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Catalytic Decolorization of Rhodamine B, Congo Red, and Crystal Violet Dyes, with a Novel Niobium Oxide Anchored Molybdenum (Nb–O–Mo)

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Abstract: In this work, a new metal-to-metal charge transfer (MMCT) heterogeneous catalyst (Nb–O–Mo) was synthesized by a chemical grafting method under an inert atmosphere. The activity of the covalently anchored oxo-bridged Nb–O–Mo catalyst was estimated for decolorization of Rh B, congo red, and crystal violet dyes in an aqueous solution under fluorescent light. The catalyst was characterized via X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray spectrometer, Fourier-transform infrared, and FT-Raman. The catalytic decolorization was evaluated from the UV spectra of dyes in aqueous solution by changing different factors, including dye concentration, temperature, and catalyst loading. Decolorization percentages were 83%–89%, 86%–95%, 97%–99% for Rh B, Congo Red and Crystal Violet in 1 min at 298 K, showing the best performance among other catalysts. Decolorization efficiency for 50 ppm of Rh B was improved from 92% to 98%, with a temperature increase to 318 K.

Keywords: metal-to-metal charge transfer; Nb₂O₅; catalytic decolorization; dyes; water purification

1. Introduction

Industrial activities bring in massive amounts of contaminants into aquatic environments, which may disturb the ecosystem. Dye organics in wastewater mainly come from dyeing, printing, textile, and food industries, resulting in negative effects [1,2]. Generally, dyes are classified into three categories, such as cationic, nonionic and anionic dyes. Rh B is a well-known xanthene dye widely used in printing, textile, and photographic industries, as well as in foodstuffs [3,4]. It is reported as harmful to human beings and animals because of its toxic nature, which causes skin irritation, eyes, and respiratory tract. Congo red is the most used dye in the textile industry, also called benzidine based anionic diazo dye [5]. This dye is harmful to the human body and causes carcinogens and mutagen. Crystal violet (Cv) is commonly used in ink industries to produce colored textiles [6]. This dye interacts easily with cell membrane surfaces in mammals and enters into cells [7], and excess inhalation causes vomiting, headache, diarrhea, dizziness, and damage to the gastrointestinal tract [8].

Several methods have been reported to purify dye contaminated water, such as biological oxidation, adsorption, and coagulation [9]. There are some problems in conventional techniques,

such as secondary pollutants, slow process, regeneration cost, high sludge production, etc. [10] To avoid such problems, photocatalyst, where a photon absorption with enough energy leads to charge separation of the photocatalyst from the valence state to the conduction state [11], has been introduced for the degradation of dyes in wastewater in the presence of external energy source [12]. This technique is more popular due to advantages such as dye degradation without producing secondary pollutants and degraded products are eco-friendly with biological systems. Zhang et al. [13] previously studied photocatalytic activities for degrading Rh B in an aqueous solution of anatase, rutile, and brookite TiO_2 , and Yin et al. [14] reported the degradation of Rh B under visible light irradiation with $\text{BiVO}_4/\text{TiO}_2$ showing 79% degradation (9 wt % $\text{BiVO}_4/\text{TiO}_2$), 1.14 times higher than that of pure TiO_2 . Kostic et al. [15] reported on solar light-induced Rh B degradation assisted by TiO_2 -Zn-Al layered double hydroxide (LDH)-based photocatalysts. Shi et al. [16] studied $\text{Ag}/\text{AgBr}/\text{ZnO}$ photocatalyst for Rh B degradation under visible light. Yang et al. [17] reported different cocatalyst by metal deposition method; among them, maximum degradation activities were observed for the $\text{Au}/\text{ZnGa}_2\text{O}_4$ catalyst with 96.7% RhB degradation in 180 min under ultraviolet light. Tian et al. [18] reported $\text{TiO}_2/\text{ZrO}_2$ composite using chitosan (CMCS) as a template, 5% $\text{TiO}_2/\text{ZrO}_2$ composite showed 90.5% Rh B degradation at $\text{pH} = 10.3$ in 4.5 h under ultraviolet light. Pica et al. [19] reported ZrP/AgBr composites for RhB degradation with a faster degradation (90% in 3 min), compared to the parent AgBr (90% in 30 min).

Advanced oxidation processes (AOPs) have recently been widely investigated as efficient routes for the destruction of organic dyes. In particular, semiconductor-based photocatalysts including iron oxide [20,21], Nb-based oxides [22,23], and titanium dioxides [24,25] are of great interest for hazardous wastewater removal to solve environmental problems. The main drawbacks of these photocatalysts lie in their limited activity and UV irradiation requirements due to their wide bandgaps. To overcome the limited activity, the doping of anions such as N, S, and C into semiconductor photocatalysts has been proposed to extend their absorption and conversion capacities in the visible light region [26–28]. In addition, various transition metals, including Ag^+ , Pb^{2+} , and Cr^{3+} were doped onto TiO_2 or SrTiO_3 semiconductors with wide band gaps, extending the photocatalytic activity to the visible region [29,30]. Among the semiconductors, TiO_2 is a well-known and promising candidate for the degradation of contaminants. TiO_2 has been made into thin layers and films based on TiO_2 nanotubes. Krbal et al. [31] reported a comparative study between sulfur treated anodic TiO_2 nanotube and parent blank TiO_2 nanotube. Sulfur treated TiO_2 nanotube showed that the photocatalytic degradation rate was 2.3 times higher than the reference TiO_2 . Motola et al. [32] developed TiO_2 nanotube layers using titanium mesh and Ti sputtered on silicon substrates for the antibiotic, photocatalytic and antimicrobial activities.

Nb_2O_5 exhibits a similar semiconductivity to TiO_2 , in addition to good chemical stability non-toxicity, and recyclability [33]. Niobium oxides are promising materials for various reactions, such as hydration, esterification, condensation, and heterogeneous photocatalysis in AOPs, due to their high Brunauer–Emmett–Teller (BET) surface areas, high selectivities, and acidic sites [34,35]. Niobium catalysts are efficient for the oxidation of organic compounds in aqueous media for the photodegradation of pollutants under UV radiation [36]. Furthermore, niobium oxides have been combined with other metals, such as Pt, Ru, and Rh, to improve their performances in many catalytic processes [37].

When two metal ions are present in different oxidation states in a complex with an oxo-bridged linkage, such as in $\text{M}_1^m\text{-O-M}_2^n$ (where m and n represent the oxidation states of metals M_1 and M_2 , respectively), a metal-to-metal charge transfer (MMCT) occurs, e.g., $\text{M}_1^m\text{-O-M}_2^n \rightarrow \text{M}_1^{m-1}\text{-O-M}_2^{n+1}$, upon absorption of visible light. Using this strategy, Frei et al. [38] developed a novel class of MMCT visible light-absorbing chromophores and mixed-valence complexes with oxygen linkages (Ti(IV)-O-Cu(I) and Ti(IV)-O-Sn(II)). Hashimoto et al. [39] also successfully developed Ce(III)-O-Ti(IV) bimetallic assemblies on MCM-41 molecular sieves that demonstrate MMCT activity under visible-light irradiation, showing the photocatalytic oxidation of 2-propanol under visible light.

Herein, based on the MMCT mechanism, a niobium oxide anchored molybdenum (Nb-O-Mo) unit using Nb_2O_5 and MoCl_5 as optimum precursors in a 1:2 ratio was successfully synthesized.

To the best of our knowledge, this is the first study to report a novel Nb–O–Mo MMCT catalyst for the catalytic decolorization of three dyes, including Rh B, Congo Red and Crystal Violet. The developed materials contain a purely inorganic redox center used for the catalytic decolorization of Rh B dye in aqueous solution. Decolorization performance was evaluated by monitoring the decrease of Rh B dye concentration in aqueous solutions under ambient conditions, using UV-vis spectroscopy. The advantage of prepared catalyst is the decolorization of Rh B by Nb–O–Mo occurred in aqueous medium under normal light (without external energy or light source) and the time required for the decolorization was reduced compared to previously reported studies. The catalyst was extensively characterized in terms of morphology, as well as structural, crystalline, and catalytic properties. The decolorization process was further confirmed by using NMR and monitoring dye concentrations, with scavengers which prevent the decolorization process.

2. Result and Discussion

There are several methods for the synthesis of catalysts such as precipitation, incipient wet impregnation, sol-gel method, physical/direct mixing, grafting, and ion exchange [40–42]. In the present study, the chemical grafting method was used for the synthesis of the Nb–O–Mo MMCT catalyst. During the synthesis, the deprotonated NbO[−] is formed on the surface of Nb₂O₅ by the basicity of TMG (1,1,3,3-tetramethylguanidine), where Mo from MoCl₅ is linked to form Nb–O–Mo MMCT linkage, which helps the photocatalytic process under fluorescent light. The XRD pattern of Nb₂O₅ was assigned via JCPDS PDF # 27-1003 [43]. The characteristic diffraction peaks of Nb₂O₅ at 22.5°, 28.3°, 36.5°, 46.1°, and 50.9°, (Figure 1) were identical to the orthorhombic structure of Nb₂O₅ reported in the literature [43]. New diffraction peaks appeared at 18.55 and 19.36° when Mo is anchored on Nb₂O₅. Moradi et al. [44] found that the intensity of the Fe-doped TiO₂ peaks was decreased compared to those of undoped TiO₂, indicating that the addition of Fe³⁺ decreased the crystallinity of TiO₂. In addition, doping of Mo in VO₂(M) barely affected XRD patterns, while the doping of Nb in VO₂(M) resulted in decreases in XRD peaks [45]. A similar trend was observed in the intensity of the XRD peaks for the Nb–O–Mo catalyst compared to pure Nb₂O₅, indicating slightly reduced crystallinity. The reduced peak intensities, with corresponding angles, are shown in Table 1.

Figure 1. X-ray diffraction pattern of pure Nb₂O₅ and Nb–O–Mo samples.

Table 1. Comparison of XRD peak intensities for Nb₂O₅ and Nb–O–Mo.

Angle (2θ)	Intensity	
	Nb ₂ O ₅	Nb–O–Mo
22.59	16,452	9156
28.36	11,108	6451
36.58	4470	2577
46.14	3107	1682
49.90	1468	965
50.98	1949	1222
55.43	2045	1258

The surface morphologies of Nb₂O₅ and Nb–O–Mo catalyst samples were identified based on SEM analysis (Figure 2). The average particle sizes, measured using ImageJ [46], were decreased from 46.2 to 29.5 μm when Mo was anchored on Nb₂O₅, while the uniformity of morphologies of Nb₂O₅ was reduced. Particle size was reduced possibly due to a physical stirring while doping MO into Nb₂O₅. A similar phenomenon was reported for Co-doped TiO₂ lattice. The particle size of TiO₂ was decreased from 15–20 nm to 5–7 nm, after Co doping with a stirring [47]. The SEM-EDS images (Figure 3) and EDS spectra (Figure S1 in Supporting Information) showed the uniform dispersion of Nb, O, and Mo elements on the sample with atomic ratios (Table S1 in supporting information) of 17.6%, 76.6%, and 5.8% for Nb, O, and Mo with a ratio of 3 to 1 for Nb and Mo.

Figure 2. SEM images of (a) Nb₂O₅ and (b) Nb–O–Mo.

N₂ adsorption-desorption isotherms at 77 K were measured for the analysis of porous structures. Before measurements, the samples were degassed for 3 h at 383 K under vacuum. The samples exhibited typical type IV curves and hysteresis loops according to IUPAC classification [40,41]. This behavior specifies the presence of mesopores. When Mo was anchored on Nb₂O₅, the BET surface area and pore volume for Nb–O–Mo were slightly decreased compared to those of Nb₂O₅ (surface area from 6.01 to 5.30 m²/g; pore volume from 0.0119 to 0.0084 cm³/g in Table S2 of Supporting Information). The pore size distribution was derived from the non-local density functional theory (NLDFT) method, based on N₂ adsorption-desorption isotherms at 77 K (Figure S2 in Supporting Information). Pore size distribution analysis for Nb₂O₅ and Nb–O–Mo exhibits that pore distribution of Nb–O–Mo was shifted to larger pore width, because the molybdenum anchored on niobium oxide resulted in [48,49].

The FTIR spectra of the Nb₂O₅ and Nb–O–Mo catalyst samples are shown in Figure 4. The peaks that appeared at 3400 cm^{−1} correspond to the OH stretching of Nb–OH in Nb₂O₅ [50] and Nb–O–Mo sample. The several peaks at 1000–1490 cm^{−1} and 1609 correspond to characteristic peaks of Mo–O linkage [51], whereas the peak at 873 cm^{−1} was assigned to Mo–O stretching. The bands between 500 and 950 cm^{−1} correspond to the angular vibrations of Nb–O–Nb and Mo–O–Mo in the Nb–O–Mo sample after anchoring Mo on the Nb₂O₅ sample [36].

Figure 3. (a) SEM image of Nb–O–Mo and corresponding EDS element mapping of (b) Nb, (c) O, and (d) Mo.

Figure 4. FTIR of the Nb₂O₅ and Nb–O–Mo samples.

To further investigate the formation of Mo on Nb₂O₅, Raman spectra of Nb₂O₅ and Nb–O–Mo were measured. The weak band at 990 cm^{−1} (Figure 5) has resulted from the vibration modes (ν_1) of NbO₆ octahedra in Nb₂O₅ [52]. The Raman band at approximately 700 cm^{−1} was assigned to orthorhombic Nb₂O₅. The strongest symmetric Nb–O stretching mode of the niobia polyhedra was related to the bond order of the niobia polyhedra and structure order [53]. After Mo doping, almost all bands disappeared, except at 700 cm^{−1}; similar behavior has been reported after the doping of metal [54].

Figure 5. Raman spectra of the Nb_2O_5 and Nb–O–Mo samples.

The UV-vis spectra in Figure 6 present the concentration decrease of Rh B in aqueous solution withdrawn from the batch reactor under the catalytic activity of Nb–O–Mo. After the addition of Nb–O–Mo catalyst to the 10 ppm Rh B aqueous solution, the absorption peak at 554 nm ascribed to a significant decrease in Rh B concentration by 80% within 1 min, indicating the decreased concentration of Rh B. The color of the Rh B dye solution almost disappeared within 10 min of the addition of the catalyst (by approximately 90%). Even with the increased concentration of Rh B, the decolorization percentages were similar to 10 ppm solution, showing 93% and 90% for 20 and 50 ppm in 10 min (Figure 7). When there is no doping of Mo, a decrease in dye concentration is negligible for Nb_2O_5 because of a lack of MMCT mechanism (Figure S3 in supporting information), showing only a 9% decrease in RhB concentration in 10 min without doping.

Figure 6. UV-vis spectra of Rh B (10 ppm) solution by Nb–O–Mo catalyst at various times.

Figure 7. Catalytic decolorization of Rh B at various dye concentrations, with different loadings of Nb–O–Mo catalyst and temperature. Error bars represent standard deviations ($n = 3$).

The effect of temperature on Rh B decolorization at a fixed catalyst loading showed that at high temperature (318 K), the characteristic absorption peak of Rh B at 554 nm diminished by 98% in 10 min after addition of the Nb–O–Mo catalyst to the 50 ppm Rh B solution (Figure S4 in Supporting Information). The dye molecules were more mobile at increased temperatures and reached the catalyst surface more rapidly for transformation, due to the increased kinetic energy of dye molecules. Yuan et al. [55] reported the effect of temperature for the oxidation of Safranin T over microporous ZnO/MoO₃/SiO₂ hybrid catalysts at 293–308 K. The decolorization efficiency reached 98% with an increase in temperature of up to 308 K.

The catalytic decolorization of Rh B was examined at different concentrations of 10, 20, and 50 ppm, to understand the influence of concentration on decolorization efficiency from the graphs of C/C_0 as a function of reaction time (Figure 7), where C_0 is the initial concentration of Rh B and C is the concentration at a certain time. It should be noted that there is no significant decrease in decolorization performance in 10 min, even with an increase in the concentration of Rh B from 10 to 50 ppm, while decolorization performances in 1 min were increased for all concentrations. Such a significant decolorization in a short time was reported for catalysts (80%–97% decolorization in 1 min for WO₃/MoCl₅ [56] with a rate constant of 104.4/min). When the temperature was increased in 50 ppm solution from 298 to 318 K, the performance was improved after 1 min. When the catalyst amount decreased from 0.8 and 0.4 g/L for 20 ppm Rh B solution (Figure 7), the decolorization performance was decreased by 53% for 1 min and 19% for 10 min. The control experiments without catalysts under a fluorescent light were carried out for all three dyes with 20 ppm concentration at 298 K (Figure S5 in supporting information), showing no significant decreases of dye concentration, due to the absence of catalysts.

The catalytic performance of Nb–O–Mo was also examined for the other two dyes of Congo Red and Crystal Violet, with 20 and 50 ppm (Figure 8). The concentrations of Congo Red and Crystal Violet

were significantly decreased by 86%–95% and 97%–99%, within 1 min, respectively. The kinetics followed a biphasic trend with an initial very fast phase followed by a slow phase. For simplicity and practical reasons, kinetics have been determined using first-order model, taking into account the experimental points of the fast degradation phase (0–1 min). The rate constant was determined using the equation, $-\ln(C/C_0) = kt$, [56], where C_0 and C are dye concentrations at time zero and t ; k is a rate constant. The rate constant (Table 2) was increased by twice for Crystal Violet when the concentration was increased from 20 to 50 ppm.

Figure 8. Catalytic decolorization of (a) Congo Red and (b) Crystal Violet at various dye concentrations at 298 K, with a fixed loading of Nb–O–Mo catalyst. Error bars represent standard deviations ($n = 3$).

Table 2. The rate constant for dye decolorization.

Dye Concentration	R ²	k [min ^{−1}]
Rh B 20 ppm 298 K	0.9948	1.944
Rh B 50 ppm 298 K	0.9995	2.220
Rh B 50 ppm 318 K	0.9993	2.226
Congo Red 20 ppm 298 K	0.9931	2.940
Congo Red 50 ppm 298 K	0.9988	1.986
Crystal Violet 20 ppm 298 K	0.9896	3.486
Crystal Violet 50 ppm 298 K	0.9834	7.116

The performance of the developed Nb–O–Mo catalyst outperforms that of the reported catalytic materials. Wang et al. [57] prepared homogeneously decorated Pt quantum dots on TiO₂ nanotube arrays, using a modified photo irradiation-reduction method for Rh B decolorization. They found that 73.47% of the Rh B was degraded after 180 min of UV irradiation. Abdel-Messih et al. [58] used TiSn₁₀ and pure titania as catalysts, achieving approximately 92% and 72% decolorization of Rh B in 3 h under UV irradiation. Kuo et al. [59] achieved photocatalytic decolorization of Rh B (~94%) in 300 min, by illuminating the surface of ZnO nanowires on silicon wafers.

To investigate the reaction mechanism of Rh B decolorization with Nb–O–Mo, different scavengers, such as benzoquinone (BQ, O₂^{•−} scavenger) of 0.108 g [60], NaHCO₃ (h⁺ scavenger) of 0.168 g [60], and isopropyl alcohol of 0.060 g (IPA, •OH scavenger) [61] were separately added to reaction mixtures containing Rh B dye solution and catalyst, where the scavengers interact with reactive radicals. Superoxide anion radical (O₂^{•−}), electron-hole (h⁺), and •OH are the primary active radicals in decolorization processes [62]. Each addition of the scavengers into Rh B solution showed decreases in concentrations (Figure 9), compared to that without scavengers, indicating that O₂^{•−}, h⁺ and •OH participate in the decolorization process. Moreover, when BQ was added into the Rh B solution with Nb–O–Mo, the decolorization of Rh B was more depressed, revealing that O₂^{•−} is likely to be the dominant active species in the decolorization process. The anchoring of Mo⁵⁺ with Nb₂O₅ broadens its visible light absorption and more electron-hole pairs are formed. The formed oxo-bridged linkage between Mo and Nb₂O₅ can accelerate the e[−]/h⁺ separation and inhibit the recombination of the generated electron-hole pairs; as a result, more generated electrons can react with O₂ to form O₂^{•−} radicals. Zhang et al. demonstrated that the photoinduced Zr(III) via the MMCT excitation of Zr(IV)–O–Ce(III) to Zr(III)–O–Ce(IV) reduced O₂ to O₂^{•−}, which was liable for the oxidation of Rh B [63]. In addition, generated •OH radicals in the reaction were monitored based on the oxidation of terephthalic acid (TA) to hydroxyterephthalic acid (TAOH) by •OH, where TA reacts with •OH to produce a fluorescent TAOH compound. The fluorescence intensity of TAOH increased with respect to time (Figure 10), representing the presence of •OH radicals generated in the catalytic reaction with Nb–O–Mo (see Figure S6 in Supporting Information for spectra changes over time).

FTIR spectroscopy was taken to identify the disappearance of Rh B due to the decolorization process (Figure 11), by comparing FTIR spectra before and after Rh B decolorization. The absence of major peaks at 2961, 2920, 2855 cm^{−1} of Rh B [64] in Nb–O–Mo after Rh B decolorization indicates that the Rh B was degraded by the Nb–O–Mo catalyst. Additionally, the structural changes of Rh B by decolorization were evaluated, by using proton NMR analysis. Four samples as one Rh B solution and three reaction mixture samples with different times of 1, 5 and 10 min were evaluated using ¹H NMR (Figure S7 in Supporting Information). The disappearance of characteristic peaks at δ 1.05, 1.99, 2.1 and 2.21 and appearance of new peaks at δ 2.07, 2.14, 2.67 and 2.92 ppm (in red color) indicates the breakdown of the Rh B structure.

Figure 9. Catalytic decolorization of Rh B (50 ppm) by Nb–O–Mo with scavengers of BQ, NaHCO₃, and IPA at 318 K.

Figure 10. TAOH formation by •OH radicals generated in the heterogeneous system.

Based on the previously reported MMCT mechanism [65], the schematic illustration of Rh B dye decolorization by Nb–O–Mo linkages is provided in Scheme 1. The oxo-bridged bimetallic linkage of Nb(V)–O–Mo(V) is supposed to be the function of the catalytic redox center. There is a possibility of MMCT transition of Nb(V)–O–Mo(V) to Nb(IV)–O–Mo(VI), which can serve as active sites for dye decolorization. The generated Nb(IV) can be trapped by the O₂ molecules to return to Nb(V), producing the superoxide anion radicals as a strong oxidizing agent for the decolorization of organic

compounds; meanwhile, the Mo(VI) is reduced to Mo(V) by receiving an electron from water molecule in dye solution, leaving H^+ and $\bullet OH$ radicals, which contribute to dye decolorization.

Figure 11. FTIR spectra of Nb–O–Mo before decolorization and Nb–O–Mo after decolorization.

Scheme 1. Schematic illustration of Rh B decolorization by Nb–O–Mo MMCT catalyst.

The reusability of a catalyst was examined by performing recycling experiments, because it is another important aspect as a catalyst in water treatment, due to which it can be used as an industrial catalyst and avoiding secondary pollution. After each reaction in Rh B solution, Nb–O–Mo was collected from the solution by a centrifuge and washed with deionized water, dried and reused for the next experiment. The decolorization activities of Nb–O–Mo (Figure 12) were effectively maintained during three cycles, with a 7% decrease in efficiency, which is similar to the reported catalysts, including $Co_xFe_{3-x}O_4$ nanocatalyst [66], Ag- Fe_3O_4 composite [67], and Ag_2CO_3 catalyst [68].

Inductively coupled plasma-mass spectroscopy (ICP-MS) analysis was performed to investigate the metal leaching. The Rh B (10 ppm) solution with 0.8 g/L catalyst loading was used for 10 min. The formed reaction solution after the decolorization was centrifuged at 1000 rpm and finally passed through a mixed cellulose ester syringe filter. For the ICP-MS analysis, 2 ml of the above solution was diluted to 4 ml, by using deionized water and comparing with the standard solution of Mo with

1, 10 and 100 ppm for a calibration curve (Figure S8 in supporting information), showing that the leaching of Mo in reaction aliquot was 7.8 ppm, less than 1% of total catalyst loading (mass of Mo leaching = 0.0078 g/L, total catalyst loading = 0.8 g/L).

Figure 12. Rh B decolorization efficiency of Nb–O–Mo for three cycles.

3. Experimental

3.1. Materials and Chemicals

Niobium oxide (Nb_2O_5 , 99.99%), 1,1,3,3-tetramethylguanidine (99%), molybdenum pentachloride (MoCl_5 , 95%), and deionized water were purchased from Sigma Aldrich (St. Louis, MO, USA). Anhydrous toluene ($\geq 99.8\%$) was obtained from Honeywell Chemicals (Harvey St., Muskegon, MI, USA). All chemicals and solvents were of analytical grade and used without further purification.

3.2. Preparation of the Catalyst

The niobium oxide anchored molybdenum (Nb–O–Mo) catalysts were prepared using a Schlenk line under a nitrogen atmosphere. In a typical synthesis, 0.5 g of Nb_2O_5 was added to a 100 mL single-necked Schlenk flask (A), capped with rubber septa. Nitrogen gas was purged and evacuated twice to remove air and the Nb_2O_5 was vacuum dried overnight at 363 K. Similarly, 1 g of MoCl_5 was placed in another single necked Schlenk flask (B) and maintained under a nitrogen atmosphere. Anhydrous toluene (25 mL) was transferred to both flasks (A and B) using a cannula tube. Further, 0.5 mL of tetramethylguanidine was added to flask A containing the Nb_2O_5 solution under a nitrogen atmosphere using a glass syringe. Both flask solutions were stirred for 1 h under a nitrogen atmosphere and room temperature. After 1 h, the MoCl_5 solution from flask B was transferred to a flask containing Nb_2O_5 solution using a cannula tube. Finally, the reaction mixture was stirred for 2 h maintaining the nitrogen atmosphere. The resulting product was filtered and washed with toluene a couple of times under inert vacuum conditions. The final product was dried under vacuum overnight at 388 K.

3.3. Experimental Procedure for Oxidative Decolorization of Rh B, Congo Red, and Crystal Violet

Dye solutions of 10, 20, and 50 ppm were prepared for dyes. In a batch reactor, 100 mL of dye solution at the desired concentration was mixed with 80 mg of the catalyst (0.8 g/L) and then stirred for 10 min. At certain time intervals from 0 to 10 min, an approximately 4 mL aliquot of the reaction mixture was withdrawn for concentration analysis by using a UV spectrometer. The absorbances of Rh B, Congo Red, and Crystal Violet were recorded at 554, 498, and 590 nm respectively (Figure S9 for calibration curves in supporting information). The catalytic activity was performed under normal light conditions and at room temperature (298 K), where there is no highly concentrated light source, such as a UV lamp, directly irradiating the reactor. The only light source was a fluorescent light 480 nm to 570 nm with a frequency of 120 Hz located at the ceiling to brighten the laboratory, providing small energy of light.

3.4. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded using an X-ray diffractometer (XPert Pro-MPD, PANalytical, Netherlands) with Cu anodes from 10 to 70° under 40 kV and 40 mA. Fourier-transform infrared (FTIR) spectra were recorded using an FT/IR 6300 spectrometer (JASCO, Japan) from 400 to 4000 cm⁻¹. KBr pellets were prepared to obtain FTIR spectra by mixing the Nb–O–Mo catalyst with KBr in a weight ratio of 1:99. The scanning electron microscopy (SEM) images and atomic percentages of Nb, O, and Mo were determined using a scanning electron microscope (Merlin compact, Oberkochen, Germany), equipped with an energy-dispersive X-ray spectrometer (EDS) to observe the specific microstructures of the prepared samples. The UV-vis spectra of the various liquid samples were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent, Santa Clara, CA, USA), from 350 to 800 nm. To measure the specific surface area of the samples, N₂ adsorption-desorption isotherms were measured at 77 K using liquid nitrogen, and the specific surface areas of the samples were calculated using the BET method with BELSORP-Mini-II BET equipment (Microtrac BEL, Japan). Then, ¹H nuclear magnetic resonance (¹H NMR) spectra of the dye solution were achieved using Bruker NMR spectrometer (San Jose, CA, USA) operating at 600 MHz at 300 K. To prepare for the samples for NMR analysis, an appropriate amount of the catalyst was added to 2 mL of Rh B solution in D₂O and vortexed for a desired time to achieve catalytic decolorization. After the reaction, the mixture was centrifuged to remove Nb–O–Mo catalyst particles and the residue was used for NMR analysis.

To investigate the presence of •OH radicals in the reaction, the oxidation of terephthalic acid (TA) was performed according to the following method: Nb–O–Mo catalyst (40 mg) was added to TA (6 × 10⁻³ M) aqueous solution of 50 ml with 0.02 M NaOH, and the reaction was carried out for 60 min. During the reaction, sample aliquots were collected and filtered at every 10 min and the formation of hydroxyterephthalic acid (TAOH) was identified by using a fluorescence spectrophotometer (HITACHI F-7000) at 350–500 nm.

4. Conclusions

Niobium oxide anchored with a molybdenum catalyst was successfully synthesized using a Schlenk line. The as-synthesized catalyst was analyzed using various characterization techniques, including XRD, SEM with EDS, FTIR, and FT-Raman spectroscopy to explore the structure, morphology, and linkage between elements. XRD studies showed the orthorhombic structure of Nb₂O₅ and EDS mapping elucidated the presence and relative proportion of each element in the catalyst. The catalytic activity was explored for the oxidation of Rh B, Congo Red, and Crystal Violet and was examined using UV-vis spectra in at 554 nm. Decolorization intensity was retained over time, achieving 91%, 93%, and 92% decolorization of Rh B at initial concentrations of 10, 20 and 50 ppm, respectively, within 10 min at 298 K. Large decolorization was also observed 86%–95% and 97%–99% in 1 min for Congo Red and Crystal Violet respectively. The obtained results indicate that the decolorization efficiency of niobium oxide anchored molybdenum was not affected by even high initial dye concentration (50 ppm). The decolorization efficiency was enhanced to 98% for 50 ppm at 318 K, with a catalyst loading of 0.8 g/L, which was the best performance among other materials, such as ZnO nanoparticles of 1 g/L (96% decolorization in 180 min) [69], CdS/AgBr-rGO nanocomposite of 0.6 g/L (96% decolorization in 60 min) [70], TiO₂/RCN heterojunction photocatalyst of 0.5 g/L (98.6% decolorization in 240 min) [71], and MnO₂ of 2.5 g/L (90% in 25 min) [72]. The decolorization of Rh B was confirmed by FTIR and NMR analysis, as well as performing scavenger experiments. In conclusion, the results presented herein indicate that the prepared catalyst is a potential candidate for the catalytic oxidation of hazardous cationic organic compounds in water to environmentally innocuous products.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/5/491/s1>, Figure S1: EDS spectrum of Nb–O–Mo, Figure S2: (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of Nb₂O₅ and Nb–O–Mo at 77 K, Figure S3: Catalytic decolourization of Rh B (10 ppm) by Nb₂O₅ and Nb–O–Mo catalyst at 298K, Figure S4: UV-vis spectral changes of Rh B 50 ppm dye solution upon addition of Nb–O–Mo catalyst at 318 K at various time intervals, Figure S5: Control experiment of dyes without catalyst

at 298K, Figure S6: Fluorescence spectra for TAOH formation with respect to reaction time, Figure S7: ¹H NMR spectra of samples with different decolourization percentages (Rh B(Gray), Blue(1 min), Green(5 min) and Red(10 min) decolourization) under a catalytic decolourization by Nb–O–Mo, Figure S8: Calibration curves for Mo(V) using ICP-MS, Figure S9: Calibration curves for a) Rh B, b) Congo Red and c) Crystal violet, Table S1: EDS elemental analysis of Nb–O–Mo, Table S2: Surface area and pore volume of Nb₂O₅ and Nb–O–Mo.

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