Article

Experimental study on performance assessment of Fenton and photo-Fenton oxidation process for methylene blue

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Abstract
This project focuses on the suitability of Fenton and photo-Fenton processes for the degradation of methylene blue dye in terms of COD removal and it is optimized for experimental parameters such as pH, H_2O_2 concentration, $FeSO_4.7H_2O$ concentration and contact time. The Fenton process and photo-Fenton process is found to be effective under pH 3. The maximum efficiency of COD removal for 50 mg/L of Methylene blue is attained at optimum concentration of 10 ml of H_2O_2, 50 mg/L of Fe^{2+} and contact time of 30 minutes. The photo-Fenton oxidation process is also being carried out and it is also optimized for experimental parameters. The efficiency of COD removal for methylene blue is attained at optimum concentration of 8 ml of H_2O_2, 50 mg/L of Fe^{2+} and at a contact time of 30 minutes. Finally, on comparing both the processes, the best method with maximum removal efficiency is identified as photo-Fenton process for degradation of dye. At fully optimized condition, the efficiency of Fenton process is 65% and that of photo- Fenton is 82%, which is 17% higher than the Fenton process.

Keywords dye; Fenton process; photo-Fenton process; COD removal.

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1 Introduction

Methylene blue (MB), $C_{16}H_{18}ClN_3S$ (MW =319.65 g / mol), a heterocyclic aromatic chemical compound is an important basic dye widely used for printing calico, coloring paper, temporary hair colorant, wools, coating for paper stock, dyeing, printing cotton and tannin, indicating oxidation-reduction, and dyeing leather, and in purified zinc- free form, it is used as an antiseptic and for other medicinal purposes. At room temperature MB appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water (Barbusinski et al., 2004; Brillas et al., 2002). In an oxidizing environment, solutions of this substance are blue but will be colorless if it is subjected to a reducing agent. Methylene blue can cause some harmful effects even if it is not strongly hazardous. Acute exposure to methylene blue causes increased heart rate, vomiting, shock, cyanosis, jaundice, quadriplegia and tissue necrosis in humans (Nideesh et al., 2012). Chemical treatments have been extensively used to treat textile waste waters. Most of the studies such as chemical precipitation, adsorption using activated carbon, photo catalytic oxidation and Fenton oxidation focused on color removal. 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 2.8eV and it can degrade the organic content easily (Patel et al., 2020; Jose et al., 2019; Gowtham et al., 2015).

Photo-Fenton process ($H_2O_2/Fe^{+2}/UV$) is one of the advanced oxidation processes involving the hydroxyl radical ($^{\cdot}OH$) formation in the reaction mixture through photolysis of hydrogen peroxide (H_2O_2/UV) and Fenton reaction (H_2O_2/Fe^{+2}). The removal efficiency of COD from dye wastewaters is high with the H_2O_2/UV or Fenton process. The peroxide dose is important for obtaining better degradation efficiency and the iron concentration is important for the reaction kinetics (Patel and Patel, 2013). The cleaveage of O-O bond in hydrogen peroxide and generation of hydroxyl radical occurs with the ultraviolet radiation in UV/H_2O_2 process (Muhammad et al., 2008). When UV light is absorbed directly by hydrogen peroxide, $^{\cdot}OH$ radicals are generated by photolysis of the peroxidic bond (Zepp et al., 1992; Rehman et al., 2018).

The major objective of this study was to assess the performance of single Fenton‘s reagent and the combination of Fenton’s reagent with UV (photo-Fenton process). Both the processes are found to have the potential to remove the COD of dyes.

2 Materials and Methods

All the chemicals used in this study were of analytical reagent (AR) grade and were supplied by Sigma Aldrich chemicals India Ltd. Glassware used in the study were manufactured by M/S Borosil Glass Works Ltd. (Bombay, India). They were washed with diluted sulphuric acid followed by distilled water and millipure water.

MB dye was purchased locally and the synthetic solution was made by dissolving one gram methylene blue in one litre of distilled water and it is stored as stock solution (Shanthi and Mahalakshmi, 2012). The solutions of Fe^{2+}, NaOH, H_2SO_4 were also prepared with the distilled water. The 15W UV lamp used for Photo-Fenton process.

2.1 Experimental setup

The study was conducted in order to obtain maximum removal of COD at optimum pH, H_2O_2, $FeSO_4$ dosage and contact time. Initially, the COD of methylene blue was determined. Then the Fenton oxidation processes for MB dye carried out as batch study (Fig. 1). The synthetic waste water solution of methylene blue with a concentration of 50 mg/L was introduced in to the beaker and the pH of the solution is varied between 2.5 and 5 using H_2SO_4 or NaOH, as the process performs better in acidic conditions (Bahmani, 2013; Meric et al., 2004). And then the Fenton’s reagent (H_2O_2 and $FeSO_{4)}$ was added to that solution. The concentration of both the H_2O_2 and $FeSO_4$ is not varied and is maintained constant. The continuous mixing of chemicals was done by the means of an aerator. The reaction was allowed a contact time of 30 minutes. The optimum pH for maximum COD removal was determined. Further for the optimised pH, the process was repeated by varying the concentration of H_2O_2 and keeping $FeSO_4$ and contact time constant. The optimum dosage of H_2O_2 was determined and in a similar manner optimum dosage for $FeSO_4$ and contact time was determined by varying it and keeping all the other parameters constant.

The photo-Fenton process was also being carried out in the similar way as explained above (Fig. 2). The only difference is that the entire reaction will be exposed to the radiations of ultra violet (UV) and hence it was named photo-Fenton. The experimental parameters like pH, H_2O_2, $FeSO_4$ concentration and contact time was optimised as that of the Fenton process.

2.2 Analytical methods

The Chemical Oxygen Demand of the sample waste water were determined by closed reflux method. 2 ml of the diluted sample of the MB dye wastewater was taken in COD cuvettes. 1 gm of mercuric sulphate ($HgSO_4$) was added to avoid the interference of chloride and 3ml of COD acid ($AgSO_4$+Conc.H_2SO_4) was also added.1ml of standard potassium dichromate solution, a strong oxidising agent 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^{O}C.

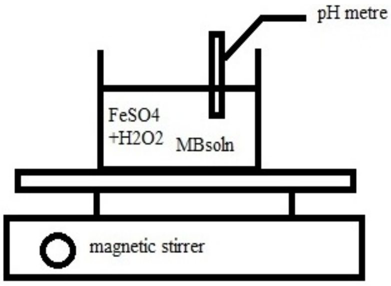

Fig. 1 Reactor setup for Fenton process.

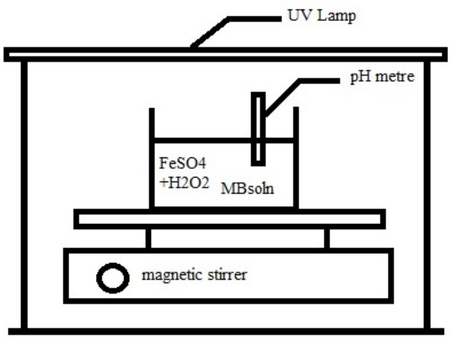

Fig. 2 Reactor setup for photo-Fenton process.

3 Results and Discussion

3.1 Effect of pH

This study was conducted for 50 mg/L initial concentration of MB dye in a batch reactor to analyse the effect of pH on the removal of COD for both the Fenton and photo-Fenton processes. 40 mg/L of $FeSO_4.7H_2O$ and 10 mL of hydrogen peroxide was added to the each reactor. The pH of the dye was increased in increasing order of 0.5 starting from 2 till 4, by adding HCL. The entire setup was then aerated for 30 minutes continuously and the sample was analyzed for COD concentration remaining in the solution as per the standard procedure explained above after the contact period of 30 minutes. The COD removal efficiency under various pH for both the Fenton and photo-Fenton process is represented graphically. It was found from the previous studies that the pH would influence the amount of OH° generation, and the preferable condition for OH° generation was under acidic conditions (Hsing et al., 2007). Therefore, the experiments were carried out at different pH values ranging from 2 to 4 by adding 1 N H_2SO_4 or NaOH to adjust the pH value. The reaction was carried out for 30 min using 40 mg/L $FeSO_4$ and 10 ml of H_2O_2 under controlled pH conditions. It is apparent from the Fig. 3, that the extent of COD removal decreased with increasing the pH and removal efficiency at pH 3 was 50% for Fenton and 67% for photo Fenton, whereas it reduced after pH 3 for both the processes. It clearly implies that the hydroxyl radical generation will be far better at the acidic pH. At low pH, we have a very high efficiency both in Fenton and Photo-Fenton processes. 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 (Dincer et al., 2008; Patel and Shah, 2013; Chen et al., 2019).

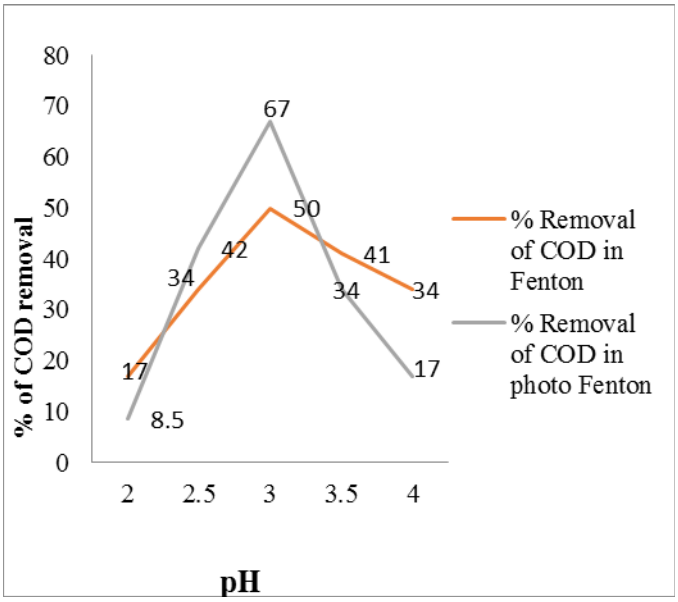

Fig. 3 Effect of pH on the removal of COD of methylene blue.

3.2 Effect of H_2O_2

This study was carried out in the batch reactor assembly for the MB dye with an initial concentration of 50 mg/L to analyse the effect of H_2O_2 on the removal of COD for both the Fenton and photo-Fenton processes. The optimised pH obtained from the previous optimization study was maintained to determine the effect of H_2O_2. The concentration of $FeSO_4.7H_2O$ was constant and the concentration of hydrogen peroxide varied from 2 to 10 mg/L in the increasing order of 2. The entire setup was then aerated for 30 minutes continuously. After the contact period, the sample was taken out from each reactor and the same was analyzed 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 and photo-Fenton process was studied and the results are shown in Figure 2. Experiments were carried out at pH 3 with the constant dose of 40 mg/L $FeSO_4$. The H_2O_2 concentration varied in the range from 2 to 12 ml. As shown in Fig. 4, the COD removal efficiency that increased from 8.4 to 50 for Fenton and 25 to 70 for photo-Fenton 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 behavior in the Fenton's process, which might be due to the hydroxyl radical scavenging effect of H_2O_2.

Addition of H_2O_2 is known to influence the decomposition of organic compounds through Fenton reaction (Xu et al., 2014; Naimi and Bellakhal, 2012; Tantak and Chaudhari, 2006).The degradation rate of organic compounds increases as the H_2O_2 concentration increases until a critical H_2O_2 concentration is achieved. However, when a concentration higher than the critical concentration is used, the degradation rate of organic compounds will decrease as a result of the so-called scavenging effect (Haddad et al., 2013; Mousavi et al., 2011).

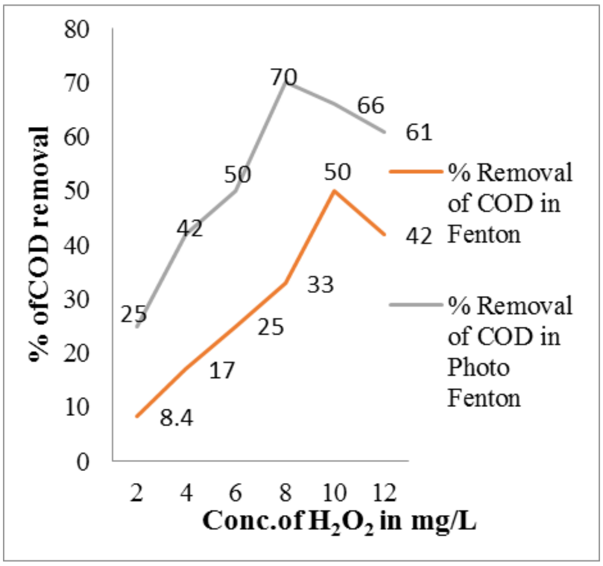

Fig. 4 Effect of H_2O_2 on the removal of COD of methylene blue.

3.3 Effect of $FeSO_4$

The effect of $FeSO_4$ on the removal of COD for the Fenton process and photo-Fenton process was analysed in this batch study. The pH and the concentration of H_2O_2 was kept constant. The reactor assembly consists of 500 mL beaker with an aerator for continuous stirring. The concentration of the dye was kept as 50 mg/L. The concentration of $FeSO_4.7H_2O$ is varied from 10 to 60 mg/L and 10 mg/L of hydrogen peroxide for Fenton and 8 mg/L for Photo-Fenton was added to the each reactor which is obtained from the optimization study of H_2O_2. The entire setup was then aerated for 30 minutes continuously. Once the contact period was completed, the sample was taken out from each reactor and it was analyzed for COD concentration remaining in the solution and a graph was plotted between the removal efficiency of COD and the varying concentrations of $FeSO_4.7H_2O$.

The effect of $FeSO_4.7H_2O$ dose on the COD removal through Fenton and photo-Fenton process was studied and the results are shown in Fig. 5. Experiments were carried out at pH 3 with the constant concentration of 10 and 8 mg/L of H_2O_2. The $FeSO_4.7H_2O$ concentration was 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. The removal efficiency decreased from 50 to 60 mg/L and the same follows for photo-Fenton oxidation process also. It was due to the redox reactions since OH radicals may be scavenged by the reaction with H_2O_2 or with another Fe^{2+} (Brillias et al., 2006; Neamtua et al., 2012)

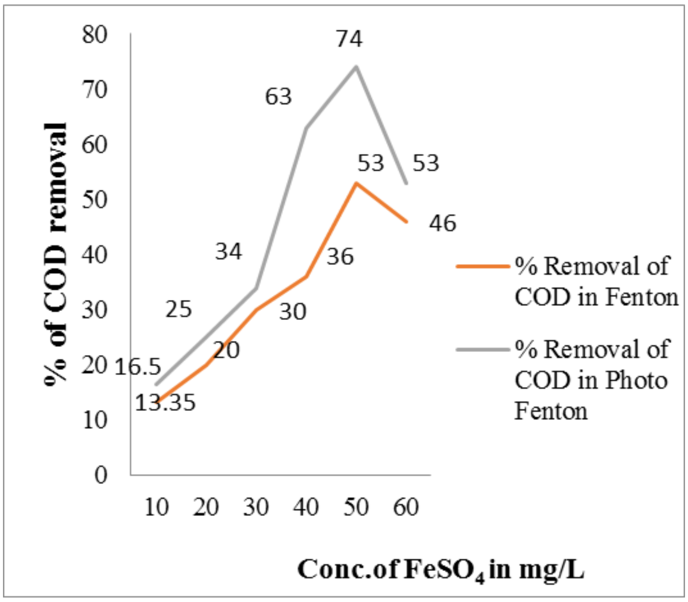

Fig. 5 Effect of $FeSO_4.7H_2O$ on the removal of COD of methylene blue.

3.4 Effect of contact time

The effect of contact time on the removal of COD was analysed with this study. The constant values of pH, concentration of H_2O_2, concentration of $FeSO_4$ were obtained from the previous optimisation studies. The reactor assembly consists of 500 mL beaker with an aerator for continuous stirring and the concentration of the dye was kept as 50 mg/L. The entire setup was then aerated for different time intervals which were varied as 10, 20, 30, 40, 50 and 60 minutes continuously. After the contact period the sample was taken out from each reactor and it was analyzed for COD concentration remaining in the solution and a graph was plotted between the removal efficiency of COD and the different contact time intervals as shown in Fig. 6.

The effect of contact time on the COD removal through Fenton process and photo-Fenton process was studied and the results are shown in Fig. 6. Experiments were carried out at pH 3 with the concentration of 10 & 8 mg/L 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. The COD Removal was increased at the contact time of 30 minutes and gradually decreased after 30 minutes. After the contact time of 30 minutes, the number of Fe molecules responsible for the generation of hydroxyl radical will be comparatively less (Chandramouli et al., 2012). Hence 30 minutes is considered as the optimum time to conduct the Fenton and photo-Fenton oxidation process.

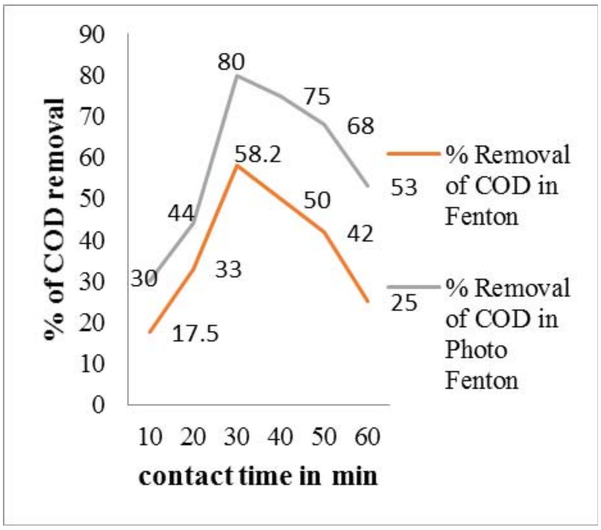

Fig. 6 Effect of contact time on the removal of COD of methylene blue.

4 Conclusion

The COD removal efficiency for both the Fenton and photo-Fenton oxidation process was studied at different experimental parameters affecting the advanced oxidation processes. The optimum pH for maximum COD removal was concluded as 3 for both the process. In the same way, the optimum H_2O_2, $FeSO_4$ and contact time was also determined. The optimum H_2O_2 for Fenton is 10 and photo-Fenton is 8mg/L. The optimum $FeSO_4$ concentration and contact time was 50 mg/L and 30 minutes for both Fenton and photo-Fenton process respectively. Performing the experiment with all the optimized values for Fenton and photo-Fenton process, the efficiency of Fenton process is 65% and the efficiency of photo-Fenton process is 82%. The percentage increase of photo-Fenton process is nearly 21%. The concentration of H_2O_2 was decreased for Photo-Fenton process and it can be suggested that Photo-Fenton process has higher removal efficiency and it will be more suitable for COD removal.

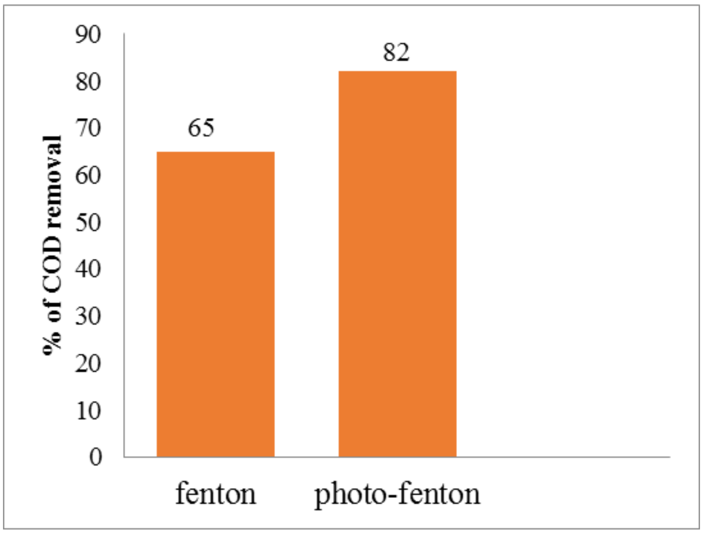

Fig. 7 Fenton *vs*. photo-Fenton.

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