Degradation of Remazol Black dye from Aqueous Solution by Heterogeneous NH₃(MoO₃)₃/H₂O₂ System

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Authors’ contributions

This work was carried out in collaboration among all authors. Author KYU conducted the experiment, data collection, and analysis of data, and helped to prepare the first edition of the manuscript. Author KO participated in the design of the study and wrote the manuscript. Author GUP helped to edit the manuscript. Author ENS provided the material and technical assistance for the study. Author TA conceived the study and coordinated the work. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2021/v22i730421

Original Research Article

ABSTRACT

Aims: The pollution of the environment by organic dyes in water is a matter of great concern. Wastewater containing dyes is difficult to treat by conventional wastewater treatment methods such as coagulation, ozonation, biological treatment, etc. This is why the implementation of an effective method by not generating pollutants secondary is necessary. The objective of this work is to study the degradation of remazol black, an azo dye, by the coupling of hydrogen peroxide - molybdenum oxide nanoparticle. The nanoparticles were synthesized by the aqueous sol-gel method using a reflux assembly.

Study Design: Random design.

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Methodology: The nanoparticles were synthesized by the aqueous sol-gel method using a reflux assembly and then characterized by X-ray diffraction and using software Origin to determine the particles size by Scherrer's formula. The influence of hydrogen peroxide, molybdenum oxide and hydrogen peroxide / molybdenum oxide coupling, and the degradation kinetics of remazol black were studied. We also studied the influence of the pH of the solution, the mass of molybdenum nanoparticles and the concentration of remazol black on the dye degradation process.

Results: The results showed that the synthesized oxide is ammonium molybdenum trioxide $\text{NH}_3(\text{MoO}_3)_3$ with a hexagonal structure and size 22.79 nm. The study of the catalytic effect revealed a degradation rate of 17%, 0.83% and 42% respectively for $\text{H}_2\text{O}_2$, $\text{NH}_3(\text{MoO}_3)_3$ and the coupling $\text{NH}_3(\text{MoO}_3)_3/\text{H}_2\text{O}_2$. The study also showed that the degradation of remazol black by the couple $\text{NH}_3(\text{MoO}_3)_3/\text{H}_2\text{O}_2$ is better at pH = 4 and for a mass of nanoparticles of 400 mg. This degradation kinetics are pseudo 1st order. In addition, the degradation rate decreases when the concentration of remazol black increases. The efficiency of the coupling ($\text{NH}_3(\text{MoO}_3)_3/\text{H}_2\text{O}_2$ showed at ambient temperature, that it was possible to remove about 60% of the initial color of remazol black from the water in a batch reaction.

Conclusion: The reflux method makes it possible to synthesize molybdenum nanoparticles. The molybdenum oxide hetero-Fenton process is effective in removing remazol black dye from water.

Keywords: Molybdenum oxide; nanoparticles; Fenton process; depollution; dyes.

1. INTRODUCTION

Dyes are widely used in printing, food, cosmetic and clinical industries, but especially in textile industries for their chemical stability and ease of synthesis and variety of colors. However, these dyes are the source of pollution once released into the environment.

The annual world production of dyestuffs is estimated to be around 7,105 tonnes/year and around 5% of the total amount is released to wastewater by the textile industries [1].

The presence of textile dyes in the wastewater discharged by the textile and dyeing industries into aquatic environments such as ponds, rivers, seas, oceans and the lack of their biodegradability, under normal ecological conditions can destroy the vital conditions of these different environments, while penetrating light into the depths of aquatic environments [2]. Consequently, there will be serious ecological consequences such as the modification of the nature of the aquatic environments and the reduction of photosynthesis in marine plants [3], by triggering the phenomenon of eutrophication, under the effect of the uncontrolled release of mineral elements such as nitrates, nitrites and phosphates, and produces long-term risks of persistence, and bioaccumulation [4]. In addition, this wastewater can generate several dangerous problems, namely aesthetic and health problems such as changes in the quality (color and odor) of the water and make it toxic, as they can cause allergies, dermatitis, skin irritations, cancers and in humans [5]. For example, a study was carried out by Nilsson in 15 Swedish industries in 1142 employees of whom 162 were exposed to dyes, 6% complained of respiratory and or nasal symptoms, which appeared 9 times out of 10 less than a year after the start of the exposure. Allergy to reactive dyes was confirmed for 3% of them. In particular, Reactive Black 5 gave all positive tests [6].

As a result, the problem of textile effluents discharged into the environment appears to be a major issue in water treatment. One of the most widely used methods is the biological method for its low cost of realization [7]. Unfortunately, microorganisms do not have the ability to degrade a wide range of organic pollutants such as azo dyes. Various other methods of treating water loaded with organic dyes such as adsorption on activated carbon, membrane filtration, photocatalysis, electrochemistry, coagulation and ozonolysis exist [8-10]. Most of these methods are expensive, have complex procedures, or promote the formation of secondary pollutants. Among these methods, the use of oxide-based nanoparticles could be of interest due to the affordable cost and the ease of regeneration of the catalyst. The oxides of titanium (TiO₂) and tungsten (WO₃) have been used for the degradation of dyes [9, 11-13]. Alone, these oxides degrade the dyes very little. Coupling with hydrogen peroxide is necessary. Powerful free radicals (OH⁻) are thus produced with these metal oxides, capable of powerfully degrading dyes.
In this work, we proposed to synthesize molybdenum oxide and use it in coupling with hydrogen peroxide to degrade the remazol black dye in aqueous solution.

2. MATERIAL AND METHODS

2.1 Synthesis

The following procedure was inspired by Redel [14], but modified to prepare molybdenum oxide nanoparticles without surfactant. First, 2 g of ammonium molybdate powder ((NH₄)₆Mo₇O₂₄·4H₂O), purity 99.98%, Applichem panreac was dissolved in 10 mL of deionized water and the mixture stirred for 15 min. Then we placed the resulting mixture in an ice bath to introduce 5 mL of nitric acid (ACS reagent, purity 70%) poured drop by drop and stirred a second time for 30 min. After this step, the mixture was refluxed at 90 °C for 12 h. After bringing the mixture to reflux, we separated the resulting precipitate using a centrifuge. We then washed the precipitate obtained three times with distilled water and then once with ethanol, then we dried it in an oven at 70 °C for 10 h and was able to obtain molybdenum oxide.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker D8 Advance X-ray diffractometer equipped with a Cu Ka radiation source (λ = 1.5418 Å). The data were collected over an angular domain 2θ varying from 5 ° to 80 ° using increments of 0.02 ° and an integration time of 1.3 s per increment with a scintillator detector. The diagrams obtained are diffractograms representing the intensity of diffracted photons as a function of 2θ. The determination of interreticular distances dhkl uses Bragg's law:

\[ 2d_{hk} \sin \theta = n \lambda \]  

(1)

Where, dhkl is the inter-reticular distance corresponding to the distance between two planes of Miller index hkl (Å); θ is the Bragg diffraction angle corresponding to the half-angle of deviation (°), n is the order of diffraction (unitless) and λ the X-ray wavelength (nm). From Bragg's law, the positions of the lines and the widths at mid-height make it possible to determine the average size of the crystallites using the origin software.

2.3 Preparation of Calibration Curve

The measurement of the absorbance of Remazol black (Table 1) was carried out using a UV-1600PC spectrophotometer in the 200-1000 nm range. Fig. 1 shows the obtained chromatogram. The chromatogram shows 2 predominant peaks. The peak at 595 nm corresponds to the wavelength of the azo bond responsible for the coloring of the dye. The peak at 316 nm corresponds to the wavelength of the aromatic nucleus characteristic of the dye [15].

In the rest of our work, the wavelength at 595 nm will be used to determine the initial and residual concentrations of the dye after treatment.

The calibration curve for remazol black (RB) was obtained from different aqueous solutions of remazol black with a concentration between 2 and 100 mg / L. Absorbance measurements were taken at 595 nm.

Fig. 2 showing the calibration curve obtained by plotting A = f (C), shows a good correlation between Absorbance and Concentration.

This curve will then be used to determine the initial and residual concentrations at each moment of the treatment.

2.4 Catalytic Tests

In a reactor capacity of 100 mL, we introduced 25 mL of remazol black (Table 1) of concentration \( C_0 \). We added a mass m of molybdenum oxide prepared and a volume V of hydrogen peroxide. The mixture is stirred using a magnetic stirrer for 120 min at room temperature. At the end of the reaction, the mixture was separated using a centrifuge at 8000 rpm. 1 mL of the supernatant was taken for analysis with a UV–vis spectrophotometer in order to determine the residual concentration of remazol black.

The percentage of remazol black removal is determined according to the formula:

\[ \% \text{ removal} = \left( \frac{C_0 - C_f}{C_0} \right) \times 100 \]  

(3)
Where \( C_0 \) and \( C_r \) are respectively the initial concentration before treatment and the residual concentration after treatment of the dye in mg.L\(^{-1}\).

Molybdenum oxide particles were recovered then washed with ethanol and water several times and dried at 60 °C overnight for reusability.

Fig. 1. Remazol absorption chromatogram

![Remazol absorption chromatogram](image1)

Fig. 2. Absorbance calibration curve as a function of remazol black concentration

![Absorbance calibration curve](image2)
Table 1. Information about Remazol black

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Remazol black</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{26}H_{21}N_{5}Na_{4}O_{19}S_{6} C_{28}H_{21}N_{5}Na_{6}O_{19}S_{6}</td>
</tr>
<tr>
<td>Molecular weight (g.mol⁻¹)</td>
<td>991.82</td>
</tr>
<tr>
<td>𝜆_{max} (nm)</td>
<td>595</td>
</tr>
</tbody>
</table>

2.5 Kinetic Study

A kinetic study was performed on all tests for the elimination of RB. During the reaction, it consisted in taking quantities of the mixture every 10 min and then analyzing them with a spectrophotometer in order to determine the corresponding residual concentrations. This study aims to determine on the one hand, the influence of concentration on degradation and on the other hand to determine the kinetic model(s) governing this process.

3. RESULTS AND DISCUSSION

3.1 Characterization of Molybdenum Oxide

Fig. 3 shows the XRD diffraction patterns of the prepared molybdenum oxide.

According to basic crystallography data, the diffractogram of the analyzed sample is indexed to the hexagonal structure of ammonium molybdenum trioxide (NH₃(MoO₃)₃) of No. 96-153-7263. For clarity, the main Bragg peaks are indexed. Indeed, all the main peaks indexed to molybdenum trioxide NH₃(MoO₃)₃, with the space group P 63 / m (176) and density 4.108 g / cm³ are shown. The mesh parameters a and c correspond to respectively 10.5680 Å and 3.7260 Å. The hkl indices show the different faces of the oxide according to Garin JL [16].

Using Scherrer’s formula (Eq.4) and the software origin allowed us to determine the size of the prepared oxide.

\[ D = \frac{\kappa \lambda}{\beta \cos \theta} \quad (4) \]

Where the wavelength \( \lambda = 0.154060 \text{ nm} \) and the Scherrer constant \( K = 0.89 \).

The particle size is 22.79 nm. The synthesized oxide is therefore a nanoparticle because the size is between 1 and 100 nm [17]. We called it NMO (nanoparticle of molybdenum oxide).

3.2 Degradation of Remazol Black by NMO/ \( \text{H}_2\text{O}_2 \)

For the catalytic tests, we tried to degrade remazol black by hydrogen peroxide alone, molybdenum oxide alone and the coupling of molybdenum oxide-hydrogen peroxide. Fig. 4 shows the percentage of remazol black degraded in each case. In the presence of molybdenum oxide alone there is a low rate of elimination (less than 1%). Molybdenum oxide, like most metal oxides, degrades dyes very little. Metal oxides have low specific surfaces. The dyes therefore adsorb very little on the metal oxides, which explains the low degradation capacity of remazol black by molybdenum oxide [12]. The use of hydrogen peroxide alone for the degradation of indigo reached about 17%. We can attribute the contribution of \( \text{H}_2\text{O}_2 \) to its strong oxidizing power (1.78 V).

When hydrogen peroxide is coupled with molybdenum oxide particles, the rate of remazol black removal is 42%. Thus, the couple NMO / \( \text{H}_2\text{O}_2 \) is therefore powerful to degrade remazol black in aqueous solution.

The degradation of remazol black by the NMO / \( \text{H}_2\text{O}_2 \) is due to the phenomenon of oxidation. This oxidation is due to the powerful reactive oxygen species (\( \text{OH}^-, \text{OH}^\bullet, \text{O}_2^-, \text{O}_2^{2-} \)) released by the action of hydrogen peroxide on the metal oxide of molybdenum [18].
Fig. 3. X-ray diffraction of the oxide and mesh parameters

Fig. 4. Effect of H$_2$O$_2$, NMO and NMO/H$_2$O$_2$ in the removal of Remazol black

Fig. 5. Evolution curve of the degradation of remazol black as a function of the catalyst
According to the review of literature, the degradation of organic dyes by metal oxide nanoparticles coupled with hydrogen peroxide is due to the decomposition of hydrogen peroxide which produce strong oxidant rather than the adsorption by metal oxide nanoparticles [19-20]. The hydroxyl radical can be formed during the degradation of hydrogen peroxide in the presence of transition metals (M) according to the following Fenton reaction (1)

\[ M^{(n-1)+} + H_2O_2 \rightarrow M^{n+} + OH^- + \cdot OH \]  

(1)

Dyes and several other organic compounds (RH) can be decomposed by these radicals formed according to the equation (2)

\[ RH + \cdot OH \rightarrow \text{Reaction intermediates} + CO_2 + H_2O \]  

(2)

The removal efficiency of remazol black by the molybdenum oxide/H\textsubscript{2}O\textsubscript{2} without optimized conditions is very similar to those observed during the degradation of organic dyes by hydrogen peroxide in the presence of cerium oxide [21].

Fig. 5 shows four characteristic spectra of remazol black, of the remazol black - H\textsubscript{2}O\textsubscript{2} mixture, remazol black - NMO mixture, remazol black - NMO/H\textsubscript{2}O\textsubscript{2} mixture after 120 min. The spectrum of remazol alone shows two peaks located at \( \lambda = 595 \) nm and at \( \lambda = 316 \) nm characteristic respectively of the azo bonds (responsible for the dark blue coloration) of the dye and of the aromatic rings [15, 22]. After addition of hydrogen peroxide, a slight decrease is observed peak at 595 nm, therefore a slight discoloration. The spectrum obtained after the addition of the oxide alone is almost identical to that of remazol black alone. However, there is a shift of the peak of 316 nm with an increase in size of the spectrum at this level. The oxide would complex with the aromatic nucleus. With the rémazol - NMO/H\textsubscript{2}O\textsubscript{2} mixture, there is a decrease in the peak located at 595 nm indicating a rupture of the azo bond (-N = N-). The decrease in the absorption band is due to a discoloration of the solution. The hydroxyl radicals generated by the coupling are able to attack the double bond of the azo group in order to ensure its breakage by producing degradation by-products which do not absorb in the same visible region. This break marks the start of the degradation of rémazol. In contrast, the absorption at \( \lambda = 316 \) nm of the benzene ring increases considerably and has shifted to \( \lambda = 300 \) nm, indicating that degradation intermediates containing a benzene ring have been generated. These results are in agreement with the work reported in the literature [23-24]. Similar results were obtained during the degradation of remazol black by the photo Fenton process [15,25].

3.3 Influence of Some Parameters on the Degradation of Remazol Black

The influence of pH on degradation of rémazol black by NMO/H\textsubscript{2}O\textsubscript{2} is shown in Fig. 6a. The result shows that the oxidation of rémazol black by the couple NMO/H\textsubscript{2}O\textsubscript{2} is strongly pH-dependent. pH value of the solution plays a significant role in the Fenton oxidation process as it influences the generation of hydroxyl radicals. The degradation efficiency increased from 52.45 to 58.76% with increasing the pH value from 3 to 4. Then the degradation decreases with increasing the pH from 4 to become 15.25% at pH 10. The optimum pH (potential hydrogen) value 4. These results are in agreement with several works concerning organic dyes degradation using nanocomposites of manganese oxide and iron oxide [26-27].

![Fig. 6. Effect of a) pH and b) mass of NOM in NMO /H\textsubscript{2}O\textsubscript{2} couple for the remazol black removal](image-url)
The effect of the mass of NMO on the degradation of rémazol black was studied by varying the mass of NMO (from 50 to 500 mg). The results obtained are shown in Fig. 6b. Experimental results show that the removal percentages of the dye increase as the amount of NMO increases. The increasing of the removal rate with the mass of NMO is due to the high amount of site available to produce more oxidative species. From approximately 400 mg of NMO the removal rate of rémazol did not change. According to the literature, there is an optimal mass of catalyst in the Fenton process beyond which the degradation rate decreases due to the undesirable reactions that consume hydroxyl radicals [28].

In this study, the relationship between contact time and dye removal efficiency at different initial concentrations of solution was conducted. Fig. 7 show that the concentrations of remazol black decrease as a function of time. This decrease indicates a discoloration over time reflecting the progressive homolytic cleavage of the remazol black molecule during the degradation process. We also observe a decrease in the elimination of remazol black when the concentration of remazol black increases from 5 mg / L to 25 mg/L, which reflects a decrease in the catalytic activity of the NMO / H₂O₂ pair with the increase in the concentration. At higher dye concentrations, the generation of hydroxyl radicals on the surface of the catalyst was suggested to be reduced since the active sites of the catalyst might be occupied by the dye molecules. An increased number of dye molecules and insufficient concentration of the active radicals decreased the efficiency of the decomposition process [29-31]. Similar results were obtained for the degradation of indigo carmine with manganese dioxide [32]. Indeed, an increase in the initial concentration of dye would increase the pollutant load, leads the decrease in catalytic activity and also prolongs the degradation time [33].

3.4 Kinetic Study of Degradation

Two kinetic models were used to study the degradation process of remazol black. In order to find out which kinetic model best describes the degradation of remazol black by NH₃(MoO₃)₃/H₂O₂ coupling, the pseudo-order 1 and pseudo-order 2 reaction models were applied. The application of the pseudo-reaction models of order 1 and 2 was done using equations 5 and 6 respectively

\[
\ln \left( \frac{C_t}{C_0} \right) = -k_1 t \quad (5)
\]

\[
\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \quad (6)
\]

Where \( C_0 \) and \( C_t \) are respectively the initial concentration of remazol black removed and at time \( t \) in (mg / L); \( k_1 \) (1/h) and \( k_2 \) (g.mg⁻¹.h⁻¹) the adsorption rate constant.

The plotted curves are respectively \( \ln \left( \frac{C_t}{C_0} \right) \) as a function of time (Fig. 8), \( \frac{1}{C_t} - \frac{1}{C_0} \) as a function of time (Fig. 9).

![Fig. 7. Evolution of remazol black concentration as a function of time](image-url)
The rate constants and linear correlation coefficients are listed in the Table 2. By observing the values in the table, it can be seen that the correlation coefficients of the pseudo 1st order model are the closest ($R^2 > 0.98$) to 1. This model is the one which best describes the process of degradation of remazol. This result is in agreement with the literature [34]. It is also noted that the rate of degradation of remazol black at 5 mg/L is greater than that of 25 mg/L. This result is in agreement with the previous one where we showed that when the dye concentration increased, then the pollutant load influenced the free radicals produced and therefore decreased the degradation of the dye [12,32].

### 4. CONCLUSION

In the present study, we synthesized molybdenum oxide nanoparticle coupled with hydrogen peroxide and applied for degrading Remazol black in aqueous solution. This study revealed that the catalytic degradation activities of remazol black with peroxide alone and molybdenum oxide alone are low. On the other hand, the hydrogen peroxide / molybdenum oxide coupling has a greater catalytic activity of
degradation of rémazol, due to the action of hydrogen peroxide which in the presence of molybdenum oxide generates very powerful and active radicals. The study also showed that the degradation of remazol black by the peroxide / molybdenum oxide depended on the concentration of remazol black. Thus, when the concentration increases, the degradation decreases. The heterogeneous Fento-like process showed performance at pH = 4. This degradation follows pseudo first order kinetic model.

DISCLAIMER
Authors have declared that no competing interests exist. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS
Authors have declared that no competing interests exist.

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DOI: 10.1002/smll.202101596


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