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Research Note

Feasibility Studies on Application of Photo-Fenton Oxidation for Methylene Blue

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A B S T R A C T

Several industries are using dyes as colouring agents. The effluents from these industries are discharged mainly in to river streams which increasingly creates an environmental problem. The removal of dyes from aqueous solution has a great potential in the field of environmental engineering. There are many methods being employed in the dye removal. Among these methods, Fenton process-based advanced oxidation processes are an emerging prospect in the field of dye removal. This project focuses on the suitability of photo-Fenton process 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 photo-Fenton process is effective under pH 3. The maximum efficiency of COD removal for 50 mg/L of methylene blue is attained at optimum concentration of 10 mg/L of H_2O_2, 50 mg/L of Fe^{2+} and contact time of 30 minutes.

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INTRODUCTION

Methylene blue (MB) is a heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}ClN_3S$ (MW =319.65 g/mol). MB is an important basic dye widely used for printing calico, colouring 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, odourless, dark green powder that yields a blue solution when dissolved in water. Solutions of this substance are blue when it appears in an oxidizing environment, but will turn colourless if exposed to a reducing agent. Though methylene blue is not strongly hazardous, it can cause some harmful effects. Acute exposure to methylene blue is found to cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans [1]. Many chemical treatments have been extensively used to treat textile waste waters. Most of the studies such as chemical precipitation, adsorption using activated carbon, and photo catalytic oxidation and Fenton oxidation focused on colour removal. Fenton oxidation process which is an advanced oxidation process capable of producing hydroxyl radicals at acidic pH with the help of hydrogen peroxide and ferrous ions, which are Fenton's reagents. The hydroxyl radicals have a high oxidation potential of 2.8V and it can easily degrade the organic content. The photo-Fenton process (H_2O_2/Fe^{2+}/UV) is also one of advanced oxidation processes. This process involves 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 H_2O_2/UV or Fenton process alone was successful in removing COD from dye wastewaters. The peroxide dose is important in order to obtain high degradation efficiency, while the iron concentration is important for the reaction kinetics. The UV/H_2O_2 process uses ultraviolet radiation to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical. When UV light is directly absorbed by hydrogen peroxide, $^{\cdot}OH$ radicals are generated by photolysis of the peroxidic bond. The major objective of this study was to investigate the performance of combination of Fenton's

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reagent with UV (photo- Fenton process) [2-5]. This process is found to have the potential to remove the COD of dyes.

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 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 methylene blue dye was purchased from Madurai and the synthetic solution was prepared by dissolving one gram of accurately weighed methylene blue in one litre of distilled water and it is stored as stock solution. The solutions of $Fe^{2+,}$ NaOH, H_2SO_4 were also prepared with the distilled water. The UV lamp used for Photo-Fenton was of 15W manufactured by Philips.

Experimental setup

Experimental study was carried out to obtain maximum COD removal at optimum pH, H_2O_2, $FeSO_4$ dosage and contact time. Initially the COD of methylene blue was determined followed by the Photo-Fenton oxidation processes. It was carried out as batch study in a 500 mL beaker. The synthetic waste water solution of methylene blue was prepared from the stock solution and it had a concentration of 50 mg/L. It was then introduced in to the beaker and the pH of the solution is varied from 2.5 to 5 using H_2SO_4 or NaOH, as the process performs better in acidic conditions followed by the addition of H_2O_2 and $FeSO_4$. The concentration of both the H_2O_2 and $FeSO_4$ is not varied and is maintained constant. The reaction was allowed a contact time of 60 minutes. For even and continuous mixing of chemicals, magnetic stirrer was used and aeration was provided by means of aerator. The whole assembly is then exposed to U-V radiation. The optimum pH for maximum COD removal was determined and for that optimum pH, the process was repeated by varying H_2O_2 while 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 schematic diagram for experimental set up is shown in Figure 1.

Analytical methods

The COD of the sample is 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. 1g of mercuric sulphate is added to avoid chloride interference.Then, 1mL of potassium di chromate is added followed by 3mL of COD acid.

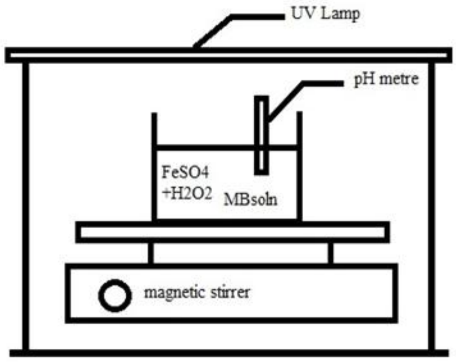

Figure 1. Schematic diagram for experimental set-up

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°C. 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.

RESULT AND DISCUSSION

Effect of pH

The batch study was carried out for the MB dye to analyze the effect of pH on the removal of COD for photo-Fenton processes. The batch reactor assembly consists of 500 mL beaker with an aerator for aeration and magnetic stirrer for continuous stirring. The initial concentration of the dye was kept as 50 mg/L. 40 mg/L of $FeSO_4.7H_2O$ and 10 mL of hydrogen peroxide was added to each reactor. The pH of the dye was varied as 2, 2.5, 3, 3.5 and 4 by adding HCl. The entire setup was then kept in an UV chamber for exposure to UV radiation and continuously aerated for 60 minutes. 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 explained above. The COD removal efficiency under various pH for photo-Fenton process is graphically represented in Figure 2.

The previous studies showed that the pH would influence the amount of OH° generation, and the preferable condition for OH° generation was under acidic conditions [6, 7]. 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 60 min using 40 mg/L $FeSO_4$ and 10 mL of H_2O_2 under controlled pH conditions. It is apparent from the Figure 2, that the extent of COD removal decreased with increasing the pH and removal efficiency at pH 3 was 67% for photo

Fenton, whereas it reduced after pH 3. The decreasing of the COD Removal rate is mainly due to the decreasing of oxidation potential of hydroxyl radicals at high pH. In addition, under alkaline conditions (pH > 4), the precipitation of hydroxide ions $Fe(OH)_3$ occurs, decreasing the Fe^{3+} concentration dissolved. Besides, in such conditions, hydrogen peroxide is less stable; therefore less hydroxyl radicals are formed reducing the process efficiency. It clearly implies that the hydroxyl radical generation will be far better at the acidic pH.

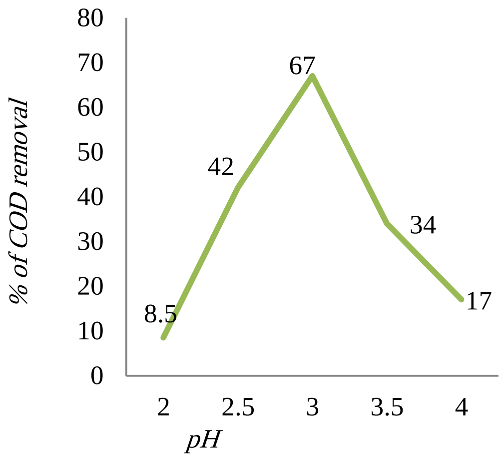

Figure 2. Effect of pH on the removal of COD of Methylene Blue

Effect of H_2O_2

This batch study was carried out for the MB dye to analyze the effect of H_2O_2 on the removal of COD for photo-Fenton processes. The pH of the dye solution was maintained at the value obtained from the previous optimization study which is 3. 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 40 mg/L and the dosage of hydrogen peroxide varied as 2, 4, 6, 8 and 10 mL and was added to the each reactor. The entire setup was then kept in UV chamber for radiation and continuously aerated for 60 minutes. 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 photo-Fenton process was studied and the results are shown in Figure 3.

Experiments were carried out at pH 3 with the constant concentration of 40 mg/L $FeSO_4$. The H_2O_2 dosage varied in the range from 2 to 12 mL. As shown in Figure 3, the COD removal efficiency that increased from 25 to 70 for photo-Fenton. And that was 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 [8-12].

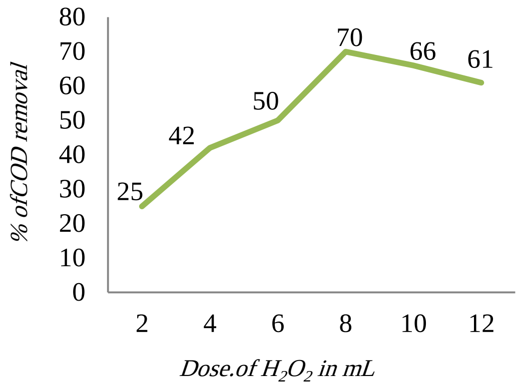

Figure 3. Effect of H_2O_2 on the removal of COD of Methylene Blue

Effect of $FeSO_4$

This batch study was carried out for the MB dye to analyze the effect of $FeSO_4$ on the removal of COD for the photo-Fenton process. The pH of the dye solution and the dosage of H_2O_2 were maintained at the value obtained from the previous optimization studies. 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 which is obtained from the optimization study of H_2O_2. The entire setup was then kept in an UV chamber for radiation and it was continuously aerated for 60 minutes. 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 and a graph was plotted between the removal efficiency of COD of the Methylene Blue for various $FeSO_4.7H_2O$. The effect of $FeSO_4.7H_2O$ dose on the COD removal through photo- Fenton process was studied and the results are shown in Figure 4.

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 mL. It was observed that the amount of ferrous ion is one of the main parameters influencing the Photo-Fenton process. The COD Removal was increased from 16.5 to 74 as the concentration of ferrous ion was increased from 10 to 50 mg/L. The removal efficiency decreased from 74 to 53 mg/L. It may be explained by redox reactions since OH radicals may be scavenged by the reaction with H_2O_2 or with another Fe^{2+} The Fe^{3+} formed reacts with the H_2O_2 and hydroperoxy radical which regenerates Fe^{2+} in the solution resulting in the decrease of COD removal [8, 13-16].

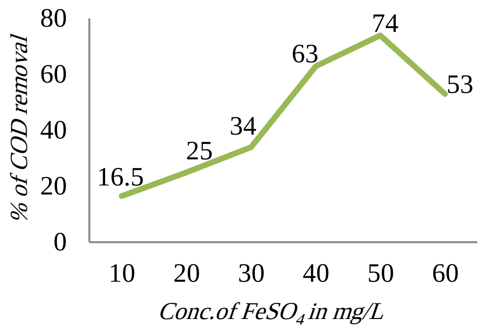

Figure 4. Effect of $FeSO_4.7H_2O$ on the removal of COD of Methylene Blue

Effect of Contact time

This batch study was carried out for methylene blue dye to analyze the effect of contact time on the removal of COD. 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 and the whole setup was kept in an UV chamber to give radiation. 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 as optimized from the previous study was added to the each reactor. The entire setup was then continuously aerated for different time intervals which were varied as 10, 20, 30, 40, 50 and 60 minutes. 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

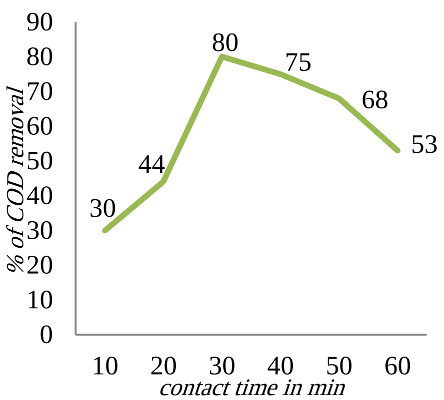

Figure 5. Effect of contact time on the removal of COD of Methylene Blue

standard procedure and a graph was plotted between the removal efficiency of COD of the Methylene Blue for various contact time intervals as shown in Figure 5. The effect of contact time on the COD removal through Photo- Fenton process was studied and the results are shown in Figure 5.

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. 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 to conduct the Photo-Fenton oxidation process.

CONCLUSION

The COD removal efficiency for 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 the process. In the same way, the optimum H_2O_2 , $FeSO_4$ and contact time was also determined. The optimum H_2O_2 dosage for photo-Fenton is 8mL.The optimum $FeSO_4$ concentration and contact time was 50 mg/L and 30 minutes respectively.

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Persian Abstract

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چکیده

صنایع متعددی از رنگ‌ها به عنوان عامل رنگ‌آمیزی استفاده می‌کنند. غالباً مسیر جریان خروجی این کارخانجات به روان‌آب‌ها و رودخانه‌ها منتهی می‌گردد که باعث تشدید مشکلات زیست‌محیطی می‌گردد. حذف رنگ‌ها از محلول‌های آبی، پتانسیل زیادی برای کار در حوزه مهندسی محیط‌زیست داراست. روش‌های فراوانی برای حذف رنگ‌ها به‌کار گرفته شده که از میان آن‌ها فرآیند اکسیداسیون پیشرفته برپایه روش فنتون، فرآیندی نوظهور در این حوزه به شمار می‌رود. این پروژه بر مناسب بودن فرآیند فتوفنتون جهت تبدیل رنگ متیلن‌بلو برحسب حذف COD تمرکز کرده و پارامترهای عملیاتی نظیر pH، غلظت آب اکسیژنه (H_2O_2)، غلظت $FeSO_4.7H_2O$ و زمان تماس را بهینه‌سازی نموده است. روش فتوفنتون در pH ۳ عملی و موثر می باشد. بیشترین بازدهی حذف COD برای ۵۰ میلی‌گرم بر لیتر متیلن‌بلو در غلظت بهینه ۱۰ میلی‌گرم بر لیتر H_2O_2، ۵۰ میلی‌گرم بر لیتر Fe^{2+} و زمان تماس ۳۰ دقیقه به دست آمد.