**Chemical Oxidation of Cosmetic Industry Wastewater by Fenton Reagents**

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**Abstract**
Cosmetic industry wastewater is high strength wastewater and it can be difficult to decompose with biological treatment due to its high stability or toxicity. The use of Fenton reagent as a Chemical pretreatment was investigated with a Factorial Experiment where the concentrations of ferrous sulfate, hydrogen peroxide and reaction duration was the main parameters examined for COD and TOC reduction. The oxidation with Fenton reagents was proven very efficient in terms of COD and TOC removal where 61% and 85 % was the removal efficiency respectively. Iron concentration was found to have the largest impact on the pollutant removal.
**Key words:** Fenton reagents, Factorial Experiment, Cosmetic industry , Wastewater.

**Introduction**

Cosmetic industry wastewater is characterised by high levels of COD, Suspended solids, Fats and Oils and Detergents [1]. Many of the organic compounds contained in waste from cosmetics industries are difficult to undergo biological treatment because of the high stability or toxicity which they contain. Additionally, some of the organic constituents of the waste exhibit large acclimatization times resulting difficult and time consuming process to biologically degraded by the method of activated sludge. Moreover it has also identified that surfactants, especially at higher concentrations, can significantly deteriorate biological treatment processes. A number of treatment methods such as ultra filtration, catalytic wet peroxide oxidation processes, advanced oxidation and coagulation/flocculation have been used to treat Cosmetic industry wastewater[2] [3].

The high demand of cosmetic is expected to further extend with increase of the role of woman in the workplace, the increasing number of male consumers, the increase of life expectancy and with the introduction of new technologies and novel products in markets.[4]

This work examines with use of the factorial experiment the effect of each individual or combined, process parameter in the Fenton oxidation process for COD and TOC removal and presents the equations which were calculated.

*Oxidation using Fenton reactions*

The Fenton oxidative process involves the use of iron salts and hydroxyl peroxide to produce hydroxyl radicals which have high standard oxidation potential (2.80 V). hydroxyl radicals have high reaction rates in comparison with other oxidants such as $Cl_2$, $O_2$, $O_3$ [5].

Fenton reagent has the advantage in wastewater treatment that iron is a highly abundant and non-toxic element and hydrogen peroxide is easy to handle and breaks down to $H_2O$ and $O_2$ which are non toxic to the environment [6]. Other advantages of the Fenton process include the low capital cost, it is easy to implement, it can be used as a pretreatment stage of the biological treatment and hydroxyl radicals is a non selective oxidant that can be used in a broad range of pollutants. However there are pollutants such as acetic acid, oxalic acid and acetone where is proven ineffective [7] [8].

The possible reaction steps are shown below.

$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+}$ (1.0)

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^{\bullet}$ (1.2)

$Fe^{3+} + HOO^{\bullet} \rightarrow Fe^{2+} + H^+ + O2$ (1.3)

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH$ (1.4)

${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HOO^{\bullet}$ (1.5)

$Fe^{2+} + HOO^{\bullet} \rightarrow HOO + Fe^{3+}$ (1.6)

${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ (1.7)

$^{\bullet}OH$+ organics→products+$CO_2$+$H_2O$ (1.8) [7]

**Experimental Methods**

*procedure*

In this experiment 500 ml Cosmetic Industry wastewater was poured on a 1000 ml Beaker. A predetermined quantity of heptahydrate ferrous sulfate was added and magnetic stirring was applied. After dissolving the ferrous sulfate in the solution hydrogen peroxide was gently added and the solution was left under continuous stirring . in order to stop the fenton reaction an aqueous $Na_2SO_3$ solution 15% (w/w) in 1:1 ratio of the corresponding added hydrogen peroxide quantity was added. in order to eliminated any interference by the addition of $Na_2SO_3$ the solution was left under rapid stirring for 60 min [9],[10].

*Chemicals and method of analysis*.

All chemical used were reagent grade. Hydrogen peroxide (30v/v) , heptahydrate ferrous sulfate, Sodium sulfite were purchased by Merck.

COD analysis was measured according to the SM 5220 C and TOC analysis was perform by the a TOC analyser which oxidise with Ultraviolet/persulfate oxidation and analyse the CO2 with the non-dispersive infrared analysis (NDIR) method. [12]

*Factorial design*

The aim of the experimental procedure was to determine the influence of some basic process parameters which were considered as the 'Controlling Parameters' on the effectiveness of the oxidation treatment in terms of % COD and % TOC removal. These parameters are the initial concentrations of ferrous sulfate, hydrogen peroxide and reaction duration. The benefits for using Factorial experiment was to determine the effect of each independent variable but also if they combine to influence the dependent variable

The effect of the controlling parameters on the optimization parameter was estimated by performing a $2^3$ factorial experiment where the significance can also be estimated and accessed. the experimental area was pre determined by preliminary tests.[13],[14].

Table 1 shows the Controlling parameters which were used and their selected controlling intervals which were used.

The number of experiments for the $2^3$ factorial experiment was 8. two additional experiments were carried out in the center of the design to determine the Repeatability and the accuracy of the experiments. Each experiment was repeated three times and the results presented are the mean values.

**Table 1.** Controlling parameters and their levels in the factorial experiment.

| controlling parameters | | | controlling intervals | | |
|---|---|---|---|---|---|
| | Units | Representation as | -1 | 0 | 1 |
| Time | min | X1 | 15 | 30 | 45 |
| FeSO4.7H2O addition | g*L-1 | X2 | 0.25 | 0.5 | 0.75 |
| H2O2 (30%) addition | mg*L-1 | X3 | 0,75 | 1,5 | 2,25 |

**Results and discussion**

Table 2 shows the COD and TOC reduction for altering each of the controlling parameters.

**Table 2.** COD and TOC removal efficiency results of the factorial experiment.

| trial | X1 | X2 | X3 | TOC concentration (mg/l) | COD concentration (mg/l) |
|---|---|---|---|---|---|
| 1 | - | - | - | 681,6 | 4640 |
| 2 | - | - | + | 675,6 | 4600 |
| 3 | - | + | - | 132 | 1760 |
| 4 | - | + | + | 94,8 | 2320 |
| 5 | + | - | - | 602,4 | 4240 |
| 6 | + | - | + | 674,4 | 4160 |
| 7 | + | + | - | 106,8 | 2160 |
| 8 | + | + | + | 111,6 | 2160 |
| 9 | 0 | 0 | 0 | 135,6 | 2560 |
| 10 | 0 | 0 | 0 | 142,8 | 2760 |

From the the experiments in the center of the design the mean values and the standard deviation where shown high reputability. The standard deviation from the experiment carried out to estimate TOC removal. The value was ±5 mg/l while from the COD experiment was ±141 mg/l.

The initial concentration of COD and TOC was 5580 mg/l and 708 mg/l respectively. The TOC removal reached up to 85persent while the COD removal reached 61 percent. In high FeSO3 concentrations it was observed iron hydroxide precipitation which enhanced TOC and COD removal. The linear equation by applying the factorial experiment theory for the COD and TOC removal were the following.

$COD = 3255+ 75X_1-1155X_2+55X_3 -135X_1X_2+75X_2X_3+65X_1X_2X_3$

$TOC = 384+11.1X_1-273X_2+4.2X_3-9X_1X_2-15X_2X_3-12.5X_1X_3+4.5X_1X_2X_3$

where

$X_1$ represent the reaction duration in min

$X_2$ represents the FeSO4.7H2O concentration in g*L-1

and $X_3$ represents the H2O2 concentration in mg*L-1

However, to identify which parameter in the equation is important to we need to calculate the dispersion of the remaining ($S_{ad}$)

$$S_{ad} = \frac{\sum_{i=1}^{N}(Yi-\hat{Y}i)^2}{f}$$

where

$Y_i$ is the actual experimental value

$\hat{Y}_i$ is the test value which is calculated from the linear relationship by using the coefficients of the linear actions only and

f = N-(K+1) = 4 is the degree of freedom where N is the number of experiment , which is 8 in our case, and K the number of factors, which is 3 in this experiment.

For estimating if the experimental model is adequate, the Fisher criteria was used. In this case the ratio $F = S^2_{ad}/S^2_Y$ should follow -F distribution with significance level 5%. From the TOC experiment the F = 1177 and from the COD experiment was F = 283.

In order to estimate the significance of each linear factor in the equation 1 and 2 we have to compare them with the following equation: $t= |b_j|*(N)^{0.5} / S_y$ where t follows student distribution, $b_j$ represent the linear factor were in order to be considered significant the t value should be greater comparing the value which results with the number on a table which follows the student deviation. From the TOC and COD statistical analysis it was estimated that only iron concentration can be considered significant. Figure 1 shows the % reduction of TOC and COD in relation to FeSO4.7H2O concentration and for the different concentrations of H2O2 and reaction time.

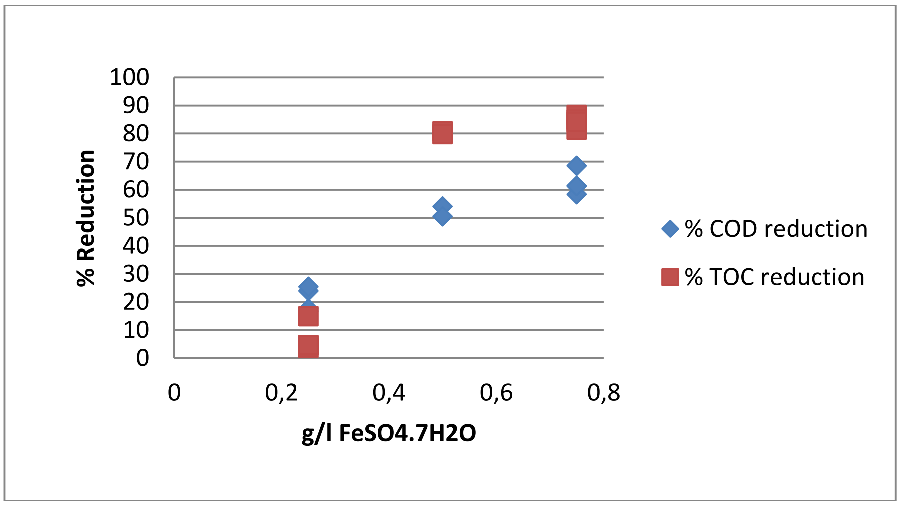


Figure 1. Effect of the FeSO4.7H2O addition in the COD and TOC reduction.

Taking into consideration the above equation it can be concluded that for low COD and TOC concentration, iron concentration is the dominant controlling parameter and by increasing dosing of iron, higher COD and TOC reduction is achieved.

**Conclusion**

In conclusion, Fenton oxidation could be a feasible method for the treatment of toxic wastewater as cosmetic processing industry wastewater and could also be used as a pretreatment stage for a biological post-treatment.

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