

Fenton activated carbon catalytic oxidation (FACCO) system for the treatment of soak liquor for reuse application

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Abstract:

Soak liquor (10 L/kg of skins/hides) of characteristics BOD,COD, TOC, Dissolved Protein, Dissolved solids and halophilic count respectively 757 mg/l, 2178 mg/l, 553 mg/l, 1011 mg/l, 20801 mg/l, 2.35×10^7 CFU/ml is discharged by leather industries with out any physico –chemical and biological treatment. Solar evaporation is the resorted method for concentration of soak liquor and to heap the scraped salt in tanneries. In the present study a treatment technique , known as Fenton Activated Carbon Catalytic Oxidation (FACCO) ,consisting of coagulation-flocculation using alum , lowering of pH to 3.0 using sulphuric acid, chemical dosed with hydrogen peroxide (0.001ml /L) and Ferrous sulphate (0.1 g/L) (known as Fenton reagent), and catalytic oxidation over mesoporous activated carbon at a residence time of 1 hour was attempted. The coagulated-flocculated and Fenton reagent added soak liquor was applied at a surface loading rate of $1.46\text{m}^3/\text{m}^2/\text{day}$ and volumetric loading rate of $0.83\text{ m}^3/\text{m}^3/\text{hr}$ to the reactor packed with mesoporous activated carbon. The packed bed reactor was operated under counter current mode , the clarified soak liquor was applied on the surface of the catalyst bed and air required for the oxidation of organics was supplied from the bottom of the reactor. The treated wastewater was characterized by BOD 15 mg/l, COD 200 mg/l and dissolved protein < 5 mg/l. The treated wastewater was concentrated in solar evaporation pan and crystallized. The crystallized salt was of reusable quality.

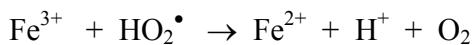
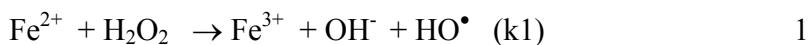
1.Introduction

Conversion of skins /hides into leather involves three major operations : pre tanning, tanning and post tanning operations. The pre tanning operations include soaking , liming , de liming and pickling. Soaking process consists of immersing the wet salted skins/hides in water for the removal of adhered common salt which was applied to preserve the raw material from microbial attack during storage/transportation. The characteristics of wastewater shown in table 1 reveals that the wastewater has BOD/COD in the range 0.37-0.42 suggesting the wastewater is amenable for bio degradation of dissolved organics in wastewater. Biological treatment of saline wastewater usually results in low BOD or COD removal performances because of adverse effects of salt on microbial flora. High salt concentration (>1% salt) causes plasmolysis and loss of activity of the cells. Several researchers have investigated the effects of salinity on bioactivity of micro organisms in biological treatment systems and found that high levels of salinity had adverse effects on treatment performance (1) . Hence, micro biological methods are insensitive to address to the treatment of salt laden wastewater discharged from tanning industries. In the absence of viable methods, segregation and evaporation of salt laden wastewater in solar evaporation pans is followed in India. The scraped salt from solar evaporation pan is collected in heaps as this salt does not meet the standards for reuse. These collected salts undergo leaching into ground water sources during run off season causing ground water pollution.

Recovery of salt from soak liquor or from the scraped salt from solar evaporation pan is a rational method for mitigating ground water pollution . As biological methods are ineffective to remove the dissolved organics from salt/soak liquor to such a level for reuse purpose ,advance oxidation processes have been considered for the treatment of wastewater..

Recently , advanced oxidation processes (AOP), which involve the in situ generation of highly potent chemical oxidants such as the hydroxyl radical (OH^\bullet), have been developed and proposed for accelerating

the oxidation and destruction of a wide range of organic contaminants in wastewater (2) (3), particularly oxidation by Fenton's reagent (4,5). Fenton's reagent is a mixture of Ferrous iron and hydrogen peroxide. The hydroxyl radicals released on mixing the reagent with wastewater facilitates the oxidation of organics.



The values of k1 ($76.5 \text{ mol}^{-1} \text{ s}^{-1}$) and k2 ($2 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$) are affected by the presence of chelators (diols, carboxylic acids, amino acids and so forth)^{4a} that are able to stabilize the cation (Fe^{3+}) slowing down the reaction or, contrarily, activate and accelerate the reaction (6). Also, the heterogeneous catalytic decomposition (on solid surfaces) of peroxides may play an important role in the degradation of organics in wastewater (7). This model incorporates a single rate limiting step controlling H_2O_2 loss and ultimately contaminant degradation, super oxide and hydroxyl radical formation, scavenging reactions of oxygen radicals with the solid surface and contaminant degradation by reaction with hydroxyl radical which is formed from both surface and solution reactions.

Sekaran el al (7) in studies on oxidation of organics in tannery effluent confirmed the formation of hydroxyl radical from molecular oxygen using the free electrons in meso porous activated carbon prepared from rice husk. The present investigation focuses on the oxidation of dissolved organics in salt laden wastewater, discharged from leather industries, using Fenton's reagent as homogeneous catalyst and meso porous activated carbon derived from rice husk as the heterogeneous catalyst .

II. Materials and Methods

2.1 RAW MATERIAL

Rice husk as the precursor material obtained from the agro industry was well washed with H₂O several times and used after oven drying at 110°C for six hours. The dried samples were then sieved to 600 micron size and the same was used for the preparation of activated carbon.

2.1 PREPARATION OF MESO POROUS ACTIVATED CARBON

Rice husk based activated carbon (RHAC) was prepared in two steps. The first step being precarbonization followed by chemical activation. In the precarbonization process the rice husk was heated to 400°C at the rate of 10°C / min for about 4 hours under N₂ atmosphere and then cooled down to room temperature at the same rate. This is labeled as precarbonized carbon (PCC). The precarbonized carbon was then subjected to chemical activation. In chemical activation process 50 g of the precarbonized material was agitated with 250 g of aqueous solution containing 85 % H₃PO₄ by weight. The ratio of chemical activating agent / pre carbonized carbon was fixed at 4.2. The chemical activant and pre carbonized carbon were homogeneously mixed at 85°C for 4 hours in a mixer. After mixing, the pre carbonized carbon slurry was dried under vacuum at 110°C for 24 hours. The resulting samples were then activated in a vertical cylindrical furnace under N₂ atmosphere at a flow rate of 100 ml / min. This is followed by heating to three different temperatures 700, 800 and 900°C to optimize the heat treatment. This was done at a heating rate of 5°C/min using a programmer and it was then maintained at a constant temperature for one hour before cooling. After cooling, the activated carbon was washed successively for several times with hot water until the pH becomes neutral and finally with cold water to remove the excess phosphorous compounds. The washed samples were dried at 110°C to get the final product. The samples heated at activation temperatures 700, 800 and 900°C were labeled as C700, C800 and C900.

2.3. CHARACTERISTICS OF ACTIVATED CARBON

CHEMICAL CHARACTERISTICS OF ACTIVATED CARBON

The activated carbon C900 prepared in this laboratory was used in this study. The chemical characteristics of the carbon C900 as illustrated in Table 1 are carbon 48.45%, Hydrogen 0.7%, Nitrogen 0.1%, and bulk density 0.405 g / cc. Samples were sieved to the size 600 μ m. The dried samples were stored for further analysis such as N₂ adsorption – desorption isotherms, FT-IR technique and surface morphology.

2.2.3 SURFACE MORPHOLOGY

Surface morphology carried out on the samples of RHAC before and after chemical activation and on organism immobilized carbon was done using Leo-Jeol scanning electron microscope. The carbon samples were coated with gold by a gold sputtering device for a clear visibility of the surface morphology.

2.2.4 FT-IR STUDIES

Perkin Elmer infrared spectrometer was used for the investigation of the surface functional groups. The carbon samples were mixed with KBr of spectroscopic grade and made in the form of pellets at a pressure of about 1MPa. The pellets were about 10mm in diameter and 1mm thickness. The samples were scanned in the spectral range 4000 – 400 cm⁻¹.

2.2.5. SOURCE OF RAW WASTEWATER:

The wastewater used in the present investigation was obtained from a tannery processing raw skins into semi finished leather. The steps involved in the process are soaking, liming , pickling and tanning. The wastewater from soaking and pickling operations were collected in a separate drain. The coarse solids

such as fleshing , trimmings and hair are screened through a metal screen of aperture 5mm. The screened effluent was collected in a tank.

2.2.6. PRIMARY CLARIFICATION

The combined soak and pickle wastewater were flash mixed with alum at a dose of 900 mg/l at a strength of 3% at 100rpm for 2 minutes. The coagulated wastewater was flocculated at 20 rpm for 15 minutes. It was allowed to stand for 2 hours in a quiescent condition. The supernatant liquor was siphoned off without disturbing the sludge interface.

2.2.7. SAND FILTER

A sand filter was used with diameter of 6 cm and height 30cm. It consisted of 2.5 cm layer of gravel (diameter 5mm) separated by a 2.5cm layer of gravel (diameter 3 mm). This was followed by a 10 cm layer of coarse sand (diameter 1mm). A 2.5 cm void space was left at the base to facilitate aeration of the system . The anaerobically treated sewage was distributed onto the surface of the top gravel layer through a PVC pipe (inner diameter 10mm) perforated with 0.8mm diameter holes. Water was drained from the base of the filter through a 10mm wide slit which was open to the air.

BATCH STUDIES ON FENTON OXIDATION OF SOAK LIQUOR

The sand filtered soak liquor was used for catalytic oxidation . The dissolved organics in the soak liquor was oxidized using air of volume 1.2 l/hr at a pressure 0.6 kg/m². The oxidation reaction was carried out with initiators H₂O₂ and FeSO₄ and meso porous ac activated carbon as the heterogeneous catalyst The experiment was carried out with different amounts of H₂O₂ (0.02 ; 0.04 , 0.06; and 0.08 ml/l) and different concentration of ferrous ion (5 , 10 , 15 , 20 mg/l) while RHAC (10 g/l) was fixed. The

oxidation reaction was continued for 24 hours. Aliquot of samples were withdrawn for every one hour, and the samples were analysed for pH, COD, TOC and dissolved protein.

2.2.8. FENTON ACTIVATED CARBON CATALYTIC OXIDATION (FACCO)

REACTOR

The reactor used in this study had a total volume of 720 ml and working volume of 356 ml, with dimensions of 5.5 cm diameter and height of 30 cm. It consisted of 2.5 cm layer of gravel (diameter 5mm) separated by a 2.5cm layer of gravel(diameter 3 mm). This was followed by a 10 cm layer of coarse sand (diameter 1mm). A 2.5 cm void space was left at the base to facilitate collection of the filtered water. The collection system consisted of header and laterals. The header was of diameter 10mm and laterals of diameter 5mm. The laterals were perforated with 0.8mm diameter holes. The reactor was filled with mesoporous activated carbon to a bed height of 15 cm. The size of carrier particles and dimensions of FACCO reactor used in this study were arbitrarily chosen for ease of observation. The oxygen required for the oxidation of organics in wastewater was supplied in the form of air at a pressure of 0.6 kg/cm² through an air diffuser placed in the carbon bed. The sand filtered sewage was distributed onto the surface of the carbon bed via a PVC pipe (10mm) perforated with 0.8mm diameter holes. The sand filtered sewage was fed to the PVC distributor using a peristaltic pump (Watson Marlow). The temperature was maintained at 30±1°C in order to minimize the change in water quality by temperature fluctuation. Treated salt laden wastewater was drained from the base of the filter through a 10mm wide slit which was open to atmosphere. The FACCO reactor was cleansed by pumping at least two void volume of sand filtered waters before each sewage sample was tested. One void volume of treated wastewater was discarded during test run.

2.2.9. CHEMICAL DOSING

The sand filtered wastewater was dosed with ferrous iron 100 mg/l in the form of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and Hydrogen peroxide 0.01ml/l at a strength of 1 % v/v solution. The contents were agitated for 15 minutes inorder to facilitate mixing. The wastewater dosed with Fenton reagent was allowed to distribute over FACCO reactor.

Physico-chemical analysis of the wastewater

pH, BOD_5 (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), DOC (Dissolved Organic Carbon), dissolved protein , TDS (Total dissolved solids) were determined in fresh water sample , coagulated , sand filtered and FACCO treated wastewater samples. COD measurements were used to determine removal efficiency of organics during chemical oxidation in Fenton process.

III Results and discussion

3.1. CHARACTERISTICS OF CARBON

Rice husk based activated carbon (RHAC) has been considered in the present investigation for its physico – chemical and electrical properties(20,21) for the generation of hydroxyl radicals from molecular oxygen that are considered to have the highest oxidation potential for dissolved organics in wastewater.

3.1.1 PORE SIZE AND PORE DISTRIBUTION

Figure 1 shows the pore size distribution of activated carbon samples. The average pore size distribution is dependent mainly on the concentration of chemical impregnation and the heat treatment temperature. The pore diameter was observed to increase with activation temperature up to 800°C and the same was reversed at a further higher temperature of 900°C. The activated carbon obtained at 700°C characterized

by an average pore diameter of 38.8Å had a marginal increase in pore diameter to 39.36Å at 800°C. The narrow increase in pore diameter suggests that up to 800°C certain unorganized carbons or residual tar materials are expelled by opening of closed pores [8] and existing pores are widened into larger pores of small magnitude through gasification of carbons in the pore walls having labile carbon structure [9]. But the decrease in the pore diameter of C900 is due to the suppression of the pore widening of stable carbon structure [10] formed during pre carbonization process. The surface morphology of the pre carbonized carbon (PCC) and activated carbon C900 is shown in Fig. 2.

3.1.2 FT-IR SPECTRA

The infrared spectroscopic data in Fig. 3 provides information on the chemical structure of activated carbon samples . All the carbon samples show a wide band at about 3350 – 3425 cm⁻¹. The O-H stretching mode of hexagonal groups and adsorbed water can be assigned to the occurrence of this band. The position and asymmetry of this band at lower wave numbers indicate the presence of strong hydrogen bonds [11]. A weak band at 3780 – 3786 cm⁻¹ may be assigned to isolated O-H group. The samples C700, C800 and C900 show absorption bands due to aliphatic C-H at 2920 cm⁻¹ and this is found to be low in the precarbonised sample (PCC). A very small peak near 1700 cm⁻¹ is assigned to C=O stretching vibrations of ketones, aldehydes, lactones or carboxyl groups. The weak intensity of this peak for all the carbons indicates that the precarbonized and phosphoric acid activated carbons contain a small amount of carboxyl group. The band near 1615 cm⁻¹ in PCC is due to aromatic stretching vibration of C=C enhanced by polar functional group. But this is not found in any of the carbons heat treated at high temperature. A broad band between 1250 and 1000 cm⁻¹ is observed. The broad peak shouldered at 1180

cm^{-1} for C700, C800 and C900 indicates the presence of phosphorous content of the samples. The occurrence of these bands are usually found with carbons activated with phosphoric acid (20,21). Appearance of bands in these regions may also be assigned to C-O stretching in acids, alcohols, phenols, ethers and esters. But in this case these bands cannot be assumed to be due to C-O stretching because the bands in these regions may disappear at higher temperatures. The appearance of these bands is therefore only a characteristic for phosphorous and phospho-carbonaceous compounds [12]. The appearance of a peak at 1190 cm^{-1} is mainly assigned due to phosphates arising due to phosphoric acid activation and the band at 1203 cm^{-1} is due to phosphoric acid esters which have been reported previously[13,14]. As reported by Puziy et al. [15] the appearance of bands at $900 - 1300 \text{ cm}^{-1}$ could be due to phosphorous species resulting from the phosphoric acid activation. The peak at 1180 cm^{-1} may be assigned to the stretching mode of hydrogen-bonded P=O to O-C stretching vibrations in P-O-C (aromatic) linkage and to P=OOH [22,23]. The shoulder at $1080 - 1070 \text{ cm}^{-1}$ may be ascribed to ionized linkage $\text{P}^+ - \text{O}^-$ in acid phosphate esters [16,17] and to symmetrical vibration in a chain of P-O-P (polyphosphate) [18,19].

3.1.3. PRIMARY CLARIFICATION

The primary treatment of wastewater reduced the dissolved protein by about 50% besides reducing the suspended solids by 90%. The BOD of the wastewater was in the range 360 to 720 mg/l and COD was in the range 1200-2300 mg/l and the BOD/COD ratio was brought down to 0.31. The decrease in biodegradability of wastewater is due to the elimination of dissolved protein during primary treatment with alum. It is known that Al^{3+} has remarkable affinity with albumin and globulin with stability constant

3.1.4. SAND FILTRATION

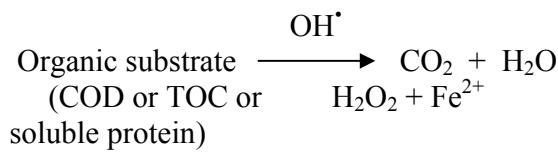
The filtration of wastewater through sand filter was able to retain the biodegradability index at 0.31 while it was able to reduce the BOD to 138-550 mg/l and COD to 528 – 1632 mg/l. Sand filtration of the primary coagulated wastewater was able to attract a removal of dissolved protein by 22%. The results indicate that the sand grains are able to strain the protein complex formed with aluminium ion. The positively charged matrix of the sand filter is very much efficient to remove the negatively charged protein complex. This suggests that the periodic cleaning of the sand grains or replacement of sand filter is highly desirable for the treatment of wastewater.

3.1.5. BATCH STUDIES ON FENTON OXIDATION OF SOAK LIQUOR

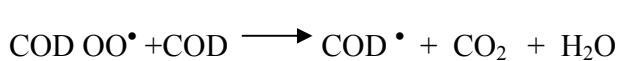
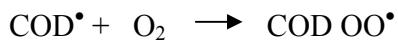
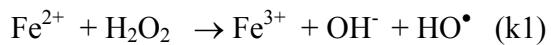
Oxidation of dissolved organics in wastewater using Fentons reagent (Hydrogen peroxide and ferrous sulphate) involves the following steps.

- Generation of hydroxy radicals from Fe^{2+} and H_2O_2
- Oxidation of dissolved in wastewater organics by hydroxy radicals and formation of end products like CO_2 and H_2O
- Oxidation of Fe^{3+} back to Fe^{2+} to sustain the reaction

The dissolved organics in soak liquor is expressed in terms of COD or TOC or dissolved protein. The oxidation of dissolved organics in soak liquor is represented by



The destruction of organics in wastewater as COD is shown as below which is followed by the following reaction



The rate of destruction of dissolved organics could be represented as

$$\begin{aligned} r &= \frac{-d[\text{dissolved organics}]}{dt} \\ &= K_o \exp [-k/RT] [\text{COD or TOC or Protein}]^m [\text{FeSO}_4]^n \\ &\quad [\text{H}_2\text{O}_2]^p \end{aligned}$$

For a given temperature and oxygen partial pressure the pseudo m^{th} order expression is

$$d(\text{COD}/dt) = K(\text{COD})^m$$

Where

$$K = K_o \exp [-K/RT] [\text{FeSO}_4]^p [\text{H}_2\text{O}_2]^q$$

The data presented could be well fitted to $m=1$ for a given a temperature and time , then

$$-d(\text{COD})/dt = K[\text{COD}]$$

$$\text{and hence } \ln \{(\text{COD}_o)/(\text{COD}_t)\} = Kt$$

The destruction of dissolved organics in soak liquor follows two consecutive steps . The first step proceeds at a faster reaction rate while the second step occurs at a slower rate. The faster rate of reaction is due to the reaction between hydroxy radical and organic substrate in the wastewater. The decrease in rate of reaction , even though the substrate is not exhausted , is due to deactivation of Fe^{2+}

formed . It is expected that hydroxyl radicals are active enough to react with Ferrous ion (reaction 1) at a rate of $3.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ which is about 5×10^7 times faster than the second reaction. The oxidation of Fe^{2+} to Fe^{3+} is accompanied with the formation of hydroxyl ions owing to the reaction as shown below. The hydroxyl ions tend to form complex with the ferric ion making it to be inactive. This could be the reason for retarded rate of second step.

The present study shows that accelerated rate step has rate constant for the destruction of COD was $9.46 \times 10^{-1} \text{ min}^{-1}$ and rate of slower step was $1.12 \times 10^{-2} \text{ min}^{-1}$ (fig 4). This appears that the overall rate and sustainability of the reaction is controlled by the second step whose contribution towards COD removal is only 20% while removal in the first step was 31.5% (figure 5) . Hence, a strategy was necessary to increase the rate of second step. The rate of reaction in the second step was considered to increase in two ways.

1. Preventing the complexation reaction of Fe^{3+} with hydroxyl ions
2. The formation of hydroxyl ion is to be prevented

In the present study the hydroxyl radicals generated by the first reaction was prevented from oxidising Ferrous ion by immobilising them in an electron rich meso porous carbon (RHAC) matrix. In addition to act as a carrier matrix RHAC also performs the following activities. RHAC is an adsorbent for the adsorption of pollutants in wastewater to be oxidized . The hydroxyl radicals and pollutants are accommodated at the proximate position onto the solid support so that oxidation of pollutants take place at a faster rate. The oxidized product are desorbed and they can diffuse to the bulk phase and the active sites of RHAC continue to adsorb hydroxyl radicals and there of for further oxidation. Hence, rate of first and second steps are expected to be high. The figure 4 illustrates the effect of RHAC for increasing the rate of reaction by preventing the deactivation of ferrous ion.

The following reactions are expected to take place in the degradation of COD in salt laden wastewater



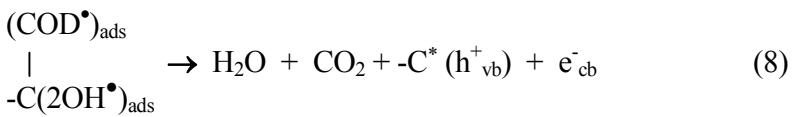
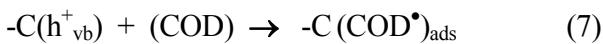
Hydroxy radicals generation from molecular oxygen



Hydroxy radicals generation from hydroperoxy radical



Destruction of COD of wastewater



where

h^+_{vb} - electron hole in the valence band

e^-_{cb} - electron in the conduction band

$-\text{C}^*$ - refers to the excited carbon active site

Effect of pH :

The effect of pH on Fentons oxidation of COD of salt laden wastewater was carried out in the pH range 2.5 to 7.0 at a Fe^{2+} 15 mg/L and H_2O_2 0.04 mg/L . The percentage removal of COD was 81.25% and the rate of removal was $6.9 \times 10^{-2} \text{ hr}^{-1}$ at pH 3.5 and the parameters were respectively 48% and $2.8 \times 10^{-2} \text{ hr}^{-1}$ at pH 7.0. The figure 6 illustrates that the optimal range of pH for operating Fenton's oxidation could be 3.0-3.5. This optimal pH range was supported by many of the researchers for oxidation of varied nature of chemicals present in wastewater system. The efficiency of Fenton's oxidation decreased with pH which could be due to precipitation of Fe^{3+} by the available hydroxyl ions at high pH. In this form, iron decomposes H_2O_2 into oxygen and water and consequently the oxidation rate decreases because less hydroxyl radicals are available. More over at high pH values the complexation of Fe^{2+} as $[\text{Fe} (\text{II}) (\text{H}_2\text{O})_6]^{2+}$ is favoured which reacts more slowly with H_2O_2 than $[\text{Fe} (\text{II}) (\text{OH}) (\text{H}_2\text{O})_5]^{2+}$, thus producing less amount of OH . The effect is reversed at low pH, the surplus hydrogen ions favor the back ward reaction leading to increase in Fe^{3+} concentration



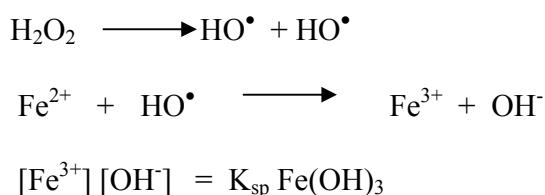
Therefore, the conversion of Fe^{3+} to Fe^{2+} is inhibited , and thus the concentration of Fe^{2+} available for generation of hydroxyl radical is retarded.

Effect of H_2O_2 on Destruction on Dissolved Organics in wastewater

The variation of percentage removal of COD with time for various concentration of H_2O_2 at constant catalytic concentration is presented in fig . A 52% of COD was removed in 24 hours with out RHAC (it was 69% with RHAC) on the application of H_2O_2 at concentration 0.04ml /l to soak liquor, while it was reduced to 34% when H_2O_2 was used at 0.06 ml/l, 0.02 ml/l of H_2O_2 registered only 12% removal. Since H_2O_2 was performed as an initiator only, an optimum amount of 0.04 ml/l of H_2O_2 was sufficient for the

oxidation of organics in soak wastewater. TOC removal was 31% for 0.04 ml of H₂O₂ and 15% for 0.02ml/l of H₂O₂. Percentage removal of TOC with time is shown in fig 7. Protein removal was 72% for 0.04ml/l of H₂O₂ and it was only 42% for 0.02ml/l of H₂O₂. The percentage removal of protein with time was shown in fig at normal temperature.

Rate of removal of COD for different concentrations of H₂O₂ at the fixed concentration of the catalyst (Fe²⁺) at 15 mg/l is given in table. Rate of removal of COD is $2.07 \times 10^{-4} \text{ min}^{-1}$ for 0.04 ml/l of H₂O₂ and it decreased to $1.47 \times 10^{-4} \text{ min}^{-1}$ for 0.08 ml/l of H₂O₂. The reason for retarded rate of decomposition of COD at high concentration of H₂O₂ is that the generated hydroxyl radicals form hydroxyl ions which in turn helps to precipitate Fe³⁺ ions. As a result of this the concentration of iron is depleted in the system leading to decrease in the rate of removal of dissolved organics in wastewater. The above sequence are in accordance with the following equation.



In other words destruction of the catalyst took place at higher H₂O₂ concentration, brownish yellow precipitate was observed for doses beyond 0.04 ml/l. Hence, 0.04 ml/l of H₂O₂ was considered to be an optimum dosage because of poisoning of catalyst was not observed upto 0.04ml/l.

Effect of Dosage of catalyst

Rate of oxidation of COD at the constant dosage of H₂O₂ (0.04ml/l) and varied catalyst concentration (5, 10 , 15, 20 mg/l) are presented in figure 8. It was observed from the table that the rate of oxidation was

maximum at 15 mg/l of Fe^{2+} and the rate decreased beyond 15 mg/l. This could be due to the fact that a greater added dose of Fe^{2+} (for a given hydrogen peroxide concentration) accelerates the rate of decomposition of the hydrogen peroxide by reaction 4, generating perhydroxyl radicals. Lower doses of Fe^{2+} favor the reaction to generate OH^\bullet that are more reactive than the HO_2^\bullet radicals. Beyond this concentration (15 mg/l) destruction of the catalyst occur on account of instantaneous formation hydroxyl ion in accordance with the following reaction



This takes place at faster rate ($3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) than the formation of hydroxyl radical from Fe^{2+} and hydrogen peroxide ($70 \text{ M}^{-1} \text{ s}^{-1}$). The reaction 3 forms the greater quantity of Fe(OH)_3 nuclei on exceeding the solubility product of ferric hydroxide (K_{sp}). Hence, an optimum concentration of iron catalyst for the removal of organics in soak liquor was selected as 15 mg/l. The variation of percentage removal of TOC, COD and dissolved protein with time for various concentration of Fe^{2+} at constant H_2O_2 concentration are presented in Figure.

Treatment of soak liquor in RHAC packed bed reactor using Fenton's reagent:

The coagulated-flocculated and Fenton reagent added SDW was applied at a surface loading rate of $1.46 \text{ m}^3/\text{m}^2/\text{day}$ and volumetric loading rate of $0.83 \text{ m}^3/\text{m}^3/\text{hr}$ to the reactor packed with mesoporous activated carbon. Table 2 reveals the characteristics of FACCO treated wastewater. The dissolved protein was eliminated preferentially by about 94%. The BOD content of wastewater was reduced to 28 mg/l and COD to 219 mg/l. The halophile content of wastewater was reduced considerably to a level of 200 CFU/ml.

4.0. SUMMARY AND CONCLUSION

The present investigation draws the following conclusion

- i. The salt laden wastewater discharged from leather industries is less amenable to biological treatment despite high BOD/COD ratio which is due to the presence of high salinity.
- ii. Primary clarification of wastewater removes suspended solids and less of dissolved organics
- iii. Fenton's reagent , a mixture of hydrogen peroxide and ferrous iron, is capable of releasing hydroxy radicals which may take part in oxidation of dissolved organics in wastewater
- iv. Fenton's reagent added salt laden wastewater was further catalytically oxidized in meso porous activated carbon packed column/
- v. The oxidation of dissolved organics by Fenton's reagent resulted in the percentage removal of BOD, COD and Dissolved protein were $81.33 \pm 9.06, 7$
- vi. 8.58 ± 15.27 and 88.13 ± 8.98 respectively.

V. References

1. Ahmet Uygur, Specific nutrient removal rates in saline wastewater treatment using sequencing batch reactor , *Process Biochemistry* 41 (2006) 61-66.
2. Eilbeck, W.J., Mattoc G. Chemical Processes in wastewater treatment.England: Ellis Horwood Series , 1987.
3. Glaze , W.H., Kang, J.W. & Chapin, D.H. The chemistry of water treatment involving ozone, hydrogen peroxide and ultraviolet radiation . Ozone: Sci. Technol., 1987, 9, 335-342.
4. Bigda RJ. Consider Fenton's chemistry for wastewater treatment. *Chem. Eng.Prog* 1995; 91: 62-6.
5. J.Beltran de Herdia, J.Torrgrosa, J.R. Dominguez, J.A.Peres, Kinetic model for phenolic compound oxidation by Fenton's reagent *chemosphere* 45 (2001) 85-90.
6. C.M.Miller, R.L.Valentine , Mechanistic studies of surface catalyzed H_2O_2 decomposition and contaminant degradation in the presence of sand *Water Res.* 33 (1999) 2805- 2816.
7. Sekaran, G., Gnanamani, A., Yogesh, P., 2004. Preparation of biocatalyst for the removal of dissolved organics in wastewater. Indian Journal of Chemical Technology 11, 95-102.

8. John kennedy, L, Mohan das, K., Sekaran, G., Integrated biological and catalytic oxidation of organics/inorganics in tannery wastewater by rice husk based mesoporous activated carbon – *Bacillus sp.* *Carbon* 42 (2004) 2399-2407.
9. Oh GH, Park CR. Preparation and characteristics of rice straw based porous carbons with high adsorption capacity. *Fuel* 2002; 81: 327-36.
10. Yulu Diao, Walawender WP, Fan LT. Activated carbons prepared from phosphoric acid activation of grain sorghum. *Bioresource Technology* 2002; 81: 45-52.
11. Marsh H, Kuo K. Kinetics and catalysis of carbon gasification In: Marsh H, editor, *Introduction to carbon science*, London:Butterworth,1989, pp107-51.
12. Zawadzki J. Infrared spectroscopy in surface chemistry of carbons. In: Thrower PA, editor, *Chemistry and physics of carbon* Vol. 21, Newyork: Marcel Dekker, 1989; pp.147 – 386
13. Jagtoyen M, Thwaites M, Stencel J, Mc Enaney B, Derbyshire F. Adsorbent carbon synthesis from coals by phosphoric acid activation. *Carbon* 1992; 30(7):1089-96.
14. Solum MS, Pugmire RJ, Jagtoyen m, Derbyshire F. Evolution of carbon structure in chemically activated wood. *Carbon* 1995;33(9):1247-54.
15. Puzy AM, Poddubnaya OI, Martinez-Alonso, Suarez-Garcia F, Tascon JMD. Synthetic carbons activated with phosphoric acid I. Surface chemistry and ion binding properties. *Carbon* 2002;40:1493-1505.
16. Bellamy LJ. The infrared spectra of complex molecules. New York: Wiley, 1954.
17. IR Wizard, <http://www.chem.uni-potsdam.de/tools/index.html>.
18. Socrates G. Infrared characteristic group frequencies: New York; Wiley, 1994.
19. Corbridge DEC. Infrared analysis of phosphorous compounds. *J Appl Chem* 1956;6:456-65.
20. Xie R, Qu B, Hu K, Dynamic FTIR studies of thermo oxidation of expandable graphite based halogen free flame retardant LLDPE blends. *Polym Degrad Stabil* 2001;72:313-21.
21. Bourbigot S, Le Bras M, Delobel R. Carbonization mechanisms resulting from the intumescence. II. Association with an ethylene terpolymer and the ammonium polyphosphate pentaerythritol fire retardant system. *Carbon* 1995;33(3):283-94

Table 1. Characteristics of rice husk based activated carbon of sample C900

S. No	Parameters	Values
1	Carbon (%)	48.45
2	Hydrogen (%)	0.7
3	Nitrogen (%)	0.1
4	Others(%)	42.61
5	Bulk density (g/ml)	0.405
6	Surface Area (BET), m ² /g	420

Table 2 : Effect of H₂O₂ on removal of Protein, COD and TOC at constant Ferrous ion Dosage 15mg/l

H ₂ O ₂ concentration ml/l (30% w/v)	Rate of Removal of protein in min ⁻¹	Rate of Removal of COD in min ⁻¹	Rate of Removal of TOC in min ⁻¹
0.02	1.74×10^{-4}	8.83×10^{-5}	4.96×10^{-5}
0.04	6.33×10^{-4}	2.49×10^{-4}	2.19×10^{-4}
0.06	5.42×10^{-4}	1.99×10^{-4}	6.96×10^{-5}
0.08	3.22×10^{-4}	1.47×10^{-4}	4.19×10^{-5}

Table 3: Percentage removal of pollution parameters at different stages of treatment

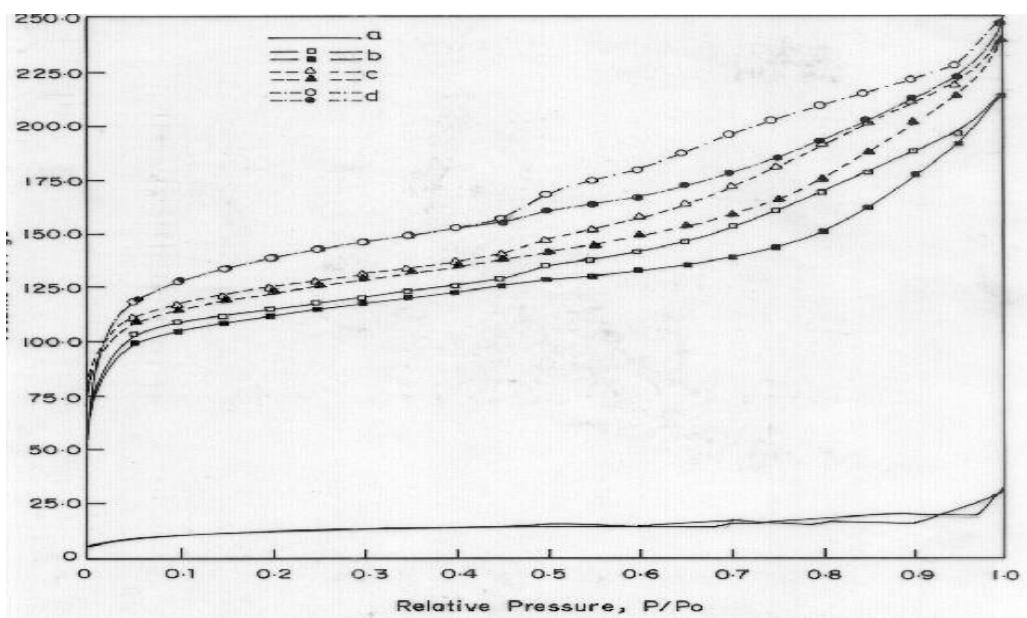


Figure 1. Pore size distribution in meso porous activated carbon

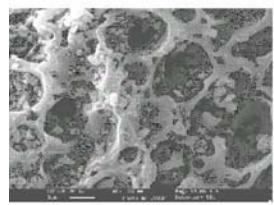
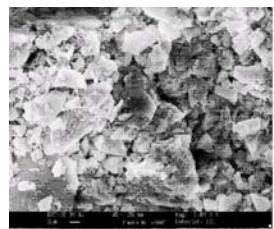


Figure 2. Scanning Electron Micrograph of Meso porous activated carbon

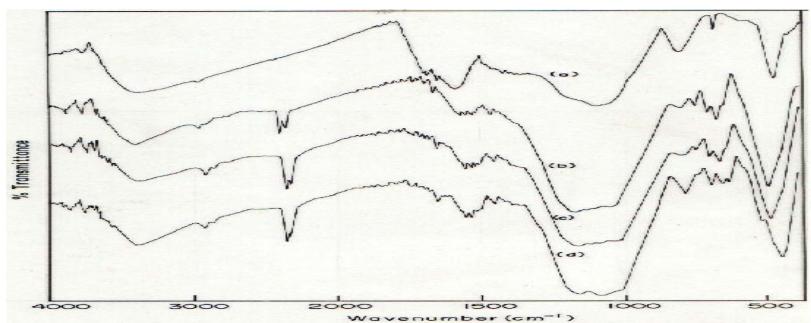


Figure 3. FT-IR spectra meso-porous activated carbon

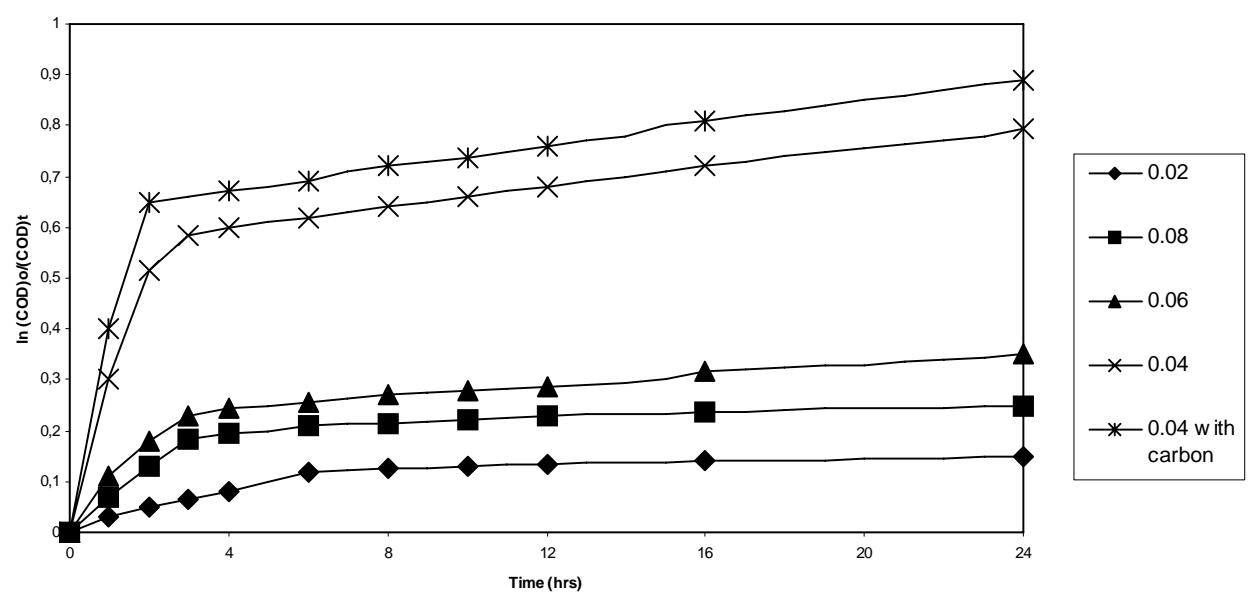


Fig. 4. COD Destruction

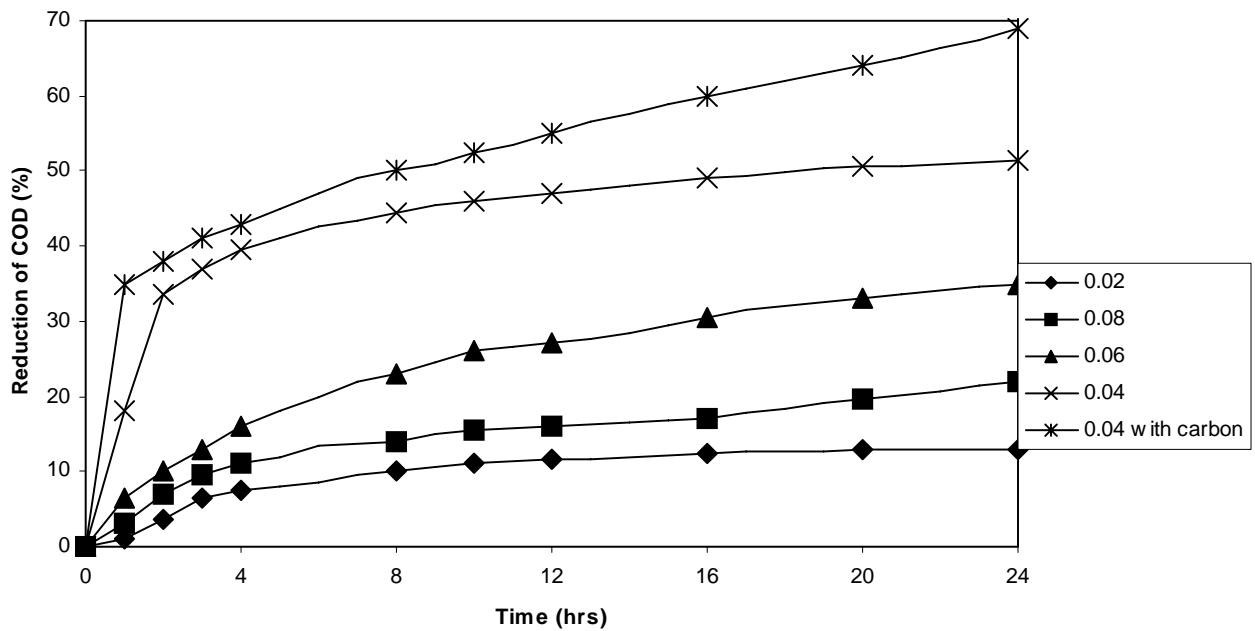


Fig. 5. Percentage removal of COD

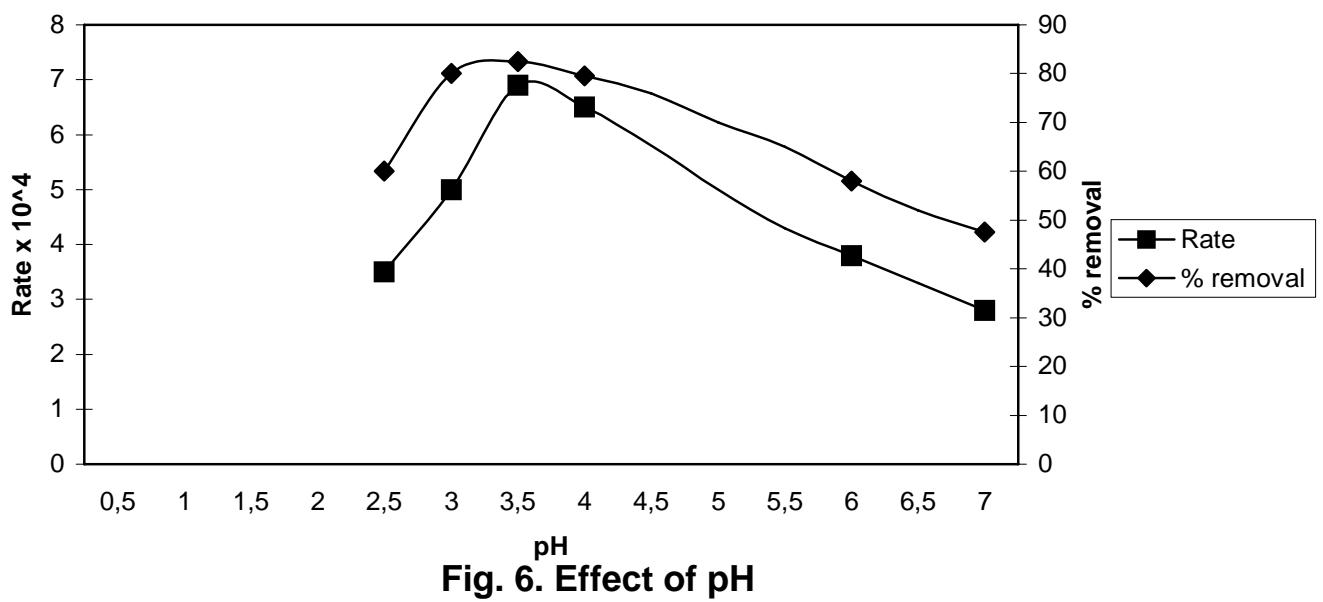


Fig. 6. Effect of pH

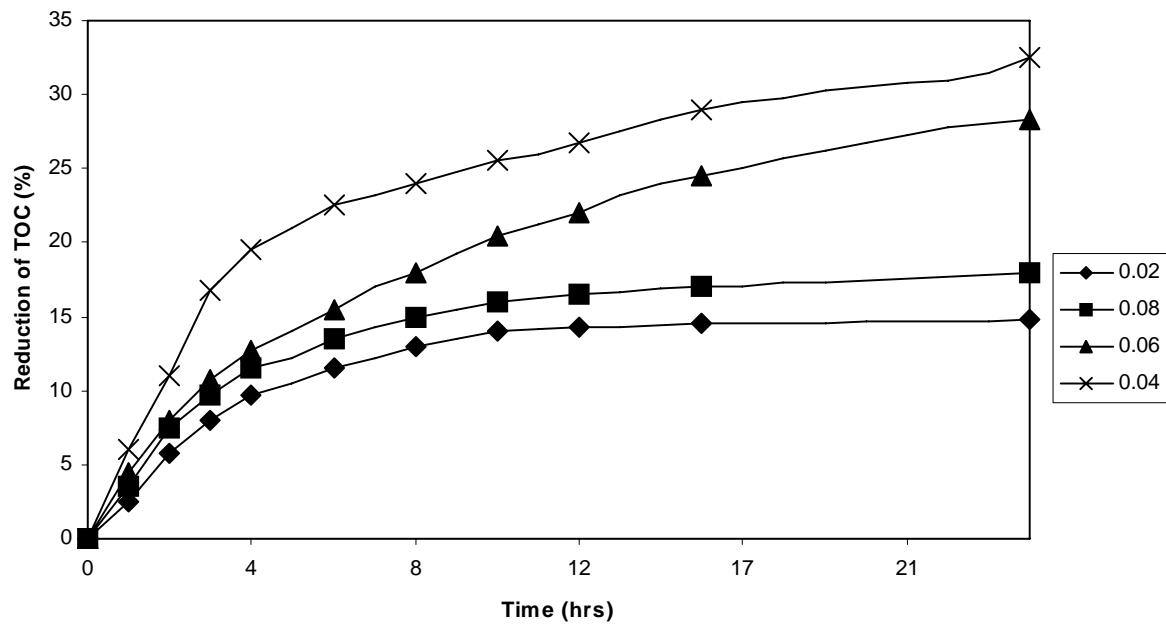


Fig. 7. Percentage removal of TOC

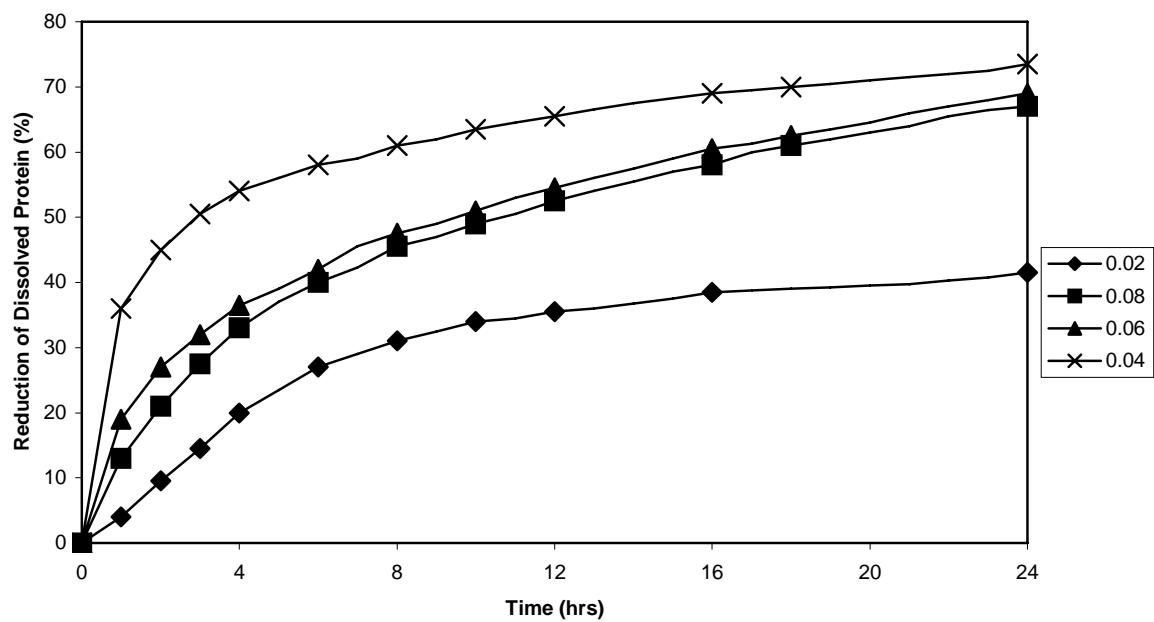


Fig. 8. Percentage removal of Dissolved protein

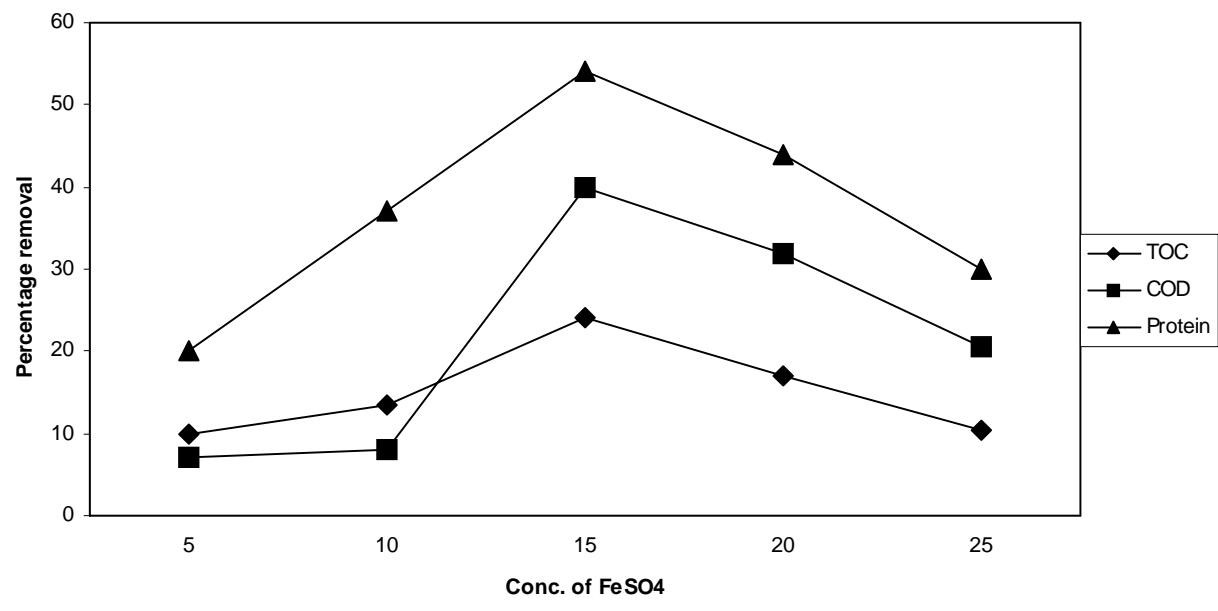


Fig. 9. Effect of FeSO₄