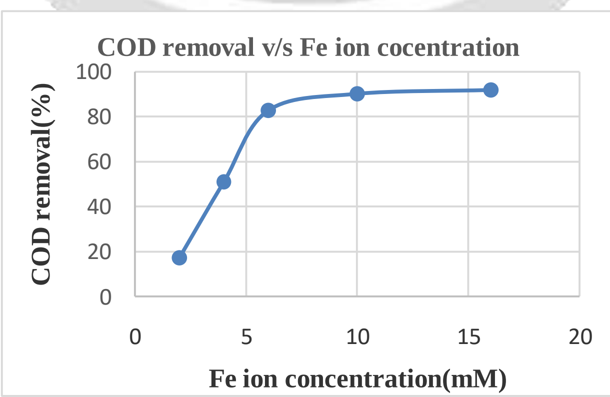

Chart 4: Effect of Fe ion concentration on COD removal

4. CONCLUSION

The effects of major parameters on the fluidized bed Fenton process were evaluated through treatment of the synthetic waste water containing Azithromycin. It was proved that the organic and inorganic compounds from the waste watercould be treated effectively using fluidized bed Fenton process. The optimal treatment condition was determined as:reaction time of 60min, pH=4, $[Fe^{2+}]$=10mM, $[H_2O_2]$=20mM, Under this condition, the maximum COD removal rate reached 90%.

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