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Performance Evaluation studies of Fenton Oxidation on Different Dyes and its Optimization of Experimental Parameters

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Abstract

This study was carried out to identify the best dye showing better removal of COD by the Fenton oxidation process. Further, optimization of experimental parameters was done for the dye showing better removal efficiency. The mode of study conducted to carry out this study was batch reactor. Four batch studies were carried out with the Fenton oxidation process to determine the COD removal efficiency of Rhodamine-B, Malachite Green, Crystal Violet and Methylene blue. At the end of contact period of one hour, COD was determined for all the dyes and Methylene Blue was found to be the better performing dye with the Fenton oxidation process. The optimization of experimental parameters like pH, Concentration of hydrogen peroxide ,concentration of $FeSO_4$ and Contact time was done for the Methylene blue .And it was found that the COD removal efficiency was satisfactory at pH 3, 30 minutes contact time, 10 mL of Hydrogen peroxide and 50 mg/L of $FeSO_4$

1. Introduction

A dye is generally a substance that bears an affinity to the substrate to which it is being applied. It is often applied in aqueous solution. It requires a mordant to improve its binding with the fabrics .It appears to be coloured because they absorb some wavelengths of light in particular than other. Various industries discharge wastewaters like chemical, refineries, textile, plastic and food processing plants .These wastewaters include dyes as residues which cause many hazards. Such residual dyes are non-biodegradable due to their complex molecular structures making them more stable and hard to biodegrade. They cause water pollution and also pose a serious threat to environment. These coloured stuffs along with being aesthetically displeasing also inhibit sunlight penetration into water bodies and thus affect aquatic ecosystem. Many of them are also toxic in nature and can cause direct destruction or can affect catalytic capabilities of various microorganisms [1, 2]

The main source of discharge of dyes is textile industries where they are used to colour products. Today there are over 1, 00,000 dyes for commercial use and around 700 tons of dyestuffs are produced annually. The types of dyes are mainly basic dyes, acid dyes, direct dyes, reactive dyes, mordant dyes, azo dyes, disperse dyes and sulphur dyes .Most of the dyes are toxic and have carcinogenic properties so they make water bodies inhibitory to aquatic systems. They don't fade by water or sunlight and owing to their complexity in structures; they can't be adequately treated in conventional treatment plants for waste waters. There are in numerous harmful effects of dyes on ecosystem such as:

(1) They pose acute as well as chronic effects on most of the exposed organisms. These effects vary depending on the time of exposure and the concentration of dyes.

(2) They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological activities.

(3) They are highly visible and even a minor amount may cause abnormal coloration of water bodies which appears displeasing to eyes.

(4) They have complex molecular structures which makes them difficult to treat with common municipal treatment operations.

(5) Consume dissolved oxygen and affect aquatic ecosystem.

To overcome the ill effects of dye waste water, many treatment methods have been adopted. They are adsorption, Membrane separation process and Advanced chemical oxidation processes. The main disadvantage with the adsorption is that it is very difficult to regenerate the adsorbents [6, 16] and the membrane separation process is too costly. Advanced oxidation processes are commonly employed in the treatment of the recalcitrant. These processes have been suggested for the partial or completely removal of pollutant in the waste water or their transformation in to less toxic and more biodegradables products (Glaze et al). Fenton oxidation process which is an advanced oxidation process is capable of producing hydroxyl radicals at acidic pH with the help of hydrogen peroxide and ferrous ions which are Fenton‘s reagent. The hydroxyl radicals have a higher oxidation potential of 2.8V and it can degrade the organic content easily. The advantage with the chemical oxidation process is that the time consumption is very less, faster reaction and less cost when compared with the membrane separation process [3, 11] .Hence, advanced chemical oxidation process is adopted to degrade the dye effluent in terms of COD removal :

$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + OH^-$

$OH^- + RH \longrightarrow CO_2 + H_2O$

$H_2O2 + Fe(OH)_3 \longrightarrow H_2O_2 + O^\cdot + Fe(OH)_3$

2. Material and Methods

The most commonly used dyes in Industries were selected for the study and the dyes were Rhodamine-B, Malachite Green, Crystal Violet and Methylene blue. The dyes were purchased from Madurai. The synthetic solution of the dyes was prepared by dissolving accurately weighed one gram of selected dye in one litre of distilled water [17, 18].The synthetic solution thus prepared was stored as stock solution and the initial concentration of COD of thus prepared solution was determined.

All the chemicals use in this study were of analytical reagent (AR) grade and were supplied by Sigma Aldrich chemicals Ltd, India. Glassware used in the present study were manufactured by M/S Borosil Glass Works Ltd. (Bombay, India) and marketed under the brand name ‘Borosil’. They were washed with diluted sulphuric acid followed by distilled water and millipure water. The solutions of $Fe^{2+,}$ NaOH, H2SO4 were also prepared with the distilled water.

The initial concentration of COD of the dye samples was determined as per the standard procedure. The Chemical Oxygen Demand of the sample waste water was determined by closed reflux method.2 ml of the diluted sample of the wastewater was taken in COD cuvettes.1gm of mercuric sulphate ($HgSO_4$) was added to avoid the interference of chloride present in the both slurries and 3ml of COD acid was also added to both diluted slurries.1ml of standard potassium dichromate solution was added and mixed. The samples in the COD cuvettes along with the blank solution prepared with distilled water were refluxed in the COD digester for two hours at 150^0C. The reflux was allowed to cool in the room temperature after the refluxing period. The blank and samples were titrated against standard Ferrous Ammonium Sulphate using Ferroin indicator. The volume of the titrant required for the samples and the blank to change colour from the bluish green to wine red was noted :

$$\text{COD (mg/l)} = \frac{(A-B) X N X 8000}{\text{ml of sample}}$$

Where,

A = ml Fe $(NH_4)_2 (SO_4)_2$ (used for blank),

B = ml Fe $(NH_4)_2 (SO_4)_2$ (used for sample)

N = normality of Fe $(NH_4)_2 (SO_4)_2$

8000 = milli equivalent weight of oxygen x 1000ml/l

3. Results and discussion

3.1 Performance Evaluation studies of Different dyes

This study was carried out to identify the best dye showing better removal of COD by the Fenton oxidation process. The mode of study conducted to carry out this study was batch reactor. The batch reactor assembly consists of 500 mL beaker with an aerator for continuous stirring. Four batch studies were carried out. Batch study 1 was carried out to determine the COD removal efficiency of Rhodamine-B and Batch study 2 was carried out to determine the COD removal efficiency of Malachite Green as shown in Fig 3.1.

Fig 3.1 Reactor Setup for Malachite Green & Rhodamine-B

Batch study 3 was carried out to determine the COD removal efficiency of Methylene Blue and the last batch study was carried out to determine the COD removal efficiency of Crystal Violet as shown in Fig 3.2.

Fig 3.2. Reactor Setup for Methylene Blue & Crystal Violet

In all the four batch studies, the initial concentration of the dye was kept as 50 mg/L. 50 mg/L of $FeSO_4.7H_2O$ and 10 mL of hydrogen peroxide was added to the each reactor. The entire setup was then aerated for 60 minutes continuously. After the contact period the sample was taken out from each reactor and the same was analysed for COD concentration remaining in the solution.

From the result, it is found that the Methylene Blue has better COD removal efficiency. Further, the work has been continued to optimise the experimental parameters like pH, concentration of hydrogen peroxide, concentration of $FeSO_4$ and contact time.

3.2 Optimisation of Experimental parameters

3.2.1 Effect of pH

This batch study was carried out using the selected dye from the previous batch studies to analyse the effect of pH on the removal of COD. The batch reactor assembly consists of 500 mL beaker with an aerator for continuous stirring. The initial concentration of the dye was kept as 50 mg/L. Then, 50 mg/L of $FeSO_4.7H_2O$ and 10 mL of hydrogen peroxide was added to the reactor. The pH of the dye was varied as 2, 2.5, 3, 3.5 and 4 by adding HCl. The pH was varied till 4 as the Fenton process works good only in acidic condition ([]Hsing et al., 2007). The entire setup was then aerated for 60 minutes continuously. After the contact period the sample was taken out from each reactor and the same was analysed for COD concentration remaining in the solution as per the standard procedure

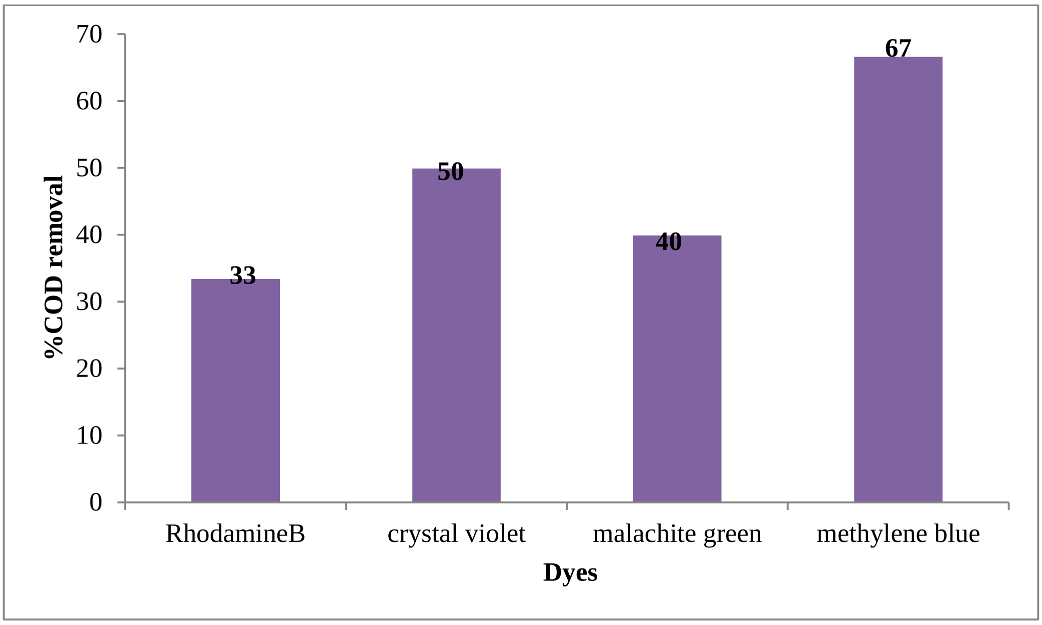

Fig 3.3. COD Removal Efficiency of Different Dyes

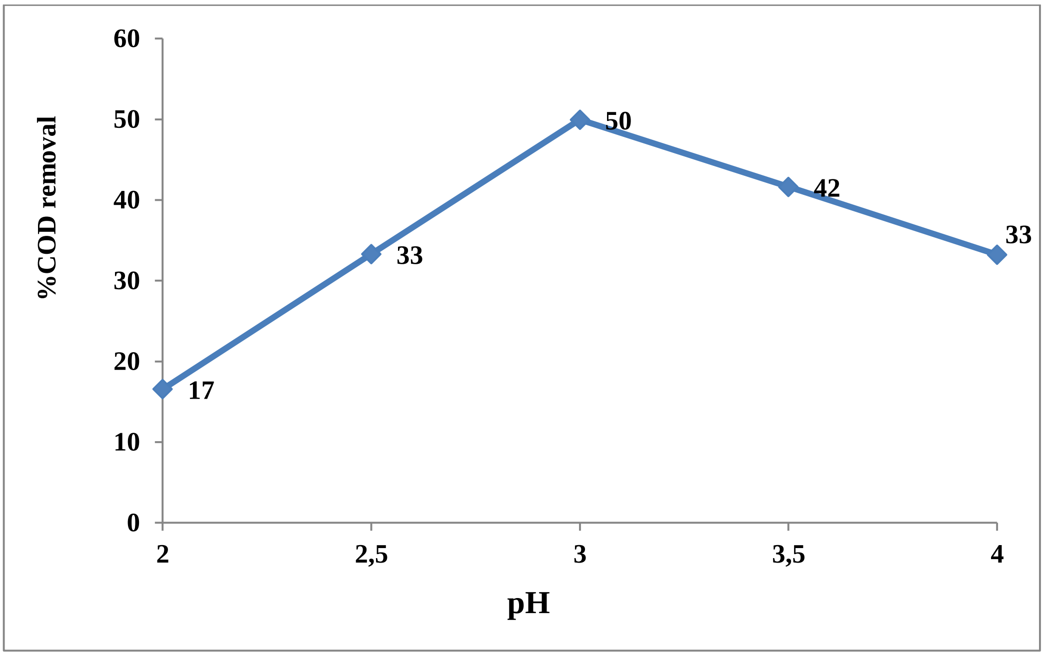

Fig 3.4. Effect of pH on the removal of COD of Methylene Blue

It is apparent from the figure 3.4, that the extent of COD removal decreased with increasing the pH and removal efficiency at pH 3 was 50% for Fenton, whereas it reduced after pH 3. It clearly implies that the hydroxyl radical generation will be far better at the acidic pH. The optimum pH was observed at pH 3.0 for both reactions. This is mainly caused by the fact that when pH is higher than 3, ferrous and ferric hydroxides are formed which inhibit the reaction between Fe^{2+} and H_2O_2 and thus the hydroxyl radicals production. On the other hand, at very lower pH, excessive H^+ reacts with H_2O_2 to produce H_3O_2+, which is stable and cannot react with iron(II) to form the HO• species[4,5,7,8].

3.2.2. Effect of $FeSO_4.7H_2O$

This batch study was carried out using the selected dye from the previous batch studies to analyse the effect of $FeSO_4.7H_2O$ on the removal of COD. The pH of the dye solution was maintained at the value of 3 which is obtained from the previous optimization study. The batch reactor assembly consists of 500 mL beaker with an aerator for continuous stirring. The initial concentration of the dye was kept as 50 mg/L. The concentration of $FeSO_4.7H_2O$ varied as 10, 20,30,40,50, 60 mg/L and 10 mL of hydrogen peroxide was added to the each reactor. The entire setup was then aerated for 60 minutes continuously. After the contact period the sample was taken out from each reactor and the same was analysed for COD concentration remaining in the solution as per the standard procedure. The effect of $FeSO_4.7H_2O$concentration on the COD removal through Fenton process was studied and the results are shown in figure 3.5. Experiments were carried out at pH 3 with the constant dose of 10 mL of H_2O_2. The$FeSO_4.7H_2O$ concentration varied in the range from 10 to 60 mg/L. It was observed that the amount of ferrous ion is one of the main parameters influencing the Fenton process. The COD Removal was increased from 13 to 53 as the concentration of ferrous ion was increased from 10 to 50 mg/L.

3.2.3. Effect of H_2O_2

This batch study was carried out to analyse the effect of H_2O_2 on the removal of COD in Methylene Blue. The pH of the dye solution was maintained at the value obtained from the previous optimization study. The batch reactor assembly consists of 500 mL beaker with an aerator for continuous stirring. The initial concentration of the dye was kept as 50 mg/L. The concentration of $FeSO_4.7H_2O$ was kept as the same value optimized in the previous study and the dosage of hydrogen peroxide varied as 2, 4,6,8,10,12 mL and it was added to the each reactor. The entire setup was then aerated for 60 minutes continuously. After the contact period the sample was taken out from each reactor and the same was analysed for COD concentration remaining in the solution as per the standard procedure. The effect of H_2O_2 dose on the COD removal through Fenton process was studied and the results are shown in figure 3.6. Experiments were carried out at pH 3 with the constant dose of 50 mg/L FeSO4. The H_2O_2 concentration varied in the range from 2 to 12 ml. As shown in figure 3.6, the COD removal efficiency increased from 8.4 to 50 is a consequence of increasing H_2O_2 dosage from 2 to 10 mL. The further increase of H_2O_2 from 10 to 12 mL caused no significant change in COD removal. This is a common behaviour in the Fenton's process, which might be due to the hydroxyl radical scavenging effect of H_2O_2. [13, 14, 15, 16]

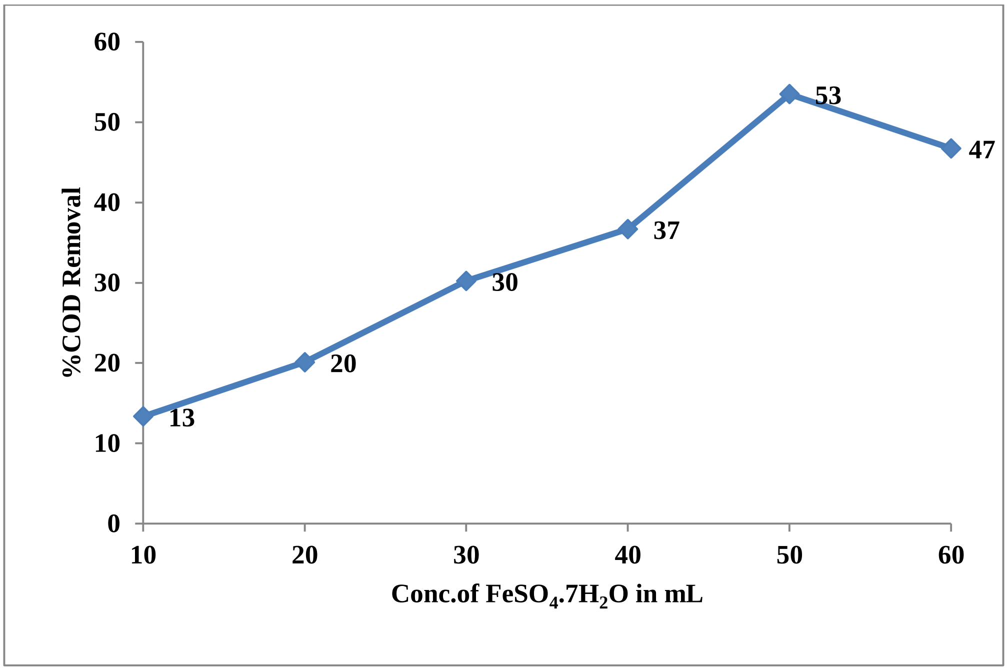

Fig 3.5. Effect of $FeSO_4.7H_2O$ on the removal of COD of Methylene Blue

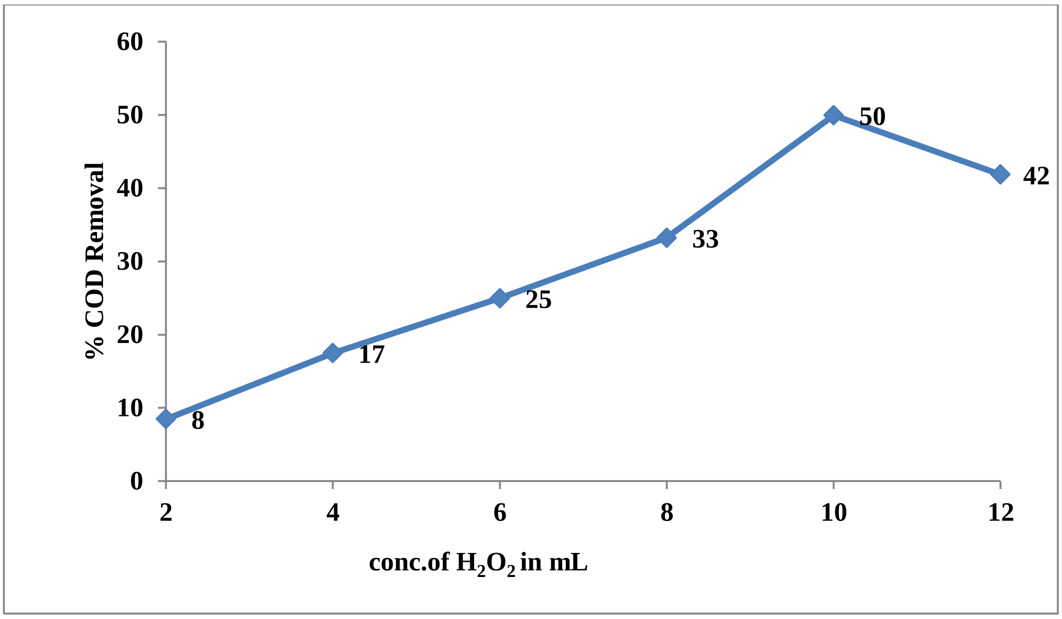

Fig.3.6. Effect of H_2O_2 on the removal of COD of Methylene Blue

3.2.4. Effect of Contact time

The batch reactor assembly consists of 500 mL beaker with an aerator for continuous stirring. The initial concentration of the dye was kept as 50 mg/L. The concentration of FeSO4.7H2O and the dosage of hydrogen peroxide was kept as the same value optimized in the previous study. The entire setup was then aerated for different time intervals which were varied as 10, 20, 30, 40, 50 and 60 minutes continuously[17,18,19]. After the contact period the sample was taken out from each reactor and the same was analysed for COD concentration remaining in the solution as per the standard procedure.

The effect of contact time on the COD removal through Fenton process was studied and the results are shown in figure 3.7. Experiments were carried out at pH 3 with the constant dose of 10 mL of H_2O_2, 50 mg/L of $FeSO_4.7H_2O$ concentration and contact time varied in the range from 10 to 60 minutes [20, 21, 22, 23]. The COD Removal was increased at the contact time of 30 minutes and gradually decreased after 30 minutes. Hence 30 minutes is considered as the optimum time.

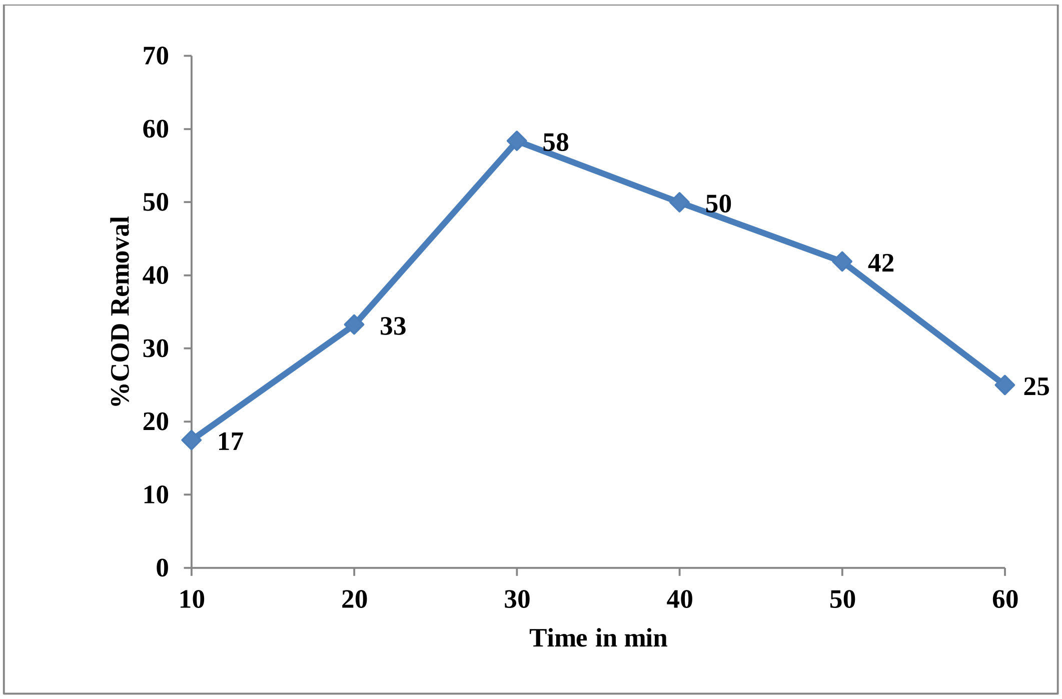

Fig 3.7. Effect of contact time on the removal of COD of Methylene Blue

Conclusion

Fenton process is one of the powerful tool for removing dyes from aqueous solution. The process very much depends on pH, catalyst concentration i.e. $FeSO_4.7H_2O$, H_2O_2 concentration and contact time. The following results can be summarized for this study.

Optimum pH and contact time was observed to be 3 and 30 minutes respectively. The optimized concentration of $FeSO_4.7H_2O$ and H_2O_2 was found as 50 mg/L and 10 mL for 50 mg/L of methylene blue dye. On conducting a batch experiment using all the optimized values by Fenton process, the overall removal efficiency of COD for methylene blue dye is found as 65%

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