

Photocatalytic Removal of Bismarck Brown G and Reactive Yellow 145 over Prepared $(\text{Co}, \text{Ni})_3\text{O}_4$ Spinel Catalyst

Abbas J. Lafta*, Salih H. Kathim and Emman J. Mohammad

Chemistry Department, College of Science, Babylon University, Hilla 51002, Iraq;
abbaslafta2009@yahoo.com, emanjassim138@yahoo.com, hadi197019@yahoo.com

Abstract

Background/Objectives: The current study is focused on the synthesis of spinel catalyst $(\text{Co}, \text{Ni})_3\text{O}_4$. This catalyst was used in removal of two textile dyes from wastewater that are charged from local textile factory. **Methods/Statistical Analysis:** This catalyst was synthesized using co-precipitation method. The obtained materials was calcinated in a furnace oven at temperature of 600°C for four hours. Then produced catalysts were investigated using different techniques such as Powder X-Rays Diffraction (PXRD), Atomic Force Microscopic (AFM). The treated industrial wastewaters that were used in this study were collected from the local textile factory in Hilla city (Iraq). **Findings:** The photocatalytic activity of the synthesized catalysts was investigated by following the photo catalytic removal of both Bismarck Brown G, (BBG) dye and Reactive Yellow145 dye (RY145) from the industrial wastewaters at normal atmospheric conditions. After one hour of reaction, the efficiency of dye removal was 94.60% and 31.11% for Bismarck Brown G and Reactive Yellow 145 dye respectively. **Applications/Improvements:** This study gives promising results in concern with treatment of industrial wastewaters before they are charged into the nearest water streams or in some cases they can be recycled to be used for industrial purposes at the same factory or at any other industrial unit.

Keywords: Bismarck Brown G, Dyes Removal from Wastewaters, Reactive Yellow145, Spinel Oxide, Textile Dyes, Wastewaters Treatment

1. Introduction

Pollution with textile dyes can cause massive pollution in the ambient environment. This arises from formation of carcinogenic products via reaction of these dyes with the other materials that may exist in the environment. Vast majority of these dyes are complex aromatic organic compounds with a complex structure that containing one or more azo groups ($-\text{N}=\text{N}-$). Currently, many industries are using azo dyes such as textile industries, food industries and color paper printing industries¹. Azo groups are responsible for the deep color in these materials, if these groups are broken; the color disappears or at least reduces to minimum intensity². In the last few years, much effort was focused to discover new methods to remove azo dyes from industrial wastewaters effectively. In this context, heterogeneous photocatalytic systems can be used effectively in removal of these dyes either by adsorption

and/or by photocatalytic processes by irradiation of aqueous solution of the industrial wastewaters with the used photocatalyst³. Different types of photocatalysts were used in this field such as TiO_2 , ZnO , CdS and many other semiconductors photocatalysts. These materials were used as neat form or modified materials³. Among these materials, Nickel Oxide (Ni_3O_4) can be used in removal of dyes from the polluted wastewaters. This oxide exhibited high activity towards removal of aromatic compounds that are found as pollutants in wastewaters. This oxide can be characterized by its distorted structure, which arises from the presences of excess of oxygen that makes holes between the neighboring ions of Ni^{2+} . This can lead to oxidizes of Ni^{2+} to Ni^{3+} and this charge makes this oxide to be colored^{4,5}. In addition to Nickel Oxide, Cobalt Oxide (Co_3O_4), is considered to be as a good photocatalyst. It has important properties such as a moderate bandgap energy, high porosity, high specific surface areas and

* Author for correspondence

non-toxicity. All these excellent catalytic properties make it suitable for environmental applications. This oxide showed high catalytic activity in many applications such as environmental and industrial applications⁶⁻⁸.

The present work aims to study the photocatalytic removal of BBG and RY145 dyes from their textile industrial wastewaters over a suspension of a prepared spinel photocatalyst Ni₃O₄.Co₃O₄ under irradiation with UV light.

2. Materials and Methods

2.1 Materials and Chemicals

All chemicals were used without any further purification. Cobalt Nitrate hexahydrate Co(NO₃)₂.6H₂O and Nickel Nitrate Hexahydrate Ni(NO₃)₂.6H₂O were obtained from (BDH Company) with a purity of 97.9% and 99.9% respectively. Sodium Carbonate anhydrous Na₂CO₃ was obtained from (GmbH Company) with a purity of 99.9%. The dyes that were used in this study were BBG dye and RY145 dye. These dyes have a molecular formula of (C₂₁H₂₄N₈.2HCl) and (C₂₈H₂₀ClN₉Na₄O₁₆S₅) respectively and they were obtained from (Al-Hilla Textile Factory-Iraq).

2.2 Catalyst Synthesis

In the current study, spinel oxide (Co, Ni)₃O₄ was prepared by a co-precipitation method with a ratio of 50:50% from their starting materials (Ni(NO₃)₂.6H₂O, Co(NO₃)₂.6H₂O). The used amounts of these salts were weighed accurately and dissolved in 400 mL of deionized water. The obtained mixture then was stirred continuously under normal atmospheric conditions. The pH of this mixture was monitored by measuring the pH of the solution using a digital pH meter (740 Inolab WTW) and a pH range of (5.5-6.2) were recorded for various mixed ratios. After that, Na₂CO₃ (1M) was added drop wisely as a precipitating agent and the temperature of this solution was kept around 70-75°C. The pH was kept approximately around 9 and the obtained solution was left for two hours at the same temperature with stirring for digestion. Then the resultant mixture was filtered using a Buchner filtration flask and a vacuum pump. The obtained precipitate was dried in an oven (Oven Bs Size Two Gallenkamp, England) for overnight at 120°C. The obtained solid was calcinated at 600°C for four hours at a heating rate of 10°C/min⁹ (Muffle Furnace Size - Tow Gallenkamp).

2.3 Photocatalytic Activity of the Prepared Catalyst

The photocatalytic reactions were carried out using a mercury vapor lamp (Philips- Holland, 250 W) without cover glass as a source of UV radiation. The cell of photoreaction was made up from Pyrex glass with quartz windows with a maximum capacity volume of 30 mL as shown in Figure 1. All photocatalytic experiments were performed by adding a required amount of the used catalyst (0.05 g) into the photoreaction cell. An aqueous solution of BBG dye and RY145 dye (50 ppm, 30 mL) were added for each experiment. The temperature of the reaction mixture was adjusted at around 23°C. The reaction was initiated by illumination with UV light from mercury vapor lamp. The temperature of the reaction was controlled by using a thermostat. Periodically, 2 mL of the reaction mixture samples were withdrawn for a period of each 10 minutes for a total reaction time of one hour for all experiments. The obtained samples were centrifuged for several times. The absorbance of the obtained supernatant liquids for each run was measured at a wavelength of 468 nm of (BBG) and at 418 nm of RY145 using UV-visible spectrophotometer (UV-1650PC Shimadzu, Japan).

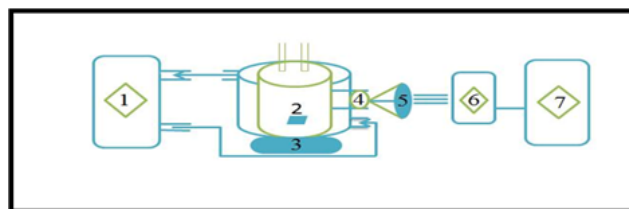


Figure 1. Application isolated dc-dc converter.

2.4. Catalyst Characterization

2.4.1 X-Ray Diffraction (XRD)

The prepared catalyst was investigated using powder X-Ray Diffraction (XRD), Phillips X-Ray Diffraction with CuK radiation (1.542 Å, 40 KV, 30 MA), in the 2θ ranged between 10-80 degrees (XRD6000, Shimadzu, Japan).

2.4.2. Atomic Force Microscopy (AFM)

The prepared catalyst was further investigated using Atomic Force Microscopy (AFM) SPM-AA3000 Atomic Force Microscope/Contact Mode Angstrom Advanced Inc., 2005, USA. This device was used to investigate the atomic configuration and topography at the surface of the prepared catalyst.

3. Results and Discussion

3.1 X-Ray Diffraction (XRD)

The results of XRD patterns of the prepared materials that were calcinated at 600°C are shown in Figure 2. From these XRD patterns of prepared catalyst, it can be seen that, sharper peaks of the XRD patterns indicate, large crystallites are almost present for these materials. Also it can be noted that there was a deviation for some peaks for the samples that were synthesized at 600°C, also there was variation in the space- d (2.8698, 2.0915, 2.4473) and 2θ (31.139, 36.691, 2.0915) for standard values for these oxides by matching with Joint Committee on Powder Diffraction Standards (JPCDS) for each of Co_2O_3 and Ni_2O_3 . These deviations can be acquired by influencing between these supported oxides¹⁰. The XRD patterns for these materials are shown in Figure 2.

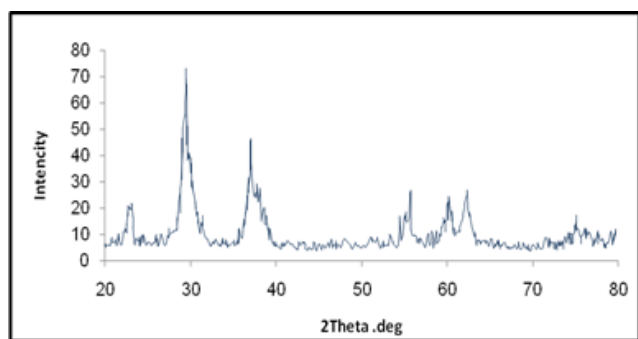


Figure 2. XRD patterns for the $\text{Ni}_3\text{O}_4\text{-Co}_3\text{O}_4$ photocatalyst.

3.2 Atomic Force Microscopy (AFM)

The image of Atomic Force Microscopy of the prepared catalyst are shown in Figure 3.

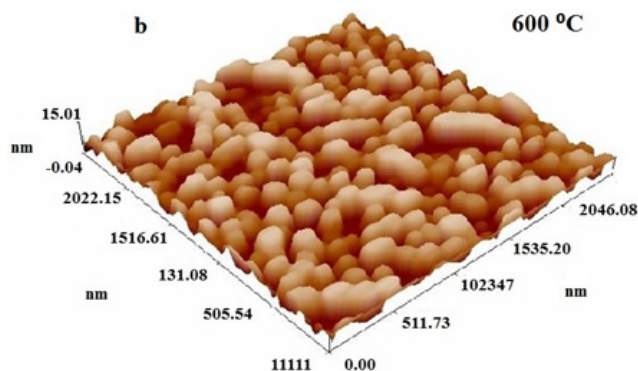


Figure 3. AFM images of $\text{Ni}_3\text{O}_4\text{-Co}_3\text{O}_4$ that was calcinated at 600°C.

From the above AFM image of the prepared catalyst that was calcinated at 600°C the average particle diameter was around 98.78 nm. This means that, these materials were prepared effectively by co-precipitation method to yield nano-scale catalyst that can be used in different industrial and environmental applications.

3.3 Study of the Physical Properties of the Prepared Catalyst

The physical properties of the prepared catalyst that was synthesized by calcination at 600°C for 4 hours were investigated using fluid saturation method^{11,12}. These investigated properties were pore size, porosity and the bulk density. The obtained results are shown in Table 1.

Table 1. The results of pore size, porosity and bulk density for the prepared catalyst

Physical property	The obtained value
Dry weight of catalyst Wt_1	0.076
Weigh of catalyst Saturated with water Wt_2	0.107
Weigh of catalyst pending in water Wt_3	0.063
Porosity%	70.45
Pore volume $\text{g}/(\text{cm}^3)$	0.407
(g/cm^3) Density	1.727

3.4 Photocatalytic Activity of the Prepared Catalyst

The photocatalytic activity of the prepared catalysts was investigated by following the photocatalytic removal of BBG dye and RY145 dye from the industrial wastewaters. From the obtained results, the efficiency of removal of BBG was 94.6% and for RY145 was 31.11%. These results are summarized in Table 2 and are plotted in Figure 4.

Figure 4 shows that the photocatalytic activity of removal of BBG and RY145 over prepared spinel oxide was increased with increase time of reaction. This was observed by monitoring a decrease of dye concentration with passing a time of reaction¹³. It was found that an optimum removal efficiency of these dyes was reached to 94.6% after 60 min of illumination time to BBG and 31.11% of RY145. This result indicates that the prepared catalyst was more effective and specific to BBG dye more than RY145. This probably arises from the chemical structure of this dye and its interaction with the surface of this catalyst more than that with the other dye. Effective interaction between adsorbate molecules and

the surface of adsorbent is essential step in photocatalytic reactions^{14,15}.

Table 2. Photodegradation efficiency % of BBG, RY145 dye for 60 min

Removal % of RY145	Removal% of BBG	Time (min.)
0.00	0.00	00
23.90	84.19	10
26.24	86.27	20
29.30	87.70	30
30.58	94.24	40
30.79	94.48	50
31.11	94.60	60

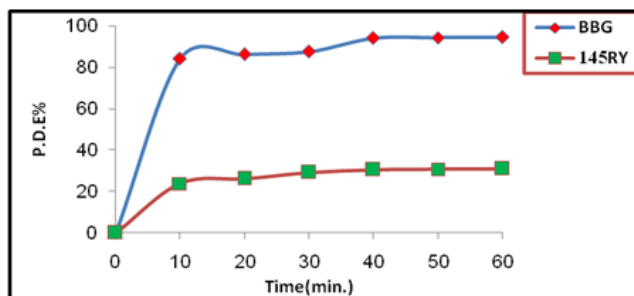


Figure 4. Photocatalytic removal efficiency % of BBG and RY145 dyes over prepared catalyst.

4. Conclusions

The photocatalytic removal of Bismarck Brown Gand Reactive Yellow 145 was investigated in this study over Ni₃O₄-Co₃O under UV irradiation. Removal of BBG was more efficient than RY145 dye under the same reaction conditions. The best removal efficiency was achieved using 0.05 g of the catalyst at normal pH and a temperature of 23°C. The prepared catalyst showed higher activity in removal BBG rather than RY145 under the same reaction conditions.

5. Acknowledgement

The authors would like to thank Babylon University, College of Science for funding this work as a part of annual staff research plan.

6. References

1. Tichonovas M, Krugly E, Racys V, Hippler R, Kauneliene

- V, Stasiulaitiene I, Martuzevicius D. Degradation of various textile dyes as wastewater pollutants under dielectric barrier discharge plasma treatment. *Chemical Engineering Journal*. 2013 Aug; 229:9–19.
2. Anpo M, Takeuchi M. Design and development of second generation titration oxide photocatalyst materials operating under visible light irradiation by applying advanced ion-engineering techniques. *Hindawi*. 2001; 3(2):89–94.
3. Robinson T, McMullan G, Marchan R, Nigam, P. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Biore-source Technology*. 2001 May; 77(3):247–55.
4. Tsuji T, Hamagami T, Kawamura T, Yamaki T, Tsuji M. Laser ablation of cobalt and cobalt oxides in liquids: Influence of solvent on composition of prepared nanoparticles. *Japan Applied Surface Science*. 2005 Apr; 243(1-4):214–9.
5. Pourbaix M. *Atlas of Electrochemical Equilibria*. New York, NY, USA: Pergamon Press; 1974.
6. Shunichi F, Yusuke Y. Catalytic activity of metal-based nanoparticles for photocatalytic water oxidation and reduction. *Journal of Materials Chemistry*. 2012; 22(46):24284–96.
7. Hussein FH, Obies MH, Ali-drea AA. Photocatalytic decolorization of bismarck brown R by suspension of titanium dioxide. *Int J Chem Sci*. 2010; 8(14):2736–46.
8. Hussain B, Kashif D, Ahmad B, Zubair A, Yousaf A, Matloob I, Muhammad U, Muhmmad Z, Asim M. Degradation study of C.I. reactive Yellow 145 by advanced oxidation process. *Asian Journal of chemistry*. 2013; 25(15):8668–72.
9. El-Bahy ZM, Ismail AA, Mohamed RM. Enhancement of titania by doping rare earth for photodegradation of organic dye (Direct Blue). *Journal of Hazardous Materials*. 2009 Jul; 166(1):138–43.
10. Atif M, Hasanain SK, Nadeem M. Photocatalytic degradation of textile dyeing wastewater using titanium dioxide and zinc oxide. *Solid State Communications*. 2006; 138:416–21.
11. Satterfield CN. *Heterogeneous catalysis in practice*. New York: McGraw-Hill Book Company; 1980.
12. John Rajan A, Anand K, Narayanan K, Ramesh B. A study on environmental sustainability in textile processing industries of South India. *Indian Journal of Science and Technology*. 2016 Feb; 9(5):1–4.
13. Ferrero F. Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust. *Journal of Hazardous Materials*. 2007 Apr; 142(1-2):144–52.
14. Nakata K, Fujishimaa A. TiO₂ photocatalysis: Design and applications. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 2012 Sep; 13(3):169–89.
15. Fan H, Jiang T, Wang L, Wang D, Li H, Wang P. Effect of BiVO₄ crystalline phases on the photo induced carriers behavior and photocatalytic activity. *The Journal of Physical Chemistry*. 2012; 116(3):2425–30.