Study of Fenton Reagent for the Removal of Chemical Oxygen Demand from Dairy Wastewater.

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Abstract-

Dairy industries have shown tremendous growth in size and number in India and other countries of the world. These industries discharge wastewater which is characterized by high chemical oxygen demand, biological oxygen demand, nutrients, and organic and inorganic contents. Such wastewaters, if discharged without proper treatment, severely pollute receiving water bodies. One of the most serious environmental problems is the existence of hazardous and toxic pollutants in wastewaters. Adsorption is considered to be one of the most promising techniques for wastewater treatment over the few decades. Attempts were made in this study to examine the efficiency of Fenton process combined with coagulation for treatment of dairy wastewater. Parameters affecting the Fenton process, such as pH, dosages of Fenton reagents and the contact time, were determined by using jar test experiments 82% of chemical oxygen demand (COD) could be removed at pH 3.0, 1000mg/L H2O2, 2041mg FeSO4 and 50 minutes contact time. The coagulation using ferrous sulfate (FeSO4) was beneficial to improve the Fenton process treated effluent in reducing the flocs settling time, enhancing turbidity and COD removal. The overall turbidity and COD reached 78%, and 85% under selected conditions, respectively. Thus this study might offer an effective way for wastewater treatment of dairy industries.

Keywords- Dairy industries, Flocs, Fenton reagent, turbidity.

I. INTRODUCTION

Last few decades, with an increase in the stringent water quality regulations due to environmental concerns, extensive research has focused on upgrading current water treatment technologies and developing more economical processes that can effectively deal with toxic and biologically organic contaminants in wastewater. [1] Industries manufacturing dairy products, cosmetics, organic dyestuff, soaps and detergents, pesticides and herbicides, tanneries and leather, paper, brewery and fermentation industry generate wastewater containing high load, toxicity or presence of bio-recalcitrant compounds having various origins and properties. Such wastewater having poor biodegradability needs a strong pretreatment method, followed by a biological treatment process. Usually, conventional chemical coagulation – flocculation methods like Alum, ferrous sulphate, polyelectrolyte etc. are very commonly used as a pre-treatment method to enhance the biodegradability of wastewater during the biological treatment.[2] Among these chemical processes, the advanced oxidation process (AOP) has been efficiently used to reduce the organic load or toxicity of different wastewater. Fenton reagent is considered as one of the AOP and used for the treatment of both organic and inorganic substances. The Fenton's reaction has a short reaction time among AOPs; therefore, it is used when a high COD removal is required.[3] Moreover, the reaction occurs at ambient temperature and pressure, involves safe and easy to handle reactants, no special equipment required, no mass transfer limitations, no energy involved and can be implemented with a great variety of compounds. The Fenton's system consists of ferrous salts combined with hydrogen peroxide (H2O2) under acidic conditions[8]. Ferrous ion reacts with hydrogen peroxide, producing hydroxyl radical ▪OH mentioned below (reaction 1).

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + °OH$ ……………. (1)

The ▪OH free radical, having a very high oxidation potential (E°=2.80 V), is capable of reacting with many organic species through a series of chain reactions.

Fe3+ + H2O2 → Fe2+ + HO2• + H+ ……………. (2)
Fe3+ + HO2• → Fe2+ + O2 + H+ ……………. (3)
Fe3+ + R• → Fe2+ + R+ ……………. (4)

Fe3+ produced can react with H2O2 and hydroperoxyl radical in the so-called Fenton-like reaction, which leads to regenerating Fe2+ (reactions 2 and 3). Fe2+ regeneration is also possible by reacting with organic radical intermediates (Reaction 4) [10].

It was also reported by Ivan et al. [11] that ▪OH reacts unselectively within a millisecond with organic substances. H2O2 and Fe2+ also had a synergistic effect on the removal of colloidal organic residues by coagulation.

In Fenton treatment, the pH value should be near 2-4 during the reaction. After reactions are completed, precipitation of the oxidized iron as Fe(OH)3 occurs by neutralizing or adjusting the pH to 7.5 - 8. Neyens et al. and Neyens and Baeyensin [9,11] studied the effects of pH, temperature, reaction time and H_2O_2 concentration with considerable reduction inorganic concentration.

As per the literature review, no study has been performed for dairy wastewater using Fenton for COD value. Therefore, the objective of present study was to evaluate the efficiency of Fenton's reagent to remove COD from industrial wastewater characterized by its value of COD (approximately 3800 mg/L) and a equal value of BOD, probably due to the presence of organic compounds, which hamper a direct biological treatment and thus require a chemical pretreatment. Effects of pH and the optimal dosages of Fenton reagent (Fe^{2+}/H_2O_2) were also determined.

II. LITERATURE REVIEW

Sureyya et al (2003) studied the degradation of Reactive Black 5 from synthetic wastewater using Fenton's oxidation (FO) process. The study was performed in a systematic approach searching optimum values of FeSO4 and H2O2 concentrations, pH, and temperature. Optimum pH and temperature for 100 mg l-1 of Reactive Black 5 were observed as 3.0 and 40 °C, respectively, using 100 mg l-1 of FeSO4 and 400 mg l-1 of H2O2 resulted in 71 % Chemical Oxygen Demand (COD) and 99 % color removal. For 200 mg l-1 of Reactive Black 5, 84 % COD removal and more than 99 % color removal were obtained using 225 mg l-1 of FeSO4 and 1000 mg l-1 of H2O2 yielding 0.05 molar ratios at pH 3.0 and 40 °C.

CelalettinOzdemir et al. (2008), states that the process of pesticide removal from industrial wastewater using which chemical, vacuum-chemical and Fenton's reactions have been analyzed. Fenton process is an attractive alternative to conventional oxidation processes in the effluent treatment of recalcitrant compounds. The aim of this study is to evaluate the efficiency of chemical, vacuum and Fenton processes for the reduction of chemical oxygen demand in wastewaters from pesticide industry. In this study wastewater from pesticide industry was used. Whereas in the chemical procedure [$Ca(OH)_2$ and $KMnO_4$], the chemical oxygen demand removal efficiency is 94.9 %; in the vacuum-$Ca(OH)_2$ + $KMnO_4$ system (with 250 mg/L $KMnO_4$, 1 mL H_2SO_4, 5 mg/L polyelectrolyte, and 2000 mg/L CaOH application) this efficiency was 97.8 %; and a 99.8 % KOI removal efficiency was obtained by the Fenton process (the optimum ratio of [Fe^{2+}] to [H_2O_2] was 1:1.56 (mM/mM), at pH 3.

Ebrahiem E. Ebrahiem et al. (2013), investigated the general strategy of this study was based on the evaluation of the possibility of applying advanced photo-oxidation technique (Fenton oxidation process) for removal of the residuals organic pollutants present in cosmetic wastewater. The different parameters that affect the chemical oxidation process for dyes in their aqueous solutions were studied by using Fenton's reaction. These parameters are pH, hydrogen peroxide (H2O2) dose, ferrous sulfate ($Fe_2SO_4.7H_2O$) dose, Initial dye concentration, and time. The optimum conditions were found to be: pH 3, the dose of 1 ml/l H_2O_2 and 0.75 g/l for Fe(II) and Fe(III) and reaction time 40 min. Finally, chemical oxygen demands (COD), before and after oxidation process was measured to ensure the entire destruction of organic dyes during their removal from wastewater. The experimental results show that Fenton's oxidation process successfully achieved very good removal efficiency over 95%.

Mahmood R. Sohrabiet al (2014), the research is designed to investigate the removal of Carmoisine from aqueous solutions by advanced oxidation processes including Fenton and photo-Fenton systems. The progress of oxidation of Carmoisine dye was monitored by UV–Vis spectrophotometer. The effect of operating parameters affecting removal efficiency such as H_2O_2, Fe^{2+} and dye concentrations as well as pH was studied and optimized using Taguchi fractional factorial design during removal of Carmoisine from 50 mL of solutions. Optimal conditions were achieved as 0.015 mmol Fe^{2+}, 0.15 mmol H_2O_2, 20 mg/L initial dye concentration and pH = 3.5, for the Fenton process and 0.0125 mmol Fe^{2+}, 0.3 mmol H_2O_2, 20 mg/L initial dye concentration and pH =3.5 for the photo-Fenton process. Also, removal yields were achieved as 92.7% for the Fenton and 95.1% for the photo-Fenton processes in optimal conditions. The result of this study showed the high efficient removal of Carmoisine by advanced oxidation processes that introduced it as a cheap, versatile and efficient method for removal of this pollutant.

Barwal A and Chaudhary R (2016), studied the effectiveness of conventional chemical coagulation and flocculation process using ferrous sulfate, alum and Fenton process for the treatment of high chemical oxygen demand (COD) industrial wastewater. Removal of organic matter (expressed as COD) was investigated for highly organic wastewater having COD of 15000 mg/L. Also, the optimum conditions for coagulation/ flocculation process, such as coagulant dosage, Fenton dosage, and pH of solution were investigated using jar-test experiment. The results revealed that in the range of pH tested, the optimal operating pH was 7.5-8 for $FeSO_4$ and alum and 3 for Fenton process. Percentage removals of 26, 42 and 88 for COD was achieved by the addition of 1.0 g/L alum, 1.2 g/L of FeSO4 and 1:20 Fe^{2+}/H_2O_2ratio, respectively.

III. OBJECTIVES

a) To characterise the dairy wastewater and preparation of synthetic dairy wastewater.
b) To study and prepare Fenton reagent.
c) To study and analyze the performance of Fenton reagent under variable parameter such as pH, reaction time and dose.

IV. MATERIALS AND METHODS

A.Materials

All chemicals employed in this study were analytical grade. All solutions were prepared in distilled-deionized water made on each experimental day. Glassware used in this work rinsed with distilled-deionized water prior to drying. Hydrogen peroxide was prepared by using the analytical grade (30% by wt.) H_2O_2 as purchased. The ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) was used as the source of Fe^{2+} in the Fenton process. Solutions of NaOH and H2SO4 were used for pH adjustments.

B. Experimental setup

The coagulation, flocculation and Fenton system experiments were conducted using Jar Test equipment, consisting of 6 jars of 1000 mL each whose contents were stirred with flat stirring paddles (25 mm × 75 mm) as shown in the figure 1.

C. Synthetic wastewater

Synthetic industrial wastewater was prepared in the laboratory with tap water by mixing different chemicals containing organic carbon, macro and micro-nutrients. The composition of stock synthetic wastewater was adjusted in such a way that COD becomes approximately about 3800 mg/L. The working synthetic wastewater containing varying COD concentrations was prepared by diluting appropriate volume of stock synthetic wastewater with tap water. The composition of synthetic wastewater is mentioned in table 1.

Table 1. Composition of synthetic dairy waste.

Compounds	**Concentration (mg/L)**
Skimmed milk powder	1400
NH_4Cl	20
$MgSO_4.7H_2O$	45
$FeCl_3.H_2O$	3
$CaCl_3.H_2O$	0.4
KCl	45
$(NH_4)_2PO_4$	5

D. Analytical procedures

Analytical procedures were monitored in accordance with standard methods [16]: COD with different coagulants. pH was measured by using a digital pH-meter. COD removal efficiency (RE) was calculated by using the following
Equation 1:

$$RE(\%) = \left(\frac{Cin - Ceff}{Cin}\right) \times 100$$

Where Cin and Ceff are the concentrations in the influent and in the effluent, respectively.

E. Sampling and analysis

For each jar test, rapid mixing conditions were 1 min at 120 rpm and slow mixing conditions were 20 min at 30 rpm in order to favor flocs aggregation. Then, the samples were allowed to settle for 30 min. After the settling period, volumes of about 10-20 mL were taken 2 cm below the surface level using a plastic syringe. For the purpose of coagulation, pH was adjusted with the lime dosing. A series of three Jar-test experiments was conducted with different coagulants with variable dosing while maintaining the optimum pH.

Figure 1. Experimental setup

In the jar-test experiment, coagulant ferrous sulphate doses were added at variable dosing with respect molar ratio 1:1, 1:2 and 1:3 with respect H_2O_2 of 600, 800, and 1000 mg/L respectively. The jar-test was performed with Fenton process (Fe^{2+}/H_2O_2). This process serves both oxidation and coagulation functions. The pH level has to be decreased to 3-4 for the effective chemical oxidation and flocculation of the complex organic materials dissolved in water. The pH level (3.0, 3.5 and 4.0) of the wastewater was set by H_2SO_4 (6N). After the setting of the pH level, desirable amounts (Fe^{2+}/H_2O_2 ratio) of $FeSO_4•7H_2O$ solution were added to the reaction solution as the ferrous iron (Fe^{2+}) source.[16] The reaction was assumed to start with the addition of H_2O_2 (ranging from 600 to 1000 mg/L). Initially the reaction time was set as 30 minutes. Later, it was extended up to 50 minutes. After the selected reaction time, the experiment was ceased with the addition of lime as to increase the pH to around 7-8, to precipitate ferrous iron out as solid $Fe(OH)_3$. Residual COD of the supernatant was measured after settling for 30 min.

V. RESULTS AND DISCUSSION

In this study for optimizing the experimental variables of COD removal for molar ratio 1:1, 1:2 and 1:3 for each molar ratio with three factors (H_2O_2 and Fe^{2+} dosages, reaction time and pH) in three levels were studied via fractional factorial design leading to nine experiments (L9 design, Table) for each molar ratio. The results of 9 experiments of Fenton and photo Fenton processes are presented in Tables 2 and 3, respectively. A range of values from 0% to 95% was obtained for removal efficiency. From the average values of the results, run 4 of molar ratio 1:1 and run 3 of molar ratio 1:3 showed the lowest and highest removal efficiency for Fenton processes, respectively.

Experimental data were analyzed using the Minitab software (version 17). The reaction time of 30, 40 and 50 min was used for all the processes because it was found from preliminary experiments that the COD removal after this time is virtually constant. The mechanism of the Fenton's reaction is quite complex, and some authors described this mechanism.

$H_2O_2 + Fe^{2+} \rightarrow OH + OH + Fe^{3+}$....... (1)

Fe (II) oxidizes to Fe (III) in a few minutes or seconds in the presence of higher amount of hydrogen peroxide. Hydrogen peroxide decomposes by Fe (III) and generates again hydroxyl radicals according to the following reactions:

$Fe^{3+} + H_2O_2 \rightarrow H+ + Fe\text{-}OOH^2+$........ (2)

$Fe\text{-}OOH^{2+} \rightarrow HO_2 + Fe^{2+}$ ……. (3)

$Fe^{2+} + H_2O_2 \rightarrow Fe3++ OH^- + .OH$ ……. (4)

Table 2. Factors and levels of an orthogonal array for molar ratio 1:1 , 1:2 and 1:3.

Levels	Factor		
	A (pH)	B (reaction time) (minutes)	C (H_2O_2 dose) (mg/l)
1	3	30	700
2	3.5	40	900
3	4	50	1100

A molar ratio of 1:1 results is tabulated in Table No.3. A maximum COD removal efficiency was observed at 3 pH hydrogen peroxide dose of 1000mg/L and ferrous sulphate dose of 2041 mg.

Table 3. The Orthogonal Array9 for optimization of Fenton process for molar ratio 1:1.

run	Factor A pH	Factor B Reaction time	Factor C H_2O_2 dose	Response % cod removal
1	3.0	30	600	51
2	3.0	40	800	58
3	3.0	50	1000	70
4	3.5	30	600	48
5	3.5	40	800	61
6	3.5	50	1000	60
7	4.0	30	600	50
8	4.0	40	800	64
9	4.0	50	1000	61

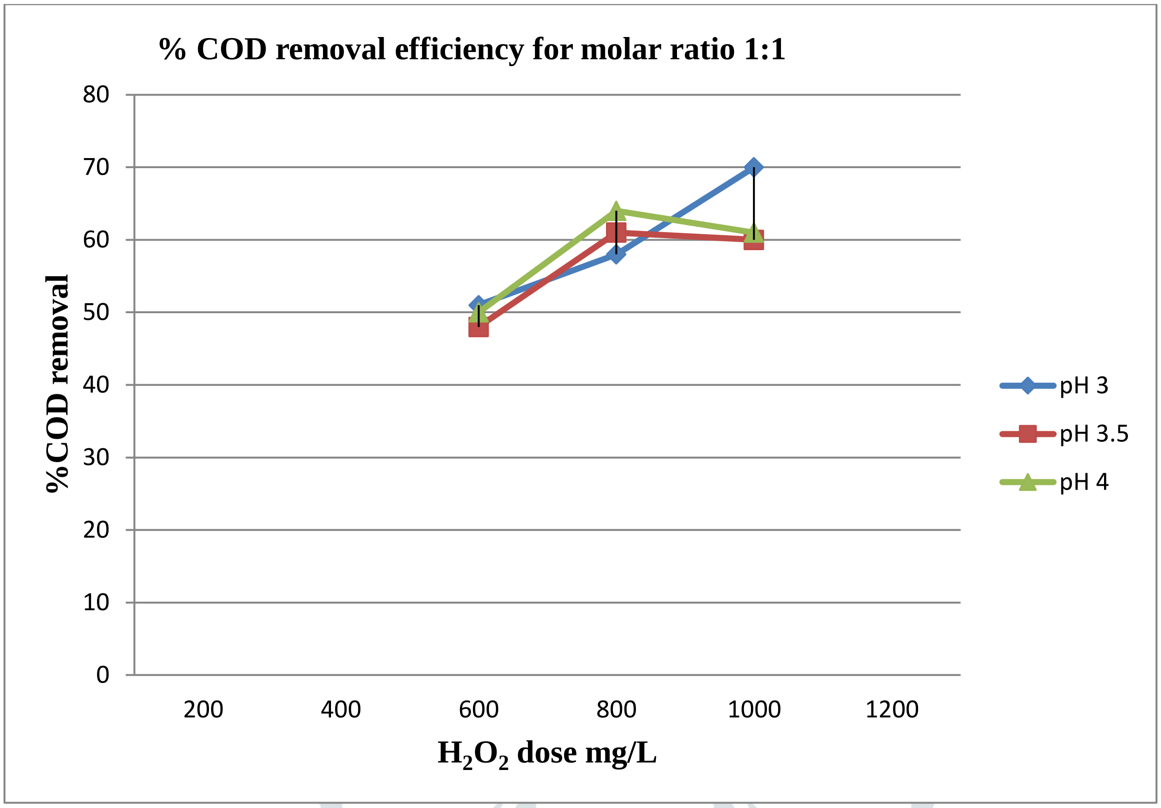

Figure2. % COD removal efficiency for molar ratio 1:1

A molar ratio of 1:2 results is tabulated in Table No. 4. A maximum COD removal efficiency was observed at 3 pH hydrogen peroxide dose of 800mg/L and ferrous sulphate dose of 816.4 mg.

run	Factor A pH	Factor B Reaction time	Factor C H_2O_2 dose	Response % cod removal
1	3.0	30	600	60
2	3.0	40	800	78
3	3.0	50	1000	74
4	3.5	30	600	68
5	3.5	40	800	71
6	3.5	50	1000	70
7	4.0	30	600	63
8	4.0	40	800	72
9	4.0	50	1000	60

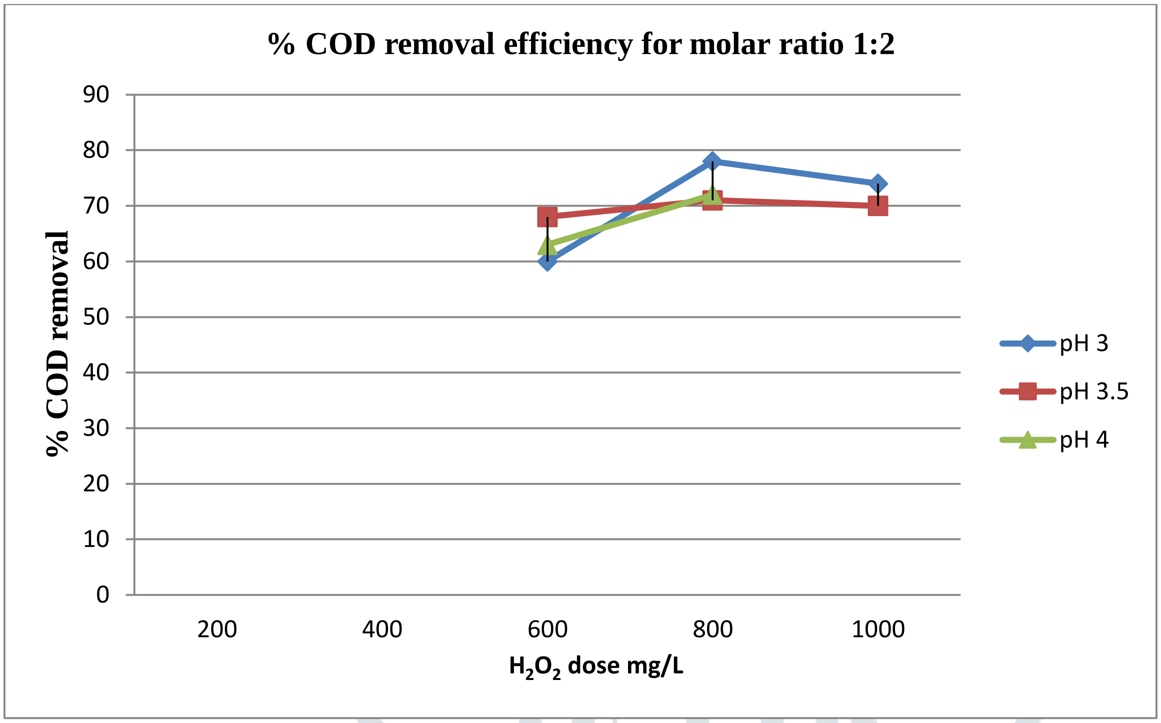

Figure 3. % COD removal efficiency for molar ratio 1:2

A molar ratio of 1:3 results is tabulated in Table No.5. A maximum COD removal efficiency was observed at 3 pH hydrogen peroxide dose of 1000mg/L and ferrous sulphate dose of 681.8mg.

Table 5. The Orthogonal Array9 for optimization of Fenton process for molar ratio 1:3.

run	Factor A pH	Factor B Reaction time	Factor C H_2O_2 dose	Response % cod removal
1	3.0	30	600	74
2	3.0	40	800	80
3	3.0	50	1000	85
4	3.5	30	600	70
5	3.5	40	800	72
6	3.5	50	1000	70
7	4.0	30	600	65
8	4.0	40	800	60
9	4.0	50	1000	62

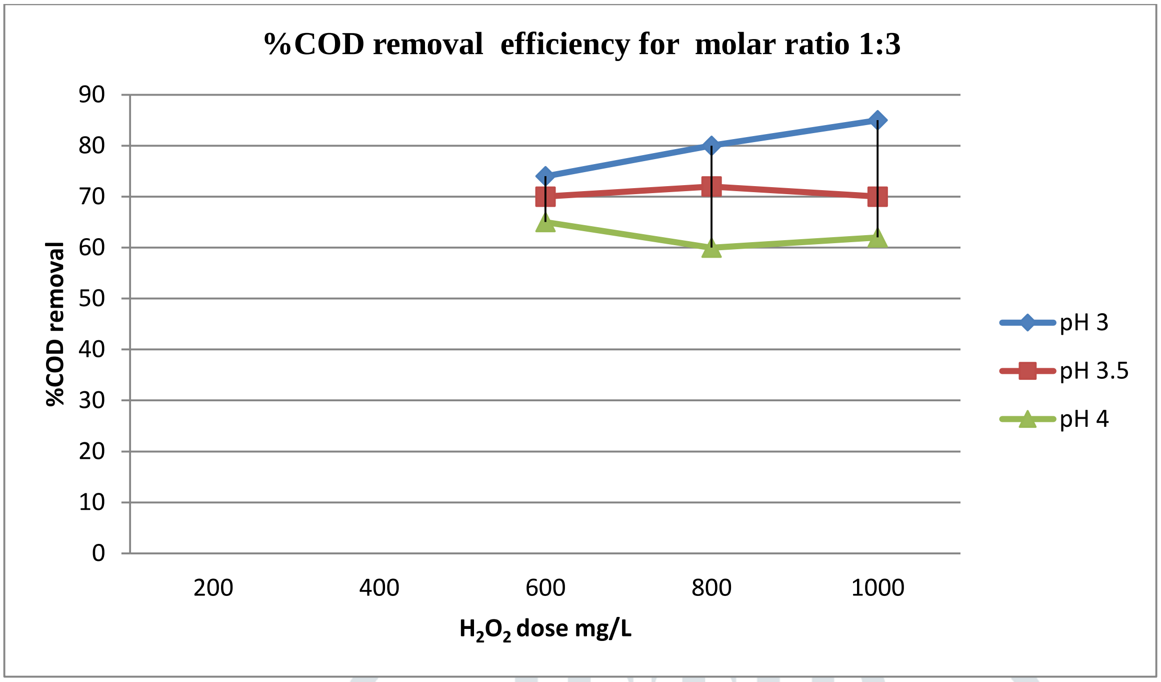

Figure 4. % COD removal efficiency for molar ratio 1:3

CONCLUSION

The Fenton's reaction was found to be efficient in reduction of chemical oxygen demand from dairy wastewater. A hydrogen peroxide dosage of 800 mg/L was found to be efficient in reducing COD for subsequent dosage of ferrous sulphate. 1:3 molar ratios gave maximum COD reduction efficiency. Further increase in the reaction time had little effect on the reduction of COD. The sludge generated from this process has potential for recovery of iron. Fenton's reaction proves to be an efficient treatment technology when biological treatment is not feasible. It is obvious that Fe2+/H2O2 had a strong synergistic effect on coagulation and achieve the best degradation in terms of COD removal and appears to be useful in increasing the biodegradability of wastewater that contains complex compounds. But, from economical point of view, Fenton process has higher cost if compared to other coagulants but this cost could be compensated by lower consumption of disinfecting agents and the lower costs of sludge handling and disposal.

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