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Use of Fenton's Reagent for Pollutants Removal in Pharmaceutical Effluent

By

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Abstract

Effluent from a pharmaceutical factory producing a single chemical product was treated on a bench scale with advance oxidation process (H_2O_2 & Fe^{2+}). The effluent was as a result of the factory treatment of the pharmaceutical wastewater by UASB (up flow anaerobic sludge bed) and a SBR (sequencing batch reactor) process. The chromatechemical oxygen demand (CODcr) range of the discharged effluent was between 8000-10,000mg/L with some residual recalcitrant compounds. The residual recalcitrant compounds which were measured by gas chromatography mass spectrometry (GC-MS) mainly consisted of alcohols, phenols and nitrogenous and sulfur compounds. The experimental variables studied include dosages of Fe^{2+}, H_2O_2 and mixing speed. The result showed that the oxidation by Fenton's reagent was best when concentration of iron (II) sulfate and hydrogen peroxide were $[Fe^{2+}]$=1.093mmol/L; $[H_2O_2]$ = 2.5mmol/L at pH = 3.0 for 30min at 80rpm; followed by conditioning with lime (1%) to pH = 8.0 where coagulation by iron hydroxide took place over 20min. Under these optimal operating conditions, the maximum removal efficiency for CODcr, Color and the aromatic compounds were 56%, 95% and 90% respectively.

Keywords: Fenton reagent; pharmaceutical effluent; hydrogen peroxide; ferrous salt; effluent treatment; chemical treatment

Introduction

The process of toxicity reduction in pharmaceutical wastewater is of paramount importance due to known fact that substances synthesized in pharmaceutical industry are either toxic inhibitory compound or structurally complex organic chemicals that are resistant to biological degradation and consequent accumulation in the environment as well as possible carcinogenic and mutagenic effect (Jia *et al***,** 2015; Ronak & Shweta, 2015***;*** Balcioglu & Otker, 2003). This makes conventional treatment methods inadequate for the treatment of pharmaceutical wastewater. One of the possible methods for their degradation and removal is chemical oxidation, especially advanced oxidation processes (AOPs) using for example O_3/H_2O_2 (peroxone); $O_3/H_2O_2/UV$; O_3/UV; H_2O_2/UV; Tio_2/UV and Fenton reactions. These processes involve the in-situ formation of highly reactive hydroxyl radicals (•OH), which react quickly and non-selectively with almost all organic pollutants (Vrushali & Gawande, 2015**;** Tijani *et al.*, 2016; Sanchis *et al.*, 2013). One of the most important advance oxidation processes used to generate hydroxyl radicals employs the Fe^{2+}/H_2O_2 system where the catalyst (ferrous ions) is dissolved in water, thus being known as Fenton process (Yuan *et al.*, 2013). Fenton's reaction is one of the most effective methods of oxidation of organic pollutants that are oxidatively degraded by hydroxyl radicals generated from H_2O_2 in the presence of Fe^{3+} as a catalyst (Hartmann *et al.*, 2010; Maezono *et al.*, 2011). $Fe^{2+} + H_2O_2$ ------------> fe^{3+} + OH + OH• equation1.

When ferrous salts are used, the hydroxyl radical is produced immediately by the rapid reaction between ferrous ion and H_2O_2 (equqtion1). Fe^{3+} can also be used to decompose H_2O_2 and to produce oxidative radicals in the Fenton-like process. With Ferric salts, the hydroxyl radical is produced in a two-stage process with the slow reaction between ferric ion and H_2O_2 (equation2) followed by the rapid reaction between the produced ferrous ion and additional hydrogen peroxide [Kiwi *et al.*,1993]. $Fe^{3+} + H_2O_2$------------> fe^{2+} +$HO_2^{\bullet}$ + H^+ equation 2.

In most applications, it does not matter whether fe^{2+} or fe^{3+} ions are used to catalyze the reaction, although some authors (Pera-Titus *et al.,* 2004; Walling & Amarnath, 1982) suggested that if low doses of Fenton's reagent are used ferrous ions may be preferable. The efficiency of Fenton's process depends on H_2O_2 and fe^{2+} concentrations and the pH of the reaction. According to some previous researcher's report, pH value should range from 3 to 5 (Mohammadine *et al.,* 2014; Navalon *et al*., 2010 and Maezono *et al.,* 2011).

Fenton reagent was found to be very effective in treating various industrial wastewater components, including aromatic & aliphatic compounds (Barbusinski & Filipek, 2001), a wide variety of dyes (Hsueh et al., 2005) as well as many other substances, including pesticides (Barbusïñki & Filpek., 2001). In this work, we present the oxidative treatment of pharmaceutical effluent that contained some recalcitrant compounds by Fenton reaction, using COD as determinand for the parameter only. This is because the pharmaceutical effluent will be subjected to critical biological treatment but effort was geared towards understanding the behavior of the effluent in a chemical treatment method hence the use of a single and most suitable parameter for efficiency determination.

Material & Methods

Wastewater:

The pharmaceutical effluent is from a medium scale drug manufacturing plant situated in Ota near Lagos State Nigeria. The presence of toxic compounds in wastewater was both due to the factory product as well as chemicals used in sterilizing the manufacturing equipment. The intermittent cleaning and disinfecting of the tanks used in the production as well as domestic utilization of the tap water make up the wastewater coming out of the plant. The plant manufacturing line is operated as batch reactor. All the characteristics of the wastewater (Table1) were measured according to procedures described in standard methods (AWWA, 1995)

Table1: **Pharmaceutical Effluent Chemical Characterization**

PARAMETERS	MEAN VALUE
pH	4,3 ± 0,3
BOD5 (mg L-1)	1370 ± 260
COD (mg L-1)	8030 ± 800
Suspended solids (mg L-1)	65 ± 10
Total solids (mg L-1)	1400 ± 400
Fats and Oils (mg L-1)	45 ± 25
Detergents (mg L-1)	100 ± 50
Odour	Noticeable, peculiar, savoury

Experimental procedure:

The following parameters of Fenton's reaction were examined and optimized; hydrogen peroxide and ferrous concentration, [fe^{2+}]: [H_2O_2] ratio, and initial pH of the reaction. A liter of wastewater was added into one liter Erlenmeyer flask which served as the reactor, acidified with H_2SO_4 (Fenton reaction is effective at acidic pH range). Since the initial pH of the wastewater is above 5.0, the sample was acidified to the desired value in the pH range of 2.5 –4.0. After which various doses of 30% H_2O_2 and solid $FeSO_4.7H_2O$ were added, the mixture was vigorously stirred for 1hour at 80rpm (oxidation process), then pH was adjusted to 8.0 with 1% lime and coagulated at 30rpm for 20min. it was allowed to sediment and chemical oxygen demand (COD) and residual H_2O_2 were determined in the clear solution. COD tests were made after total removal of residual H_2O_2. The residual H_2O_2 can increase the COD value since it acts as a reductant, especially in the chromate based analysis of COD determination. Talinli and Anderson (1992) investigated the reducing effect of H_2O_2 on

$K_2Cr_2O_7$ and they showed linear relationship between concentration of H_2O_2 and COD.

Residual H_2O_2 removal

This was achieved by raising the pH of the solution (pH=10.5) at high temperature (45) in the presence of fe^{3+} with stirring at 65rpm and was sit overnight (Walling & Amarnath, 1982; Krzysztof Barbusinski, 2009).

Analytical methods

Aromatic and aliphatic compounds were analyzed by Infrared spectrometer (FTIR spectrometer) and confirmed with gas chromatography – mass spectrometry (GC– MS) as shown in fig1. The trace element analyses were carried out with inductive coupled plasma (optimal emission spectrometer, optima 5300DV). COD (closed reflux, trimetric method). Concentration of residual H_2O_2 was analyzed by the $KMnO_4$ method.

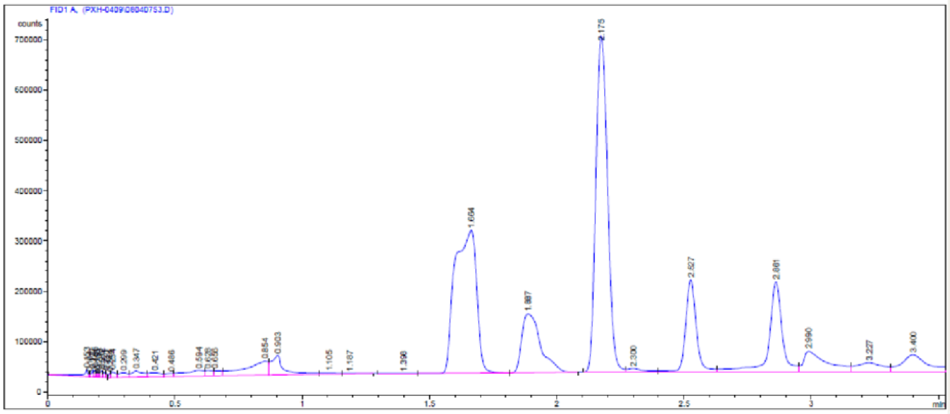

Fig.1: **GC Chromatogram of the pharmaceutical Effluent**

Statistical Analysis

Data are presented as mean ± SD of triplicate determinations and descriptive statistics was conducted using Microsoft Excel (2016).

Result and Discussion

Effect of Fe^{2+} concentration.

It was shown that as the concentration of Fe^{2+} increased, the COD removal increased until a point where further addition of iron becomes inefficient. The feature of an optimal dose range for the iron catalyst is characteristics of Fenton reagent although the range varies for different wastewater. Typical ranges are $[Fe^{2+}]:[H_2O_2] = 5– 25$ (Pere-Titus *et al.*, 2004). Figure2 shows the effect of iron dosage on COD removal using different initial H_2O_2 concentrations. The result showed that the efficiency of Fenton reaction depends on the concentration of fe^{2+} as occurs in the classical Fenton reagent process. (Rajesh & Raman, 2013) have demonstrated that the COD removal is nearly the same using either fe^{2+} or fe^{3+} in the degradation of a textile wastewater by the Fenton process. The maximum COD removal achieved in this study was between 40 – 56% depending on the hydrogen peroxide dosage.

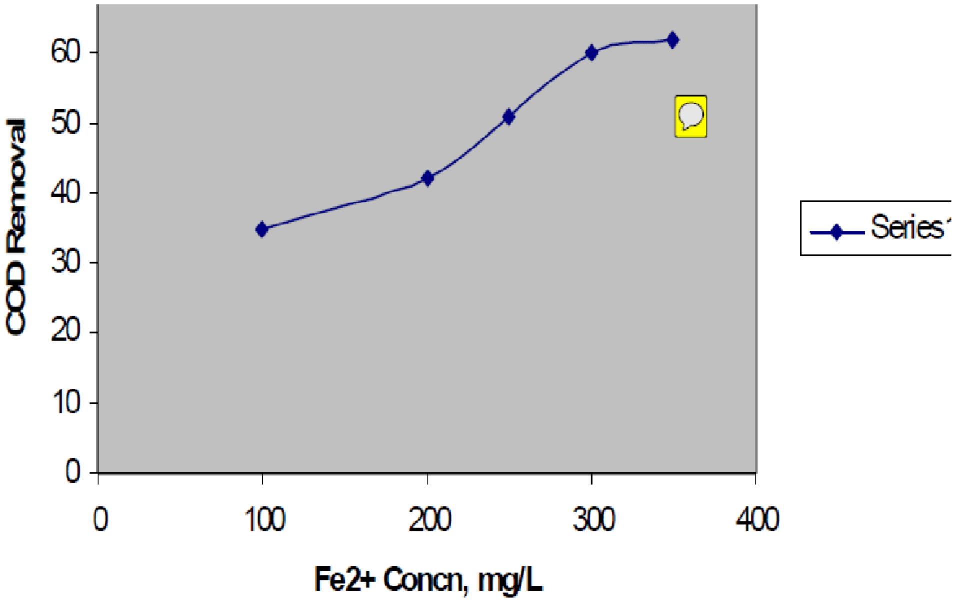

FIG. 2:: **Effect of Fe^{2+} Concentration variation**
H_2O_2 @ 1.6M; pH = 2.5; Mixing speed = 100rpm @ 30min

Effect of temperature and pH

An initial experiment was carried out at room temperature and at 50°C, to show the effect of temperature on COD removal efficiency but no significant differences were observed in the treatment efficiency for the tested temperatures (data not shown). Thus all further work was carried out at room temperature. Research findings indicate that the temperature of the wastewater almost does not affect the efficiency of COD removal in Fenton’s oxidation (Peral *et al.*, 2002; Casero *et al.*, 1997), although the redox reaction can be accelerated by rising the temperature as expected. The time required for the oxidation to be completed at room temperature was about 15–20 times longer than at 50°C which required several minutes (data not shown). When tested with initial pH range of 2.5 – 4.5, no significant differences in the treatment efficiency were observed although pH 3.5 showed slightly better results. This finding is in adherence with the recent research reports that suggest that the optimum pH for Fenton oxidation is between 3–5 and that it is independent of the nature of the wastewater. (Tambosi *et al.,* 2006; Hsueh *et al.,* 2005) all observed that pH affects significantly the degradation of organics by Fenton reaction and acidic condition is required to produce sufficient hydroxyl radicals by the decomposition of hydrogen peroxide catalyzed by ferrous ions. In a recent study, (Zhang *et al.,* 2005) reported the optimum pH as 2.5 for the treatment of landfill leachate by Fenton's oxidation.

Effect of H_2O_2 concentration

The degradation rate of organics in wastewater increases as the concentration of H_2O_2 increases until a critical H_2O_2 concentration is achieved (Huseh, *et al.*, 2005). Above this critical concentration, the degradation rate of organic compounds decreases as a result of the scavenging effect, according to equation3 $H_2O_2 + OH\bullet$ ------------> $HO_2{}^{\bullet} + H_2O$ (3) Fig.3 clearly shows that as the concentration of H_2O_2 increases, there was an increase in the COD removal efficiency up to the optimum concentration of 15ml/L. Above this amount of H_2O_2, there was decrease in the efficiency removal.

Conclusion

The Fenton process could be applied to pharmaceutical effluent. The COD removal efficiency using oxidation was greatly affected by the initial pH of the solution. The most efficient reaction was observed at a pH of 3.0 and the optimum coagulation pH range to maximize the COD removal efficiency was between 6.0 – 8.0. For a pharmaceutical wastewater with a COD range of 8000 – 10000mg/L, average COD removal efficiency was highest when the ratio of H_2O_2/Fe^{2+} was about 150–250. At 0.3M H_2O_2 and 0.012M the optimum COD removal efficiency of 65% was achieved. Fenton reagent could be used to treat pharmaceutical wastewater that contains some constituents that are extremely toxic to biological processes hence viewed as biocides. Fenton's reaction proves to be an efficient treatment technology when biological treatment is not feasible.

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