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Research article

Ultrasonic, photocatalytic and sonophotocatalytic degradation of Basic Red-2 by using Nb_2O_5 nano catalyst

Vilas K. Mahajan [1], Sandip P. Patil [2], Shirish H. Sonawane [3] and Gunvant H. Sonawane [1],*

[1] Department of Chemistry, Kisan Arts, Commerce and Science College, Parola, Dist-Jalgaon-425111 (M.S), India
[2] Nano-chemistry Research Laboratory, G. T. Patil College, Nandurbar-425412 (M.S), India
[3] Department of Chemical Engineering, National Institute of Technology, Warangal (T.S), India

* Correspondence: Email: drgunvantsonawane@gmail.com; Tel: 919422213977; Fax: 02597-293688.

Abstract: The ultrasonic, photocatalytic and sonophotocatalytic degradation of Basic Red-2 accompanied by Nb_2O_5 nano catalysts were studied. The structure and morphology of synthesized Nb_2O_5 nano catalyst was investigated using scanning election microscopy (SEM), Electron dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD).The effects of various experimental parameters such as the Basic Red-2 concentration, catalyst dose, pH and addition of H_2O_2 on the ultrasonic, photocatalytic and sonophotocatalytic degradation were investigated. Photocatalytic and sonophotocatalytic degradation of Basic Red-2 was strongly affected by initial dye concentration, catalyst dose, H_2O_2 addition and pH. Basic pH (pH-10) was favored for the ultrasonic (US), photocatalytic (UV + Nb_2O_5) and sonophotocatalytic (US + UV + Nb_2O_5) degradation of Basic Red-2 by using Nb_2O_5 nano catalyst. The ultrasonic degradation of Basic Red-2 was enhanced by the addition of photocatalyst. Then, the effect of Nb_2O_5 dose on photocatalytic and sonophotocatalytic degradation were studied, and it was found that increase in catalyst dose increase in the percentage degradation of Basic Red-2. In addition, the effects of H_2O_2 on ultrasonic, photolytic, photocatalytic and sonophotocatalytic degradation was also investigated, and it was found that H_2O_2 enhances the % degradation of Basic Red-2. The possible mechanism of ultrasonic, photocatalytic and sonophotocatalytic degradation of Basic Red-2 reported by LC-MS shows generation of different degradation products.

Keywords: Basic Red-2; photocatalyst; sonophotocatalyst; ultrasonic degradation; kinetics

1. Introduction

With industrialization and population growth, the environmental contamination caused by organic pollutants, along with the rapid increase in greenhouse gas emissions, is becoming an increasing problem around the world [1,2]. In the past decades, conventional biological and physical treatment methods (like adsorption, ultrafiltration, coagulation, etc.) have been the mainstream techniques to remove pollutants from water and the atmosphere [3,4]. Nevertheless, the decontamination of many synthetic organic pollutants requires novel techniques to chemically transform them into non/less hazardous compounds. These techniques should be sufficient to remove the organic pollutants efficiently and rapidly.

Recently, with increasing concerns for eco-conservation, advanced oxidation processes (AOPs) have received great deal of attention for the destruction of organic pollutants commonly found in wastewaters. AOP is a process that involves in situ generation of free radicals such as hydroxyl radicals. In addition to conventional AOP; processes such as Fenton reaction [5], ozonation [6], sonophotocatalysis [7], electrochemical oxidation [8] and heterogeneous photocatalysis [9], ultrasound sonication are the emerging AOPs. Among all the above mentioned methods, photocatalysis is the suitable method. From the point of view of semiconductor photochemistry, the role of photocatalysis is to initiate or accelerate specific reduction and oxidation reactions on the surfaces of irradiated semiconductors. Semiconductor materials, such as TiO_2, [10,11], ZnO [12,13], Fe_2O_3, [14,15], CdS [16,17] and ZnS, [18,19] etc. are mostly used in the heterogeneous photocatalysis. Nb_2O_5 and its compounds are also found to be very interesting because of its outstanding chemical as well as physical properties. This may lead to promising applications in magnetic devices, biotechnology, gas sensing, nanotechnology, photocatalysis and photo electrodes etc. [20,21,22]. In addition, pure or doped Nb_2O_5 are gaining attention for the photocatalytic degradation of organic contaminants [23,24]. The synthesis of Nb_2O_5 with different nanostructures and morphologies by nano-chemical synthesis could enable detailed elucidation of structure-activity relationships.

The sonophotocatalytic process of oxidation shows interesting advantages at kinetic level, due to the presence of a synergistic effect between sonolysis and photocatalysis. The combination of sonolysis with photocatalysis [25], called as sonophotocatalysis is often considered to be a suitable adjustment because sonolysis can degrade the hydrophobic products and photocatalysis can degrade the hydrophilic products [26]. Most AOPs use ultraviolet (UV) irradiation to catalyze catalysts that involve in the generation of an extremely powerful and non-selective oxidizing agent, the hydroxyl radical (•OH), to destroy hazardous pollutants. In the practical application of dye wastewater treatment with ultrasonic, photocatalytic and sonophotocatalytic degradation, there is a need to determine the optimal conditions of experimental parameters.

Present study involves the synthesis of Nb_2O_5 nano catalyst which was characterized by scanning electron microscopy (SEM), electron dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) techniques. The effect of various parameters like pH of dye solution, addition of H_2O_2, initial dye concentration, catalyst dose in ultrasonic (US), photocatalytic (UV + Nb_2O_5), sonophotocatalytic (US + UV + Nb_2O_5) degradation and the kinetics of degradation for Basic Red-2 using Nb_2O_5 nano catalyst were studied.

2.   Materials and Methods

2.1. Materials

Basic Red-2 is a cationic dye. The properties and structure of Basic Red-2 are shown in Table 1 and Figure 1. All chemicals used for the synthesis of nano Nb_2O_5 are of A.R. grade and were obtained from Loba Chemie Pvt. Ltd. India. Sonication was performed with ultrasonic Probe Sonicator-20 KHz, 150 W (Dakshin Ultrasound, Mumbai, India) which was equipped with a titanium probe (10 mm of diameter), a water-circulating unit and a temperature controller. The pH of dye solution is maintained by 0.1M NaOH and 0.1M HCl using pH meter (Equiptronics model EQ-615). The double distilled water was used to prepare all the solutions.

Table 1. Properties of Basic Red-2.

Properties	Basic Red-2
C.I.	50,240
Color	Reddish
Formula	$C_{20}H_{19}N_4Cl$
Molecular Weight	350.85 g.mol^{-1}
λ_{max}	520nm
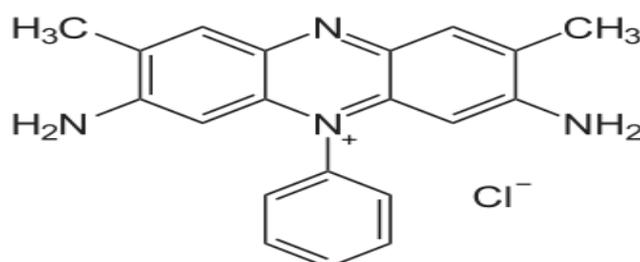
Figure 1. Structure of Basic Red-2.

2.2. Synthesis of the Nb_2O_5 nano catalyst

Commercial Nb_2O_5 powder was used as a starting material and used without further purification. In a typical synthesis, fresh niobic acid prepared by mixing 0.5 g Nb_2O_5 with 3 mL 25% $NH_3 \cdot H_2O$ and 40 mL 30% H_2O_2 to give a clear and homogeneous solution. NaOH solution in ethylene glycol (0.4 M, 5 mL) was then added to the mixed solution to provide a mild alkaline concentration. The prepared solution was transferred into a Teflon-lined stainless steel autoclave of 100 mL capacity

and sealed. The reaction was performed at 240 ℃ for 24 h and then cooled to room temperature. In the post treatment, the white precipitate was centrifuged, to separate the powder from the liquid. It was then washed for several times with deionized water and alcohol and dried at 60 ℃ for 5 h in air. Finally, the Nb_2O_5 modified samples were obtained by the calcination of resulting precipitate in air atmosphere at 500 ℃ for 2 h [27].

2.3. Characterization of Nb_2O_5 nano catalyst

The synthesized Nb_2O_5 nano catalyst was characterized by scanning electron microscopy (SEM) using HitachiS-4800 (Japan), electron dispersive X-ray spectroscopy (EDS) was performed by using Bruker X Flash 5030, and the X-ray diffraction (XRD) pattern of the samples were measured on a Bruker D 8 Advance X-ray diffractometer (Germany) using Monochromatized Cu Kα (λ 0.15418 nm) radiation under 40 kV and 40 mA and scanning over the range of $10\degree \leq 2\theta \leq 80\degree$. LCMS was taken by Varian Inc (USA) Model- 410 Prostar Binary LC with 500 MS IT PDA Detectors.

2.4. pH study

Determination of pHzpc was done to investigate how the surface charge of catalyst depended on pH. Nb_2O_5 nano catalyst for the determination of pHzpc, 0.01 M NaCl was prepared, and its initial pH was adjusted 3.0 to 12.0 by using 0.1 M NaOH and 0.1 M HCl in each batch. Then, 50 ml of 0.01 M NaCl was taken in 20 ml Erylenmeyer flasks and 0.10 g of Nb_2O_5 nano catalyst added to each solution. These flasks were kept for 48 h. and the final pH of solution was measured by using pH meter. Graph was plotted between "pH_{final} vs. $pH_{initial}$". The point of intersection of the curves of pH_{final} vs. $pH_{initial}$ was recorded as pHzpc.

2.5. Ultrasound (US) degradation study

100 mL aqueous solution of Basic Red-2 was sonicated with ultrasonic probe sonicator for 5 second off time and 30 second on time up to 15 min. at 25 ℃. Sonication was performed with ultrasonic probe sonicator operating at 20 KHz, 150 W (Dakshin Ultrasound, Mumbai, India) which was equipped with a titanium probe (10 mm of diameter). The aqueous solution saturated with pure air before and during the sonication. The reactor was sealed and connected to a gas burette to ensure a constant pressure for 1atm. The reactor cell was provided with cryostat in order to maintain the desired reaction temperature. The sonicated solution suitable amounts of sample were withdrawn at regular intervals to measure the absorbance using absorbance recorded on UV-VIS spectrophotometer (Systronics model-2203) at the λ_{max} 520 nm.

2.6. Photolytic (UV) degradation study

The photolytic degradation of Basic Red-2 was carried out in photocatalytic reactor, by irradiation with 400 W mercury lamp. Temperature (25 ℃) inside the reactor was maintained by using cooling water jacket. 100 mL dye solution (10–40 mg/L) placed in a photocatalytic reactor and concentration of the dye solution was determined using absorbance recorded on UV-VIS spectrophotometer (Systronics model-2203) at the λ_{max} 520 nm.

2.7. Photocatalytic (UV + Nb₂O₅) degradation study.

The photocatalytic degradation of Basic Red-2 was carried out in photocatalytic reactor, having 400 W mercury lamp. Temperature (25 ℃) inside the reactor was maintained by using cooling water jacket. Different nano catalyst doses were added in 100 mL dye solution (10–40 mg/L dye conc.) and placed in a photocatalytic reactor. Concentration of the dye solution was determined using absorbance recorded on UV-VIS spectrophotometer (Systronics model-2203) at the λ_{max} 520 nm.

2.8. Sonophotocatalytic (US + UV + Nb₂O₅) degradation study

Sonophotocatalysis is carried in a sequential manner in which 100 mL aqueous solution of Basic Red-2 with different concentration (10–40 mg/L) and addition of different catalyst doses was sonicated for 15 min with 5 sec off time and 30 sec on time at 25 ℃. Sonication was performed with ultrasonic probe sonicator operating at 20 KHz, 150 W (Dakshin Ultrasound, Mumbai, India) which was equipped with a titanium probe (10 mm of diameter). The aqueous solution saturated with pure air before and during the sonication. The reactor was sealed and connected to a gas burette to ensure a constant pressure for 1 atm. The reactor cell was provided with cryostat in order to maintain the desired reaction temperature. The aqueous solution is sonicated then after sonication the solution placed in photocatalytic reactor for a 40 min. During photocatalysis suitable amount of sample was withdrawn at regular intervals and sample was centrifuged to measure the absorbance using absorbance recorded on UV-VIS spectrophotometer (Systronics model-2203) at the λ_{max} 520 nm. The degradation percentage of Basic Red-2 was calculated by following equation.

$$\text{Percentage degradation} = \left(\frac{C_i - C_t}{C_i}\right) 100 \tag{1}$$

Where C_i (mg/L) and C_t (mg/L) are the initial dye concentration and concentration of dye at time t.

## 3. Results and Discussion

3.1. SEM and EDX analysis

Morphological characteristics of Nb₂O₅ nano catalyst was studied by using SEM. The Nb₂O₅ nano catalyst have analyzed before degradation of Basic Red-2 by SEM micrograph. Figure 2(a) shows the SEM micrograph of Nb₂O₅ nano catalyst. SEM micrograph showed that Nb₂O₅ nano catalyst having round shape and cluster-like nanostructures with non-uniform size distribution. The EDX analysis Figure 2(b) shows that Nb₂O₅ nano catalyst contains Nb K (62.89%), O K (37.11%). It confirms the existence of Nb₂O₅.

3.2. X-ray diffraction analysis

The XRD diagram of Nb₂O₅ is shown in Figure 3. The sample was scanned from 20° to 80° (2θ) at a scanning rate. It shows main peak at 2θ of 30.2°, 30.8°, 33.5°, 50.1°, 58.7°, 61.0°, 65.5°, 74.6° and 75.6° respectively. The high intensity of peaks indicates the highly crystalline nature of the Nb₂O₅ nano catalyst [28].
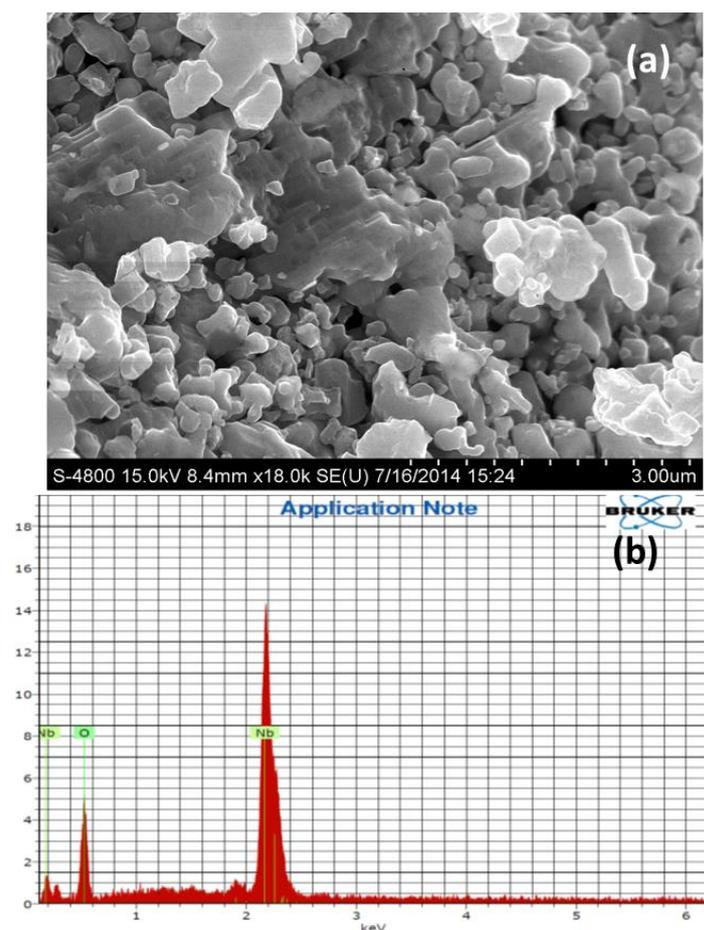
**Figure 2.** (a) The SEM image of Nb_2O_5 nano catalyst; (b) EDS spectra of Nb_2O_5 nano catalyst.
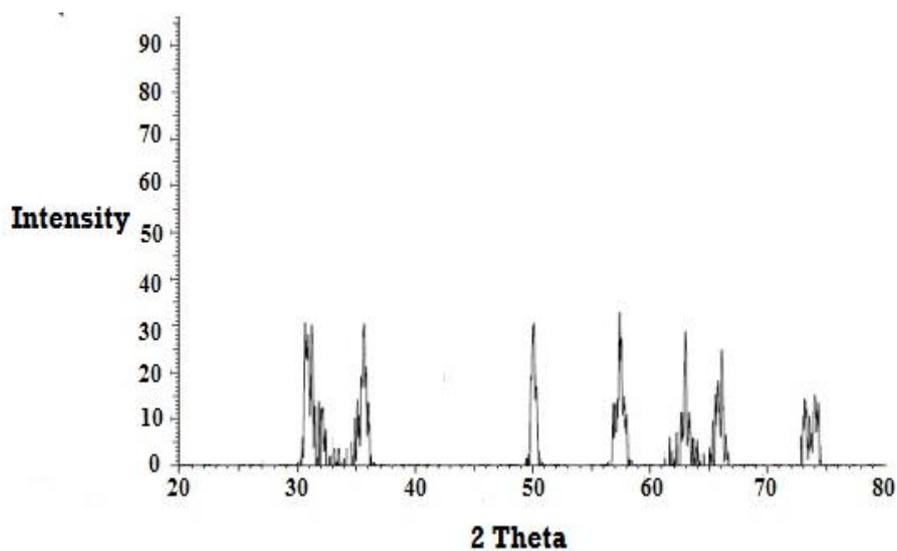
Figure 3. XRD diagram of Nb_2O_5 nano catalyst.

3.3. Effect of pH

The pH of dye solution plays an important role in photocatalytic, sonophotocatalytic and ultrasonic degradation of the dye. The effect of pH on photocatalytic, sonophotocatalytic and ultrasonic degradation were studied from pH 3 to 12 with the initial dye concentration 40 mg/L using 1 g/L photocatalyst dose and 15 min sonication in presence of catalyst and absence of catalyst. The initial pH of dye solution is 8.11. It was observed that percent degradation of Basic Red-2 was increases with increase in pH 3 to 10 and the higher percentage degradation was observed at pH 10 and again decreases in percentage degradation on increasing pH up to 12. Figure 4 shows that the rate of degradation was observed to be 5%, 10% and 26% at pH 3 which further increases up to 18%, 73% and 94% at pH 10 then it again decreases down to 52%, 57% and 63% at pH 12 for ultrasonic, photocatalytic and sonophotocatalytic degradation respectively. This indicates that ultrasonic, photocatalytic and sonophotocatalytic degradation enhances degradation of Basic Red-2 at pH 10. Since the zero point charge (pHzpc) of Nb_2O_5 nano catalyst is 4.95 $\pm$ 0.3 catalyst surface is positively charged in acidic media (pH < 4.95) whereas it is negatively charged under alkaline condition (pH > 4.95). Meanwhile, Basic Red-2 has an amine group in its structure, which is positively charged therefore, dye cannot be degrade on photocatalyst surface effectively in the acidic solution (pH $\leq$ 4.95). Maximum amount of dye degrade on the photocatalyst surface was observed at the pH 10.
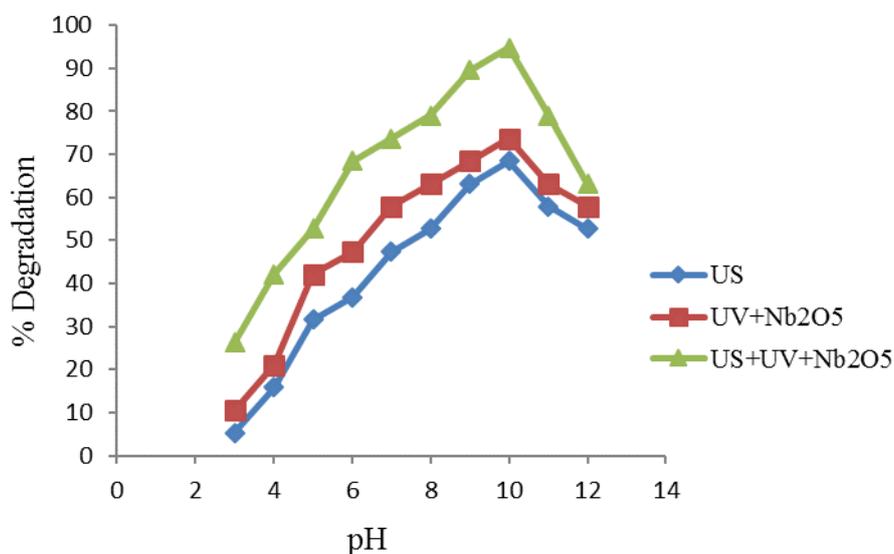

Figure 4. Effect of pH on ultrasonic, photocatalytic and sonophotocatalytic degradation of Basic Red-2 conc. 40 mg/L, catalyst dose 1 g/L, 15 min ultrasound and irradiation time 120 min.

3.4. Effect of photocatalyst and sonophotocatalyst dosage

Photocatalyst and sonophotocatalyst dose is an important parameter which determines the capacity of photocatalyst and sonophotocatalyst to degrade dye from aqueous solution. The effect of photocatalyst and sonophotocatalyst dose on dye degradation was studied by keeping all other

parameters constant (Basic Red-2 conc. 40 mg/L, pH-10). Experiments were performed to study the variations in the degradation of Basic Red-2 at different catalyst loading. It was observed that the degradation of dye increases with increase in catalyst loading from 0.5 to 2.0 g/L for 40 mg/L, at constant pH 10. Due to more availability of more catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst, increase in number of hydroxyl radicals and super oxide ions ($O_2^{\cdot-}$). A further increase in catalyst loading increases the percentage degradation. The percentage degradation was 40 to 74 % for photocatalyst and 59 to 94 % for sonophotocatalyst in catalyst dose 0.5 to 2.0 g/L (Figure 5).
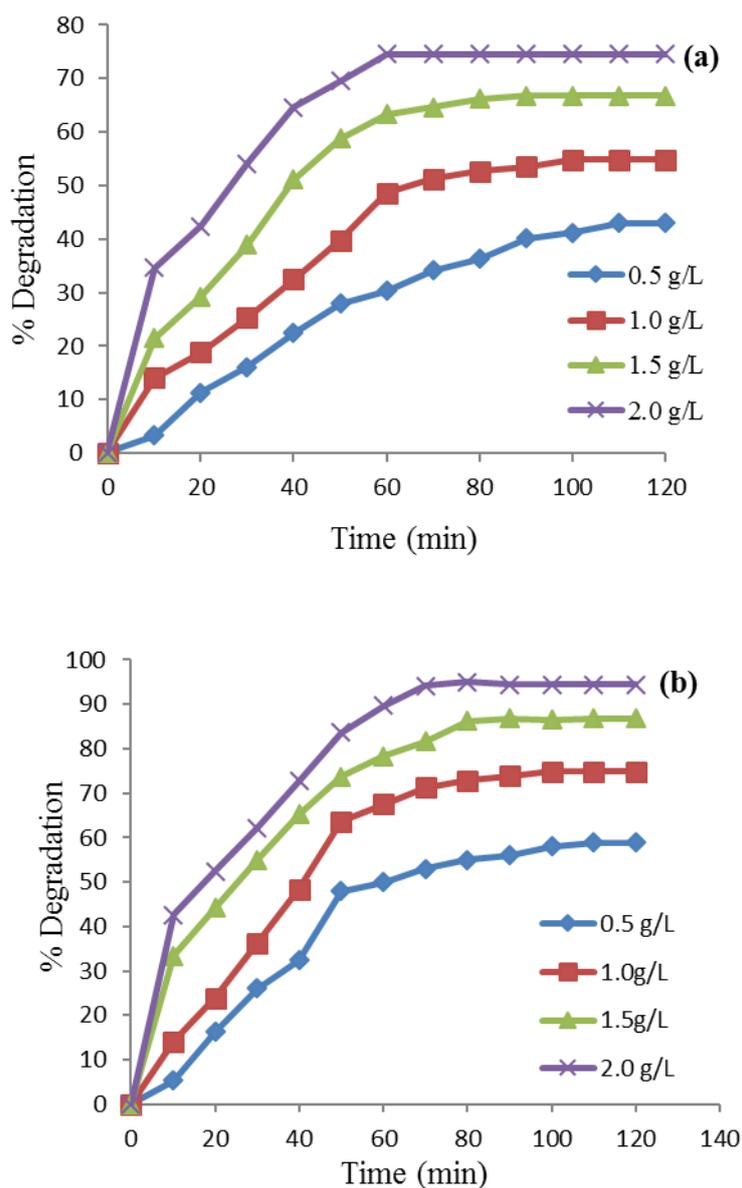
Figure 5. Effect of catalyst loading on percentage degradation. (a) UV + Nb_2O_5; (b) US + UV + Nb_2O_5 Initial dye concentration 40 mg/L, pH 10.

3.5. Effect of initial dye concentration on percentage degradation

The effect of initial dye concentration on percentage degradation of Basic Red-2 was investigated at pH 10 with initial concentration 10, 20, 30, and 40mg/L. The treatment of ultrasound for each concentration is 120 min after interval of 15 min. The results indicate that initial concentration decreases from 10 mg/L to 5.26 mg/L, 20 mg/L to 12.10 mg/L, 30 mg/L to 20.52 mg/L, 40 mg/L to 31.57 mg/L and percentage degradation decreases 47 %, 39 %, 31 %, 21 % respectively. From these results it is clearly indicated that, as the concentration of Basic Red-2 increases, the degradation percentage decreases. As initial concentration of Basic Red-2 increases the concentration of unabsorbed dye also increases. It causes less penetration of light through the solution on catalyst surface to decrease down the •OH. Hence percent degradation decreases with initial dye concentration. Ultrasonic degradation of Basic Red-2 proceeds by the reaction of •OH with the dye molecules adsorbed at the bubble interface. Also there is evaporation of dye molecules into the cavity during expansion cycle and degradation via pyrolytic reaction within the collapsing bubble. Thus as sonication time increases, there is increase in the degradation of dye molecules, which further enhances the percentage degradation.
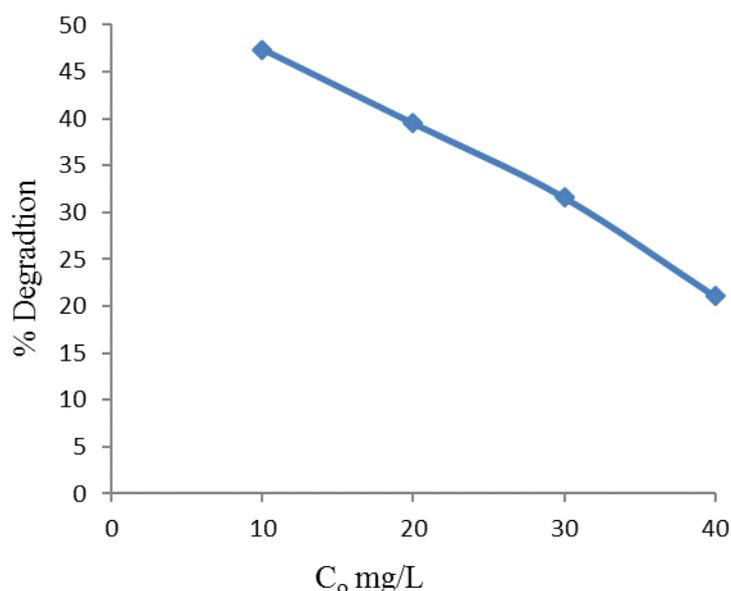

Figure 6. Effect of initial dye concentration on percentage degradation (pH 10, US power 150 W and sonication time 120 min).

3.6. Comparison for photolysis, sonolysis, photocatalysis and sonophotocatalytic degradation

Under optimized conditions of dye concentration (40 mg/L), catalysts concentrations (1 g/L) and pH 10, further experiments were conducted under photolysis(UV), sonolysis (US), photocatalysis (UV + Nb_2O_5) and sonophotocatalysis (US + UV + Nb_2O_5) processes to study their effect on percentage degradation. Adsorption study was carried out for 40 min in order to determine percentage degradation due to adsorption. It was observed that 13% Basic Red-2 was removed by adsorption. It was found from the result that after 120 min, 89 %, 84 %, 21 % and 0.22 % Basic Red-

2 degradation take place under sonophotocatalysis, photocatalysis, sonolysis and photolysis degradation processes respectively as shown in Figure 7.

The dye degradation under photocatalysis is enhanced by ultrasound. Both in photocatalysis and sonophotocatalysis the dye is degraded mainly through the generation of •OH radicals. In sonophotocatalysis process, •OH radicals are generated from splitting of water molecules under extreme conditions created by collision of cavitational bubbles. In photocatalysis process the •OH radicals are generated by UV radiation causes the photo excitation of a semiconductor catalyst. The combine effect thus increases the amount of reactive radical species inducing oxidation of dye molecules [29].
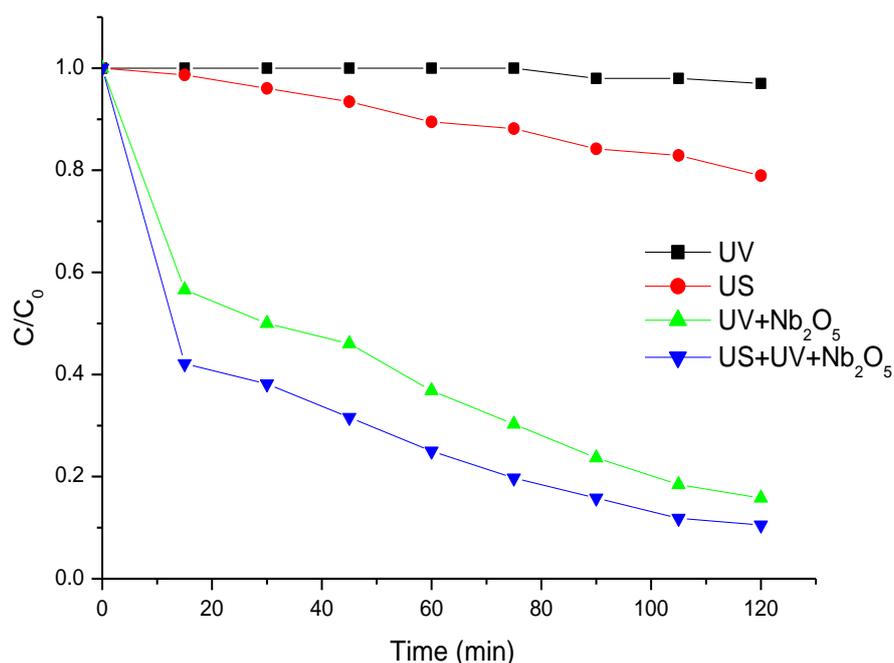

Figure 7. Comparison of photolysis, sonolysis, photocatalysis and sonophotocatalysis processes for degradation of Basic Red-2 (40 mg/L) at pH 10, Nb_2O_5 dose 1 g/L and US power 150 W.

3.7. Effect of H_2O_2 on sonophotocatalytic systems

One of the most popular advanced oxidation process (AOP) methods for degradation of organic compounds is the oxidation with H_2O_2. Presence of H_2O_2 is a key parameter for dye degradation in AOPs technique, depending on its nature of reactants [30]. The degradation of Basic Red-2 in US, H_2O_2, US/H_2O_2, $US/UV/Nb_2O_5$ and $US/UV/Nb_2O_5/H_2O_2$ systems are compared in Figure 8. The maximum degradation of Basic Red-2 98.47% was observed in $US/UV/Nb_2O_5/H_2O_2$ system after 15 min of ultrasonic irradiation and 120 min UV irradiation. Degradation efficiency was observed to be 21% in US system, 28% in H_2O_2 system and 45% US/H_2O_2 system where as in $US/UV/Nb_2O_5$ system 94% was observed. H_2O_2 has led to an enhancement of the ultrasound performance for heterogeneous sonophotocatalytic reaction. The highest degradation was observed 98.47% in $US/UV/Nb_2O_5/H_2O_2$ system compared with others systems which was mainly attributed to the promotion of ultrasound on Nb_2O_5 catalyzed degradation of H_2O_2 to form more active free radicals,

such as •OH radicals [31]. The increase in degradation efficiency is due to increased production of •OH radicals [32]. H_2O_2 increases the formation rate of •OH radicals by two ways. Firstly, the reduction of H_2O_2 at the conduction band would produce •OH radicals. Secondly, the self-destruction as a result of ultrasound irritation would also produce •OH radicals [30].
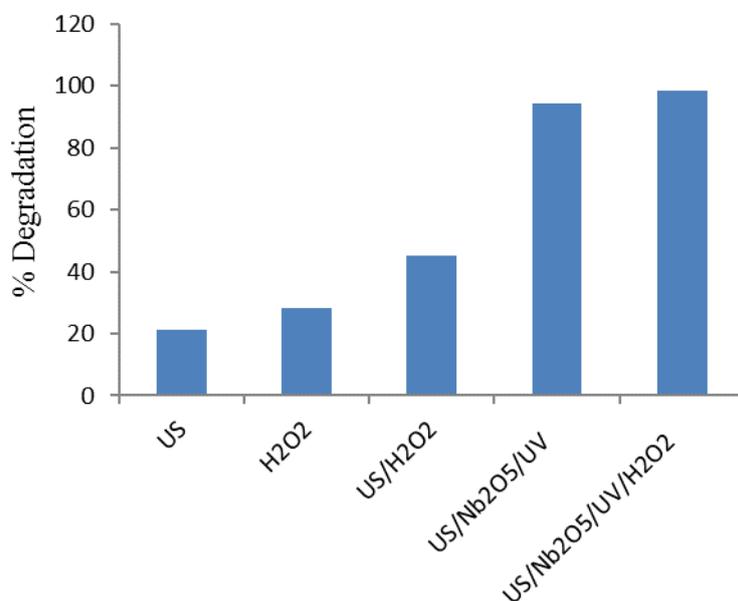
Figure 8. Effect of H_2O_2 on sonophotocatalytic system (Basic Red-2 conc. 40 mg/L, Nb_2O_5 dose 1 g/L, pH 10, 50 mg/L of (20 V/V) H_2O_2 and reaction time 120 min).

3.8. Kinetics Studies

Basic Red-2 degradation by means of sequential ultrasound and visible light in the presence of pure Nb_2O_5 catalyst is shown in Figure 9. The correlation between –ln (C/C_0) and treatment time is linear. This is a typical first order reaction plot. The slope of plots show the rate constant (k) of the reaction. The regression coefficient r^2 obtained for first order reaction at different experimental conditions which ranges from 0.98 to 0.99, confirming that degradation of Basic Red-2 under different experimental conditions i.e. sonolysis, photocatalysis and sonophotocatalysis follows the first order reaction. The sonophotocatalytic degradation generally occurs faster than the respective individual processes. The beneficial effect of coupling photocatalysis with sonolysis may be attributed to several reasons. First, increase the amounts of hydroxyl radicals (•OH) by photocatalysis and sonolysis. Second, enhancement in the mass transfer of organics between the liquid phase and the catalyst surface [33]. Third, excites the catalyst by ultrasound-induced cavitation. Fourthly, increase in surface area due to ultrasound de-aggregating catalyst particles [34]. Interestingly, there appears to be a synergistic effect between visible light and ultrasound irradiation in the presence of pure Nb_2O_5 since rate constants of the combined photocatalysis with sonolysis process were greater than rate constants of the individual processes.
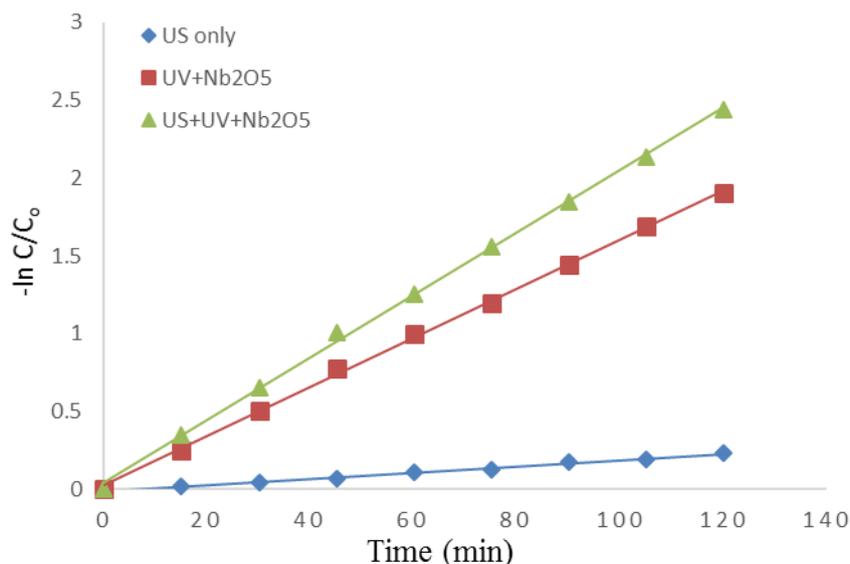
Figure 9. First order kinetics plot of Basic Red-2 degradation under sonolysis (US), photocatalysis (UV + Nb_2O_5) and sonophotocatalysis (US + UV + Nb_2O_5), Reaction conditions: pH = 10, dye conc. = 40mg/L, Nb_2O_5 = 1 g/L, US power = 150W.

3.9. Degradation mechanism

The non-selective nature of the reaction between the radicals and organic pollutants leads to the formation of number of products in the AOPs. LCMS was used to separate and identify the produced intermediates during the sonophotocatalysis process. The structures of degraded products are assigned on the basis of analysis of molecular ion peaks and their corresponding fragmentation patterns. The probable degradation pathway of Basic Red-2 is shown in Figure 10. Figure 10 indicates deamination, followed by breaking of azo linkage, to cause ring opening and electrophilic addition of $^{\bullet}OH$ radicals which subsequently mineralizes to CO_2 and H_2O.

4. Conclusion

In this study shows that US + UV + Nb_2O_5 that is sonophotocatalyst exhibited at a high activity to degradation of Basic Red-2. The percentage degradation was very slow by sonication alone and the presence of photocatalyst enhanced the rate of Basic Red-2 degradation. The extent of degradation depends on the operating conditions employed such as concentration of catalyst, initial dye concentration and solution pH. The degradation of Basic Red-2 increases with increase in catalyst dose, while the percentage degradation decreases with increase in initial concentration of Basic Red-2 and the degradation efficiency increases with increase in pH up to 10. The study showed that ultrasound was quite effective for degradation of Basic Red-2 when applied in the presence of additional catalyst. In addition, the effect of H_2O_2 on sonophotocatalytic systems was investigated for Basic Red-2 at 1g/L catalyst dose, pH 10 and compared the H_2O_2 enhanced the degradation efficiency of sonophotocatalytic degradation processes. The kinetics study shows that the reaction follows first order kinetics because the regression coefficient r^2 obtained for first order reaction at different experimental conditions which ranges from 0.98 to 0.99. LC–MS analysis shows the non-

generation of secondary waste after degradation of Basic Red-2 by Nb_2O_5 nano catalyst. .All the above results concluded that the sonophotocatalysis is effective degradation technique than sonolysis and photocatalysis.
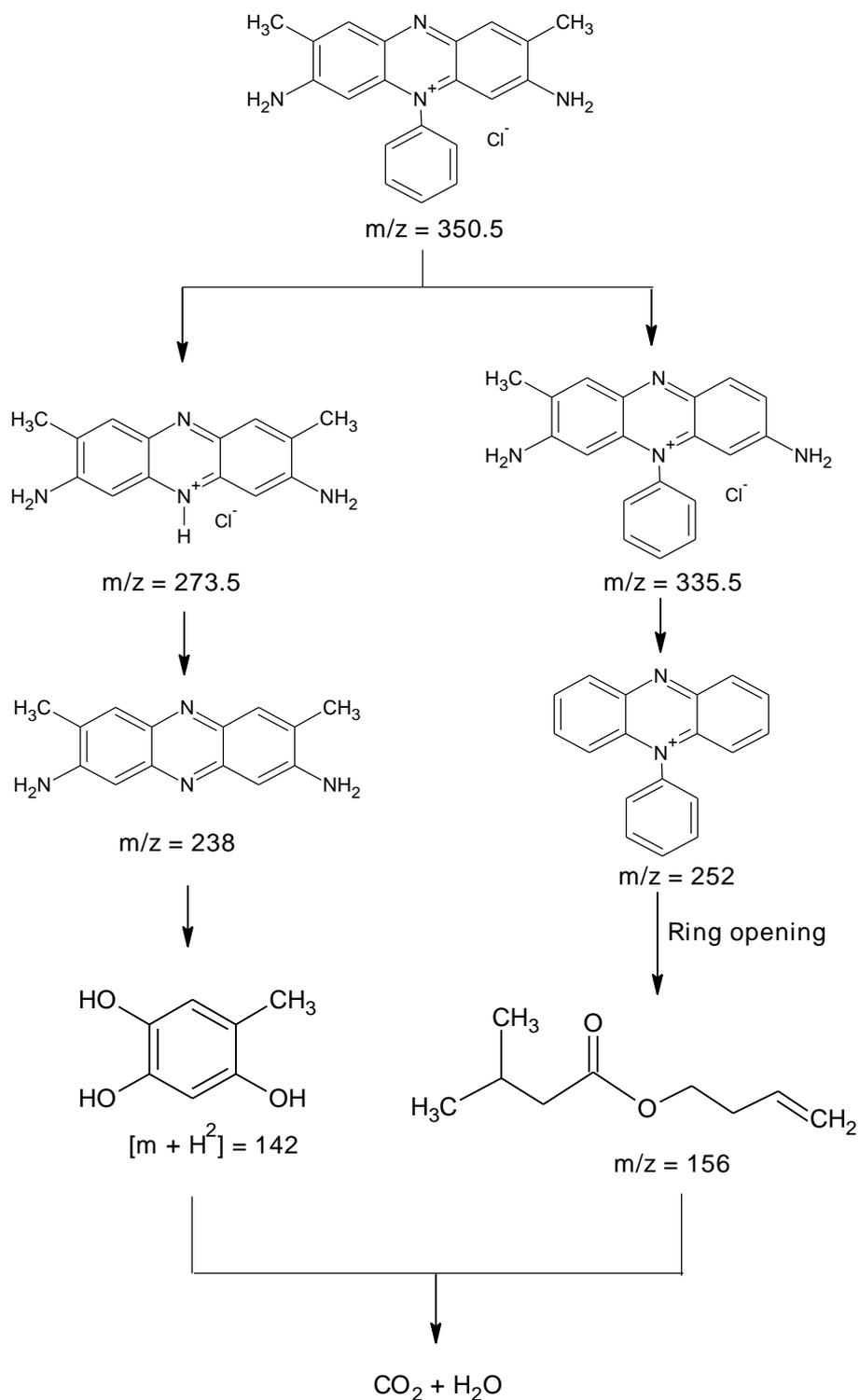
Figure 10. The possible reaction intermediates formed during ultrasonic, photocatalytic and sonophotocatalytic degradation of Basic Red-2 using Nb_2O_5 nano catalyst.

Acknowledgements

Conflicts of Interest

All authors declare no conflicts of interest in this paper.

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