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Comparative studies of degradation of dye intermediate (H-acid) using TiO_2/UV/H_2O_2 and Photo-Fenton process

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ABSTRACT

The present work is focused on the homogeneous and heterogeneous photo-catalytic degradation of H-acid, a non-biodegradable dye intermediate from dye manufacturing industries, using Advanced Oxidation Processes (AOPs) such as UV, UV/H_2O_2, UV/H_2O_2/Fe^{2+} (photo-Fenton process), UV/TiO_2 and UV/H_2O_2/TiO_2. Degradation experiments were carried out to optimize the amount of catalyst, effect of H-acid concentration, contact time, effect of pH on chemical oxygen demand (COD) etc., using UV-visible spectrophotometer, and further analysed with High Performance Liquid Chromatography (HPLC) technique. The nano catalyst was characterized with Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). The degradation rate was strongly influenced by the pH, initial concentrations of H_2O_2 and catalyst. The maximum degradation of was achieved at pH 3 to 4 in all AOPs experiments. The optimum H_2O_2 concentration is 300 mg/L achieved with heterogeneous AOPs as well as homogeneous AOPs in maximum of 90 min reaction time. The Maximum 84% degradation achieved with TiO_2/UV/H_2O_2. The order of COD reduction is UV/H_2O_2/TiO_2 > photo-Fenton > UV/TiO_2 > UV/H_2O_2 > UV.

Keywords: AOPs, Dye intermediate, Photo-Fenton process, Photocatalysis, Titanium Dioxide (TiO_2).

INTRODUCTION

Environmental pollution associated with dye and dye intermediates originate with low biodegradability and have strongly in their hydrophilic nature which enable to introduce into the aquatic environment through natural, as well as man-made without any structural alteration [1,2].

Dyes are classified by their chemical and dyeing properties however, the release of these dye compounds into the environment can be undesirable, not only because of their color, but also because some dyes and their breakdown products are toxic. Commonly, the degradation of dyes from wastewater, a biological treatment strategy based on anaerobic reduction, followed by aerobic transformation of the formed aromatic amines, holds promise. However, the first stage of the process, anaerobic dye reduction, proceeds relatively slowly. Dye and dyes have been widely used in a variety of products such as textiles, foodstuffs and leather. About one-half of the dyes used in textile industry include acid, reactive, azo and direct dyes, and as a consequence toxicity problems have arisen due to the release of some of these products into the environment. Industrial use of these dyes and its derivatives over the past decades has led to severe environmental pollution.

H-acid (1-amino, 8-napthol, 3,6-disulfonic acid) is one of the dye intermediates used in the manufacture of acid, reactive, direct and azo dyes. In particular, H-Acid is having two sulpfonated groups, involved considerably high amounts in the production of sulpfonated textile dyes, dispersants, pesticides, pharmaceuticals etc. [3,4]. The H-acid production involves the usage of high-strength acids and alkalis thus the wastewater contains high chloride and sulphate with toxic naphthalene based dye intermediates, therefore which are non-biodegradable substances.

Wastewaters from textile industries can be degraded through conventional treatment such as coagulation and hydrolyzing metals followed by flocculation and filtration with sedimentation thus produces a large amount of sludge which is difficult to dispose in an environmental secure manner. Usually, the use of one individual process may not be sufficient to obtain complete decolorization because each technique has its limitations. Adsorption onto activated carbon is also an effective method, but activated carbon may have a very short life which again depends on the type and nature of dye intermediates [5]. However, it is very expensive and inefficient to regeneration of activated carbon.

Advanced oxidation processes (AOPs) are technologies based on the intermediary of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end-products. The AOPs include chlorination, bleaching, ozonation, Fenton oxidation, photocatalytic oxidation and wet-air oxidation [6,7]. The environmental applications of AOPs are numerous, including water and wastewater treatment (i.e. removal of organic and inorganic pollutants and pathogens), air pollution abatement and soil remediation. Among the emerging technologies in textile wastewater treatment processes, AOPs have emerged as potentially powerful methods that are capable of transforming the pollutants into harmless substances [8]. They offer a high degree of process flexibility and the ability to degrade pollutants and concentration levels than the treatment processes like physical & biological treatment. There are currently a wide range of AOPs being extensively researched and developed for the treatment of aqueous wastewaters, and single treatment processes or combinations of ozonation, UV, Fenton processes, hydrogen peroxide and catalysts such as TiO_2 [9,10].

In view of the previous reports on degradation of dyes wastewaters, one of the most promising routes is to degradation of dye intermediate (H-acid) using Advanced Oxidation Processes

(AOPs). Because of the complex structures of these dyes and dye intermediates biological, physical and chemical treatment of dye effluents are inefficient. Although some of the dyes may produce toxic products, however removal of dyes in textile wastewater by photo oxidation is more efficient due to the complete degradation until CO_2 and H_2O depending on the period of photo oxidation. Nevertheless, this method is inexpensive and nontoxic for treatment of wastewater.

In general, the photo-activated chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the solution, with or without the presence of the catalyst. The radicals can be easily produced using UV radiation. UV light has been tested in combination with H_2O_2, TiO_2, Fenton reagents, O_3 and other solid catalysts such as for the decolorization of dye solutions [11]. While the UV/ H_2O_2 process appeared too slow, costly and little effective for potential full-scale application, the combination UV/TiO_2 seems more promising.

A well known Fenton process is the mixture of ferrous ion with H_2O_2 which oxidize the organic compounds, however it may take place in the presence of Fe^{3+} or Fe^{2+} and sometimes combination with coagulation method. Studies were carryout on this method and reported that this method is used in degradation of pollutants. Many years ago it was found that fenton reaction is improved with UV-vis irradiation which produces additional hydroxyl radicals and leads to reduction of the photo-catalyst [12].

Among the various reports on degradation of dye intermediates and dyestuffs only a few have investigated to compare the homogeneous and heterogeneous AOPs. The aim of the present study is to investigate the degradation of H-acid using homogeneous AOPs like UV, UV/H_2O_2, photo-fenton (UV/H_2O_2/Fe^{2+}) and heterogeneous AOPs like UV/TiO_2, UV/H_2O_2/TiO_2 and to compare the degradation behavior of above oxidation processes. The influence of pH, dosage of nano catalyst, H_2O_2 concentration and contact time on the rate of degradation were studied. The nano catalyst was characterized with Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). The degradation of compound was examined by UV-visible spectrometer and further confirmed with HPLC technique.

EXPERIMENTAL SECTION

1.1 Reagents

The commercial nano powder TiO_2 and H-Acid (1-amino 8-naphthol 3,6-disulfonic acid) was purchased from Sigma-Aldrich. The other chemicals like H_2O_2 (30% w/w), Ferrous Sulphate and $(NH_4)_2S_2O_8$ AR grade (Merck) were used. Acetonitrile AR Grade used in HPLC analyses was purchased from Merck.

1.2 Photo-reactor setup

A cylindrical quartz glass photo reactor with a total volume of 1.0 L (diameter 12 cm and height 13.3 cm) has been used for the experiments. The reactor was covered with an aluminum sheet to prevent loss of UV light. Inlets were provided to feed reactants and ports for withdrawing samples. A Teflon-coated magnetic stirring bar was placed at the bottom for homogenization. The UV irradiation source was a 16W low-pressure mercury vapor lamp (maximum emission at

270 nm) encased in a quartz tube. The lamp was surrounded with a water-cooling jacket to maintain a constant temperature. It was axially centered and immersed in the sample solution. Figure 1 shows a typical schematic diagram of the laboratory scale photochemical installation used for the purpose of this study.

1.3 AOP Experiments

Degradation of the selected H-acid aqueous solution using various AOPs is examined at different operational parameters. A series of experiments were carried out to evaluate the degradation studies.

1.3.1 Photo-degradation using UV light (Direct photolysis)

The experiments were conducted with immersion type of the photo reactor is filled with 0.75L of aqueous solution of known concentration of H-acid with an initial concentration ranging between 50-250ppm. The samples are irradiated for a period of 3hrs (180 min.) with a sampling interval of 30min**.** The sample was immediately analyzed for percentage of degradation.

Table 1: Characteristics and properties of H-Acid

Common Name	1-amino 8-naphthol 3,6-disulfonic acid
Molecular Formula	$C_{10}H_8NNaO_7S_2$
Molecular weight	341.29
Concentration	100 mg/L
COD	91 mg/L
pH	4.1

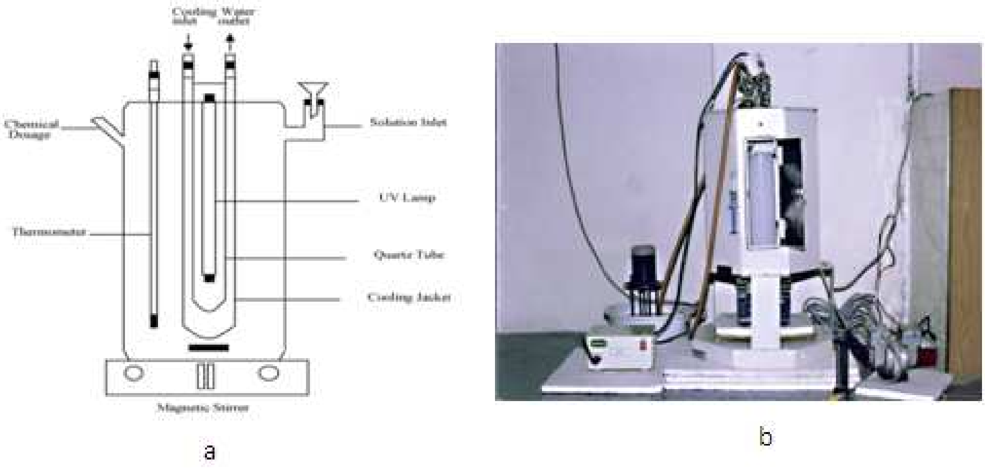

Figure 1. (a) Schematic representation of photo reactor (b) Photographic view of 16W UV Photo Reactor

1.3.2 Photo-degradation using UV/H_2O_2/TiO_2

The experiments were carried out with known concentration of H-Acid taken in the reactor. Predetermined amount of nano TiO_2 catalyst and H_2O_2 was dripped into the sample and initial pH was adjusted using 2N solution of H_2SO_4 and NaOH. The sample was stirred rapidly for 15min using magnetic stirrer in order to get maximum adsorption of the H-Acid on the catalyst surface hence the photocatalytic reaction was initiated by switching the UV lamp. After the reaction completed, the samples were centrifuged and therefore filleted with 0.2µ nylon membrane filters to remove catalyst particles from the sample and also reaction was stopped by adding 10% aqueous solution of $Na_2S_2O_3$ and therefore the sample was immediately analyzed for percentage of degradation. Experiments were repeated to get data of reproducible change of about U ± 2%. However, the experiments were carried out with UV/H_2O_2 to study the effectiveness of the catalyst. Similarly, the same experiments were carried out for photo-fenton process ($UV/H_2O_2/Fe^{2+}$).

1.3.3 *Photo-degradation using UV light in the presence of Hydrogen peroxide (UV/H_2O_2)*

Similar experiment was conducted with the reactor is filled with 0.75L of aqueous solution of H-acid with an initial concentration of 100ppm of H-acid. In order to choose the effective concentration of hydrogen peroxide for the degradation studies the concentration of hydrogen peroxide is varied to fixed concentration of H-acid. To study the effect of initial pH, a series of experiments are carried at different pH values ranging from 3 to 9. All the experiments are carried out in batch mode operation. Samples are withdrawn at regular intervals of 30min and analyzed for percentage of concentration removed and COD reduction.

1.3.4 Degradation using Photo-Fenton process ($UV/H_2O_2/Fe^{2+}$)

The photo-fenton experiments were carried out in the reactor with 0.75L of an aqueous solution of 100ppm of H-acid and varied with different concentrations of H_2O_2 and Fe^{2+} in the ratio of 10:1 are used for optimization. Results reported in the relevant literature clearly indicate that the operation pH determines the degree of oxidation reached in the treatment, with pH 3-4 being the most effective value [13,14]. Hence in the present study the photo-fenton experiments are performed at an acidic pH of 3.0±0.1. The reaction mixture is homogenized by magnetic agitation for 15min before introducing in to the photo reactor. Samples are withdrawn at regular intervals of 30 min and centrifuged, followed by filtration through 0.25μm syringe filters. The samples are then analyzed for percentage of concentration removed and COD reduction.

1.4 Comparison of various AOPs studied

A comparative assessment of H-acid degradation by various AOPs (UV, UV/ H_2O_2, $UV/Fe^{2+}/H_2O_2$, UV/TiO_2 and $UV/H_2O_2/TiO_2$) is performed in terms of compound and COD reduction after optimization of all the parameters.

1.4.1 H-acid Concentration and COD reduction

The quantitative decrease in the concentration of H-acid is measured by Systronics-1272 UV-Vis Spectrophotometer at 234nm absorption maxima. The compound reduction is further validated with high performance liquid chromatography (HPLC). COD is measured according to standard methods. Percentage reduction of compound and COD is calculated by the equation.

$$\% \text{ Degradation} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Where $\mathbf{C_0}$ represents initial concentration/ COD of the compound
$\mathbf{C_t}$ represents final concentration/ COD of the compound

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1.5 Analysis

1.5.1 Characterization of TiO_2 with FTIR

Nano TiO_2 catalyst was characterized by FTIR spectra (Perkin Elmer Precisely Spectrum One Model Spectrometer) using potassium bromide pellet in the range of 400-4000 cm^{-1}.

1.5.2 HPLC Analysis

HPLC analysis was carried out with Agilent technologies by reverse phase column C18. The mobile phase was mixture of Acetonitrile and buffer (ammonium acetate) in the ratio of 85:15 and flow rate was 1ml/min. the wave length of UV absorbance detector was 234 nm with retention of time of 30min.

1.5.3 SEM analysis

Before the SEM analysis the sample was dried in oven at 100^0C for 1hr. The sample was sputter coated with platinum. Image of free nanoparticles captured using SEM. EDAX (Energy Dispersive X-ray Analysis) of the sample of the catalysts TiO_2 have been carried out in JEOL JSM-6380LA SEM. The micrographs allowed visualizing the surface and the texture of the analyzed nanoparticles.

RESULTS AND DISCUSSION

The trends in degradation capacities of H-acid using various oxidation methodologies is presented by showing the effect of pH, initial H_2O_2 concentration and effect of TiO_2 dosage in case of $UV/H_2O_2/TiO_2$ process and Fe^{2+} concentration in case of photo-fenton process.

1.6 UV Photolysis

Optimization experiments on direct photolysis of H-Acid were initially carried out by irradiating the aqueous solution to determine the effect of initial concentration. Photolysis is a common method for generating free radicals through sigma bond cleavage. These radicals are most often the precursors that generate other free radicals [15]. The first step in a photochemical reaction is the excitation of a molecule through absorption of one photon. The excited molecule leads to a chemical reaction. Thus the organic substrate is progressively degraded. In order to choose the effective concentration of H-acid, studies are conducted in the range of 50-250ppm of H-acid (Figure 2). From the concentration screening experiments, it is concluded that 100ppm of H-acid is efficiently degraded of about 30% and at higher concentrations the degradability diminished to 13%. Hence their direct photolysis by UV light is quite slow. Therefore, for all further AOP experiments 100ppm of the H-acid is considered as optimum degradable concentration and taken as initial concentration.

1.7 Effect of pH on the degradation of H-Acid

In order to study the effect of initial pH on H-Acid degradation, a series of experiments are carried at different pH values ranging from 2 to 8 shown in Figure 3. The maximum degradation was achieved at pH 3 to 4 in all homogeneous and heterogeneous AOPs experiments. The degradation trend was observed as similar with all the homogenous AOPs (UV, UV/H_2O_2, & $UV/Fe^{2+}/H_2O_2$). However, at pH 3 the percentage degradation is very high when compared with heterogeneous process (UV/TiO_2 & $UV/H_2O_2/TiO_2$). The highest degradation is achieved at pH 3 to 4 with $UV/H_2O_2/TiO_2$ process. However, at pH>4, the degradation decreased with increasing pH from 4 to 9. This decrease is probably due to the fast decomposition of hydroxyl radicals and hydrogen peroxide at high pH ranges.

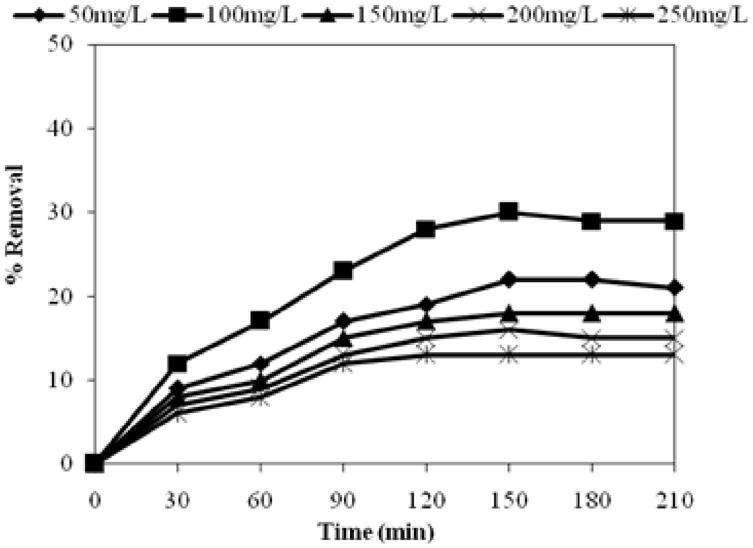

Figure 2. Optimization of the concentration of H-Acid
Experiment Conditions: pH = 3.0

In the heterogeneous AOPs, the semiconductor oxide particles are generally amphoteric in nature and the photocatalytic process takes place on the surface of TiO_2. The pH of the solution strongly influences on the surface properties of TiO_2 particle [16]. Therefore, the effect of pH on the removal of H-acid over photo-catalysis, it is observed that the percent removal increases in acidic pH and decreases in basic pH. The same trend was observed for both the heterogeneous processes. The strong influence of pH on the adsorption of H-acid depends on the specific nature of TiO_2 surface and its intrinsic behavior of TiO_2 particle [17] and also nature of the H-acid. As H-acid has two negatively charged sulfonic groups, it is expected that at low pH, attractive forces are developed between H-acid and TiO_2 surface, resulting in high adsorption in acidic medium. As the pH increases, TiO_2 surface is negatively charged, resulting in repulsive forces between the H-acid and TiO_2 surface thus decreasing adsorption [18,19].

Previous studies revealed that the pH range at 3 to 4 has been reported as the effective range for degradation of synthetic dye wastewater using Fenton's and photo-Fenton' reaction [20,21] due to which acidic pH improves the formation of extremely hydroxyl radicals with intense oxidation efficiency [22]. From the results the maximum removal was obtained at pH 3 in case of photo-fenton reaction, resulting that Fe^{3+} ion and $Fe(OH)^{2+}$ ion are actively appeared however at acidic conditions $Fe(OH)^{2+}$ ions decreased whereas at alkali conditions Fe^{3+} ion precipitates as oxy hydroxide, which reduces the UV radiation [23].

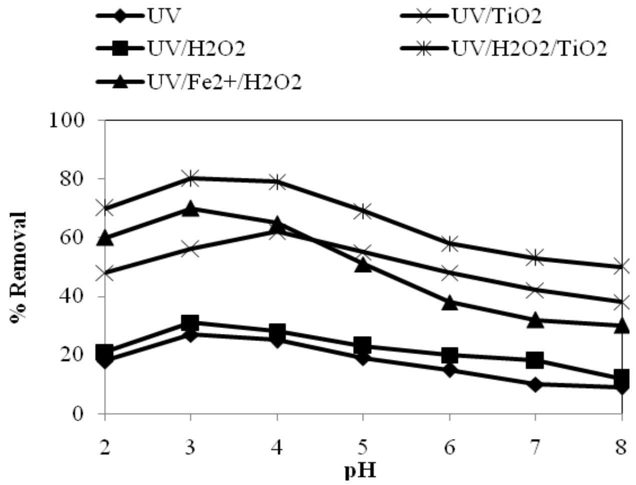

Figure 3: Effect of pH on degradation of H-acid
Experiment conditions: H-Acid - 100 ppm, H_2O_2 = 250 mg/L, TiO_2 = 0.2 g/L, Fe^{2+} = 20 mg/L, Reaction time = 90 min.

1.8 Effect of H_2O_2 concentration on the degradation of H-Acid

The effect of initial H_2O_2 concentration on the degradation of H-Acid is illustrated in **Figure 4**. Hydrogen peroxide doses are varied from 100 -500 mg/L. In the presence of UV/H_2O_2 process, the H-Acid photo degradation increased when compared to direct photolysis even at low initial H_2O_2 concentrations. The efficiency increased with increasing H_2O_2 concentration. However, increasing the initial hydrogen peroxide concentration enhanced the oxidation up to a certain level. On further increase of concentration, hydrogen peroxide inhibition on the photolytic degradation of the H-Acid was observed.

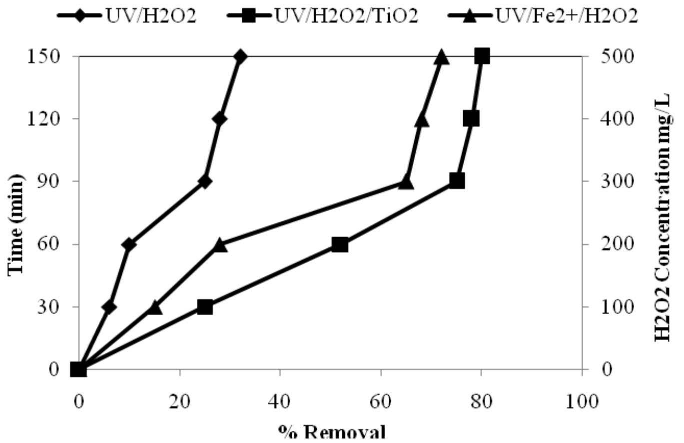

Figure 4: Effect of H_2O_2 concentration on degradation of H-acid
Experiment conditions: H-Acid - 100 ppm, pH = 3.0, TiO_2 = 0.2 g/L & Fe^{2+} = 20 mg/L

From the experiments it is concluded that the optimum H_2O_2 concentration is 300 mg/L at which maximum percentage removal of the H-acid is achieved with heterogeneous AOPs as well as homogeneous AOPs in maximum of 90 min reaction time. Further addition of H_2O_2 did not improve the degradation rate due to self-decomposition of H_2O_2 hence the degradation rate becomes very slow after 90 min reaction time. Moreover, at higher concentrations, hydrogen peroxide acted as a free-radical scavenger itself and to form oxygen and $^{-}O_2H$ radicals [24], thereby decreasing the hydroxyl radical concentration and reducing compound removal efficiency. From the previous reports indicated that degradation process is due to the electrophilic attack of the chromophoric groups by OH^{-} radicals [25] might be a primary step. From the results it is observed that, in case of photo-fenton process addition of excess H_2O_2 did not improve the removal efficiency due to as the H_2O_2 coverts to oxygen and water [26].

1.9 Effect of TiO_2 dosage

Similarly, to study the effect of TiO_2 concentration on heterogeneous AOPs (UV/TiO_2 & $UV/H_2O_2/TiO_2$), the experiments were carried out by varying the TiO_2 concentration from 0.1 g/L to 0.5 g/L with fixed reaction time i.e. maximum of 90 min.

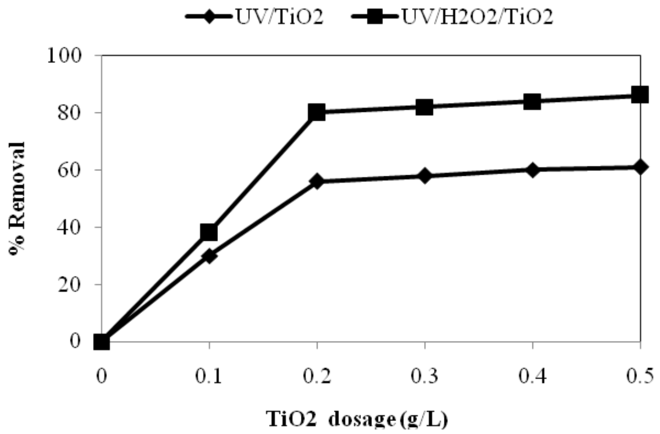

Figure 5: Effect of TiO_2 dosage on degradation of H-acid
Experiment conditions: H-Acid - 100 ppm, H_2O_2 = 300 mg/L, pH = 3.5, Reaction time = 90 min.

This experiment results shown in **Figure 5** reveal that at 0.2 g/L of TiO_2 concentration the maximum of 84% removal was achieved in $UV/H_2O_2/TiO_2$ and 58% removal in UV/TiO_2 hence same degradation trend was observed in both AOPs. However, at higher TiO_2 dosage the percentage removal is stable due to the TiO_2 suspended particles preventing the penetration of light [18,19]. Also, addition of H_2O_2 in photo-catalysis, the fraction of light absorbed by the photo-decomposition increases and thus photolysis rate [24], therefore from the results it is observed that $UV/H_2O_2/TiO_2$ is much effective than the UV/TiO_2 process.

1.9.1 Characterization of TiO_2 using FTIR

The FTIR spectrum of Nano TiO_2 is exhibited in **Figure 6.** The strong and wide weak at 3399.69 cm^{-1} and Ti-OH with which physisorbed water molecules are bound by weak hydrogen bonds. The strong absorption centered at $711.13 cm^{-1}$ is the typical Ti-O-Ti Vibration. The absorption at

2200 cm^{-1} is attributed to CO_2 in air and the bending vibrational mode of water may appear as shoulders on the spectrum such as 2920.02 cm^{-1}. Peaks located at 700cm^{-1} was likely due to the vibration of the Ti-O bond in the TiO_2 lattice. Hence, FTIR measurement firmly suggested the presence of Ti-O bounds, peroxo groups and OH groups.

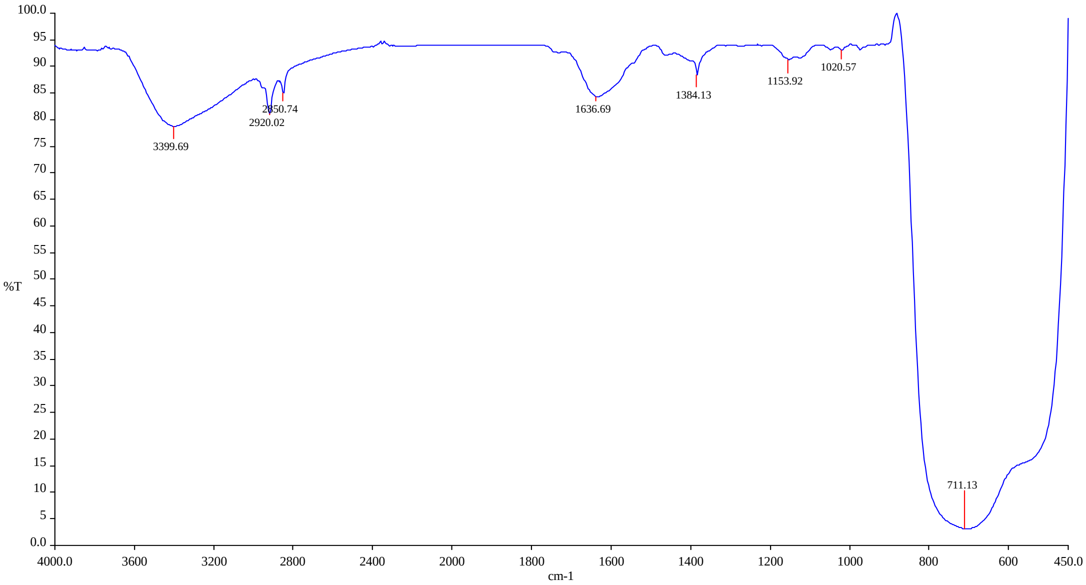

Figure 6: FTIR Spectrum of TiO_2

1.9.2 Scanning Electron Microscopy (SEM) analysis of TiO_2

The SEM analysis of TiO_2 has been shown in **Figure 7.** The morphologies of the TiO_2, samples consist of spherical particles in sizes varying from 50nm in diameter. The size of spheroids observed that each spherical particles observed from SEM is not a single crystalline of TiO_2 but the agglomerates of many single crystallites. The presence of porous structure might favor the improvement of the photo-catalytic activity of TiO_2 but only increases the specific surface area of TiO_2 but also facilitates the pass of reactants and degradation products.

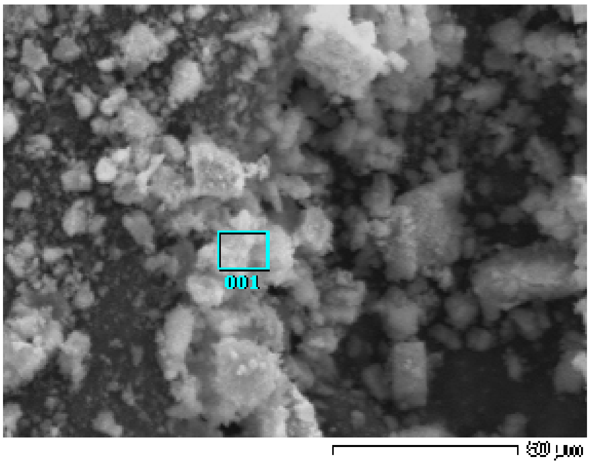

Figure 7: SEM analysis of TiO_2

1.10 Effect of Fe^{2+} concentration in Photo-fenton oxidation

The effect of initial Fe^{2+} concentrations on the removal of the H-Acid in Photo Fenton processes is presented in **Figure 8** by varying Fe^{2+} concentration from 10 mg/L to 50 mg/L. Previous literature clearly indicates that the operation pH determines the degree of oxidation in degradation process, with pH 3.0 being the most effective value [27] the efficiency of the treatment experiencing strong reductions as the pH is set to acidic medium [28]. At higher pH levels, iron precipitates as hydroxide and at lower levels self-decomposition of hydrogen peroxide are promoted [29].

The present results indicated that the degradation rate of the H-Acid increased with an increase in iron concentration. With Photofenton process, only 76 % degradation is achieved with 20 mg/L of initial Fe^{2+} concentrations. Further increase in iron concentration did not show any change in the degradation rate. This is due to the fact that, at a Fe^{2+} concentration higher than the optimum, most of the hydroxyl radicals are utilized in the side reactions effectively and thereafter removal is ineffective. Moreover, it resulted in brown turbidity that hindered the absorption of the UV light required for photolysis and caused the recombination of OH radicals [26]. Also, the removal with UV/H_2O_2 process is reported about 26% hence it is concluded that only light exposure and H_2O_2 are not enough to catalyse the H-acid. This can be explained by the complete oxidation of all Fe^{2+} to Fe^{3+} enhanced by UV.

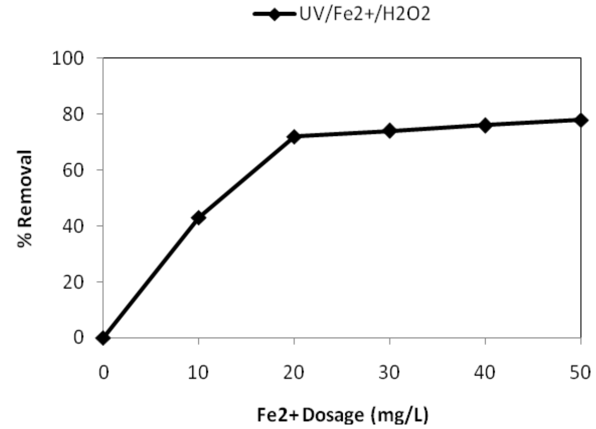

Figure 8: Effect of Fe^{2+} dosage on degradation of H-acid
Experiment conditions: H-Acid - 100 ppm, H_2O_2 = 300 mg/L, pH = 3, Reaction time = 90 min.

1.11 Comparison of various AOPs against COD removal

A comparison of UV, UV/ H_2O_2, Fenton, and UV/Fenton processes in terms of COD reduction is determined to find the efficiency of the treatment systems. Percentage reduction of COD with different AOP's is shown in **Figure 9.** The degradation with UV alone and UV/H_2O_2 processes could not totally remove COD. However, UV in combination with TiO_2 and Fe^{2+} with H_2O_2 showed considerable reduction in COD. However in the presence of catalysts based AOPs like UV/TiO_2, UV/H_2O_2/Fe^{2+} (photo-Fenton), and UV/H_2O_2/ TiO_2 an increased reduction in COD is observed when compared with UV and UV/H_2O_2 processes. The COD reduction with photo-Fenton process and UV/H_2O_2/TiO_2 (upto 80% maximum with UV/H_2O_2/ TiO_2) are found to be more efficient of all the AOPs. The order of COD reduction is UV/H_2O_2/TiO_2 > photo-Fenton > UV/TiO_2 > UV/H_2O_2 > UV.

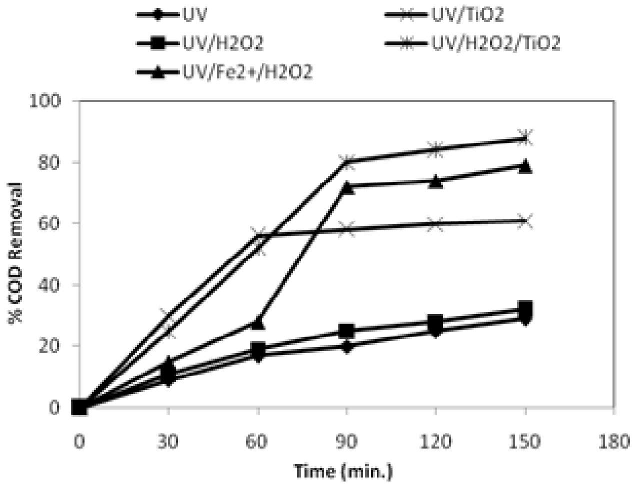

Figure 9: COD removal on the degradation of H-acid
Experiment conditions: Initial COD = 93 mg/L of H-Acid (100 ppm conc.), H_2O_2 = 250 mg/L, pH = 3.5, Fe^{2+} = 20mg/L, TiO_2 = 0.2 g/L & Reaction time = 90 min

1.12 HPLC Analysis

Reduction in H-Acid is monitored using spectrophotometric analysis and further confirmed by HPLC. It is observed from the HPLC chromatograms shown in Figure 10 that mineralization achieved by UV is almost minimal.

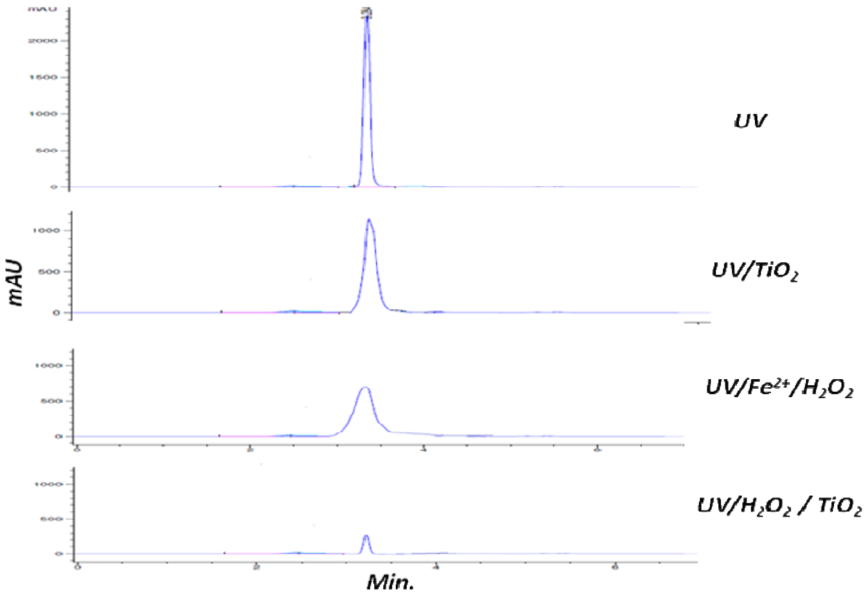

Figure 10: HPLC results for the degradation of H-Acid using AOPs (after 90 min.)

The degradation increased to almost upto 84% when UV is used in combination with peroxide and catalysts. However, the time required for degradation in both the cases is 90min. In Photo-Fenton process, 76% of H-Acid is degraded. Among all the AOPs studied, UV/H_2O_2/TiO_2

process is found to be most efficient in degradation of H-Acid i.e., a maximum of 84 % degradation is achieved.

CONCLUSION

The degradation of H-acid was investigated with homogeneous (UV, UV/H_2O_2, UV/H_2O_2/Fe^{2+} (photo-Fenton process) and heterogeneous (UV/TiO_2 and UV/H_2O_2/TiO_2) AOPs. The influence of pH, dosage of nano catalyst, H_2O_2 concentration and contact time on the rate of degradation were studied. The experimental results reveal that:

(1) The maximum degradation was achieved at pH 3 to 4 in all AOP experiments. At pH 3 the percentage degradation is achieved maximum when compared with heterogeneous process (UV/TiO_2 & UV/H_2O_2/TiO_2) of maximum observed at pH 4.
(2) The optimum H_2O_2 concentration is 300 mg/L at which maximum removal of the H-acid is achieved with heterogeneous AOPs as well as homogeneous AOPs in maximum of 90 min reaction time.
(3) The maximum removal achieved with 0.2 g/L of TiO_2 dose in heterogeneous processes where as in photo-fenton process maximum removal achieved with 20 mg/L of Fe^{2+} concentration. The maximum of 80% COD removal achieved with (UV/H_2O_2/TiO_2) heterogeneous AOPs. The order of COD reduction is UV/H_2O_2/TiO_2 > photo-Fenton > UV/TiO_2 > UV/H_2O_2 > UV.
(4) The degradation process only UV exposure (as the direct photolysis by UV light is quite slow) and H_2O_2 are not enough for complete degradation. However addition of catalyst makes faster the reaction and achieved the maximum percentage removal of compound concentration as well as COD reduction in short reaction time.
(5) The heterogeneous photo-catalysis is a prominent method for degradation of dyes and dye intermediates contained industrial wastewaters, in aqueous system under simple handling with no specific technical equipments is necessary, and also in-expensive with less investment, less energy demand and produce harmless byproducts. Among all the treatment processes studied operating cost of UV is considerably more expansive than others; however, the cost of UV can be decreased for AOPs when solar light is used.

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