HYBRID ADSORPTION AND PHOTOCATALYSIS PROCESS FOR WATER TREATMENT BY NICKEL MOLYBDATE

T. Aloui[1,2] N. Fourati[2], H. Guermazi[1], C. Zerrouki[2], S. Guermazi[1]

[1] Laboratory of Materials for Energy and Environment, and Modelling, Faculty of Science, University of Sfax, Soukra Road km 4 BP, 1171- 3038, Sfax, Tunisia, hajer.guermazi@gmail.com
[2] UMR 8029, SATIE CNRS, ENS Paris-Saclay, Paris-Saclay University, 292 rue Saint-Martin, 75003, Cnam Paris, France, thamer.aloui@univ-nantes.fr; fourati@cnam.fr and zerrouki@cnam.fr

Abstract:

Nickel molybdates were synthesized and tested in photocatalytic applications. Experiments conducted in the dark for one hour, showed a degradation efficiency of 44% of methylene blue (MB), considered as a model pollutant. This high value was related to the strong adsorption of MB on the oxide particles, due to the synergistic effect of the 2D shape (revealed by scanning electron microscopy) developing a large surface area and their high roughness (estimated from atomic force microscopy measurements). Under visible light for one hour, the degradation efficiency reaches 87%, an improvement of almost 100% compared to darkness. Attempts to regenerate and reuse nickel molybdate are made four times. The recovery process, which consists of washing particles only with distilled water, is encouraging enough even if not yet optimized.

Keywords: Nickel Molybdate; photocatalytic performance; MB degradation.

1. INTRODUCTION

Environmental issues have never been as important as in recent years. A recent study, published in the Lancet planetary health, pointed that pollution is responsible for about one in six deaths worldwide [1]. Awareness of the cumulative effects and irreversible consequences of various forms of pollution has led most countries to adopt increasingly drastic policies to preserve ecosystems [2, 3]. At the same time, research has intensified in the areas of depollution and remediation, with the synthesis of materials that are efficient for the photocatalytic depollution of water, air, or soil [4]. Besides the most used titan oxide TiO_2 and related compounds [5, 6], several other materials were elaborated and applied in photocatalytic environmental applications. We mainly found doped and undoped transition metal ferrites [7, 8], Molybdates [9, 10], tungstates [11, 12], and copper, nickel, and their composites [13-15]. Among these materials, metal molybdates (MMM) constitute a so-called multifunctional class, as they can be used for both energy and environmental applications [16, 17]. It is with this in mind that we worked on the synthesis of nickel molybdates using a simple, low-cost, and eco-friendly co-precipitation method [18]. Photocatalytic reactions are interpreted in terms of oxidation/reduction, and more precisely in terms of charge transfer between the photocatalyst and the pollutant. This leads to the characterization of both in energetic terms, with the determination of the gaps and the different energy levels involved in the possible electronic transitions. However, a favorable positioning of the different energy levels alone cannot ensure good photocatalytic efficiency. It is indeed necessary to have the largest pollutant/material contact surface, to favor adsorption [18]. This structure/properties relationship is therefore closely linked to the size and shape of the particles, which can be modulated by acting on the synthesis conditions and/or by changing the method.

The present work focuses on nickel molybdate (α-form $NiMoO_4$) which we synthesized by the co-precipitation method and fully characterized before considering it in photocatalytic experiments.

2. DESCRIPTION OF THE WORK

2.1 Surface characterization

The efficiency of photocatalysis requires two combined synergistic effects, the efficient adsorption of the pollutant on the catalyst and the relative matching of energy levels that facilitates charge transfer. The first one is mainly controlled by the catalyst's active area, which must be as high as possible. This aim can be reached by acting on shape/size of catalyst particles. So, surface examination is of primary importance. For this purpose, we first used scanning electron microscopy (SEM) to reveal the shape of α-$NiMoO_4$ particles. These examinations showed a nanosheets like shape (Fig.1a). This quasi-2D structure is quite favourable as it develops high specific surface. Besides, we considered atomic force microscopy (AFM) to reach the nanosheets roughness's in the nanometric scale (Fig.1b).

Thus, we can estimate the active surface including roughness and all geometric defects, which constitute the real interface between the catalyst and the pollutant in the solution.

As can be seen from the AFM image (Fig.1b), the topography of the nanosheets is far from being as regular as suggested by the SEM image taken at a lower magnification. These surface irregularities strongly contribute to an increase in the active surface, the place of interaction between the catalyst and the pollutant in the solution. In this case, the root means square roughness was found at about 40 nm and a mean height between peaks and valleys of the order of 350 nm (in the spatial frequency range of 10^{-3} – 1 nm^{-1}). These relatively high

values suggest that the active surface is large enough to give rise to strong adsorption, suitable for photocatalysis.

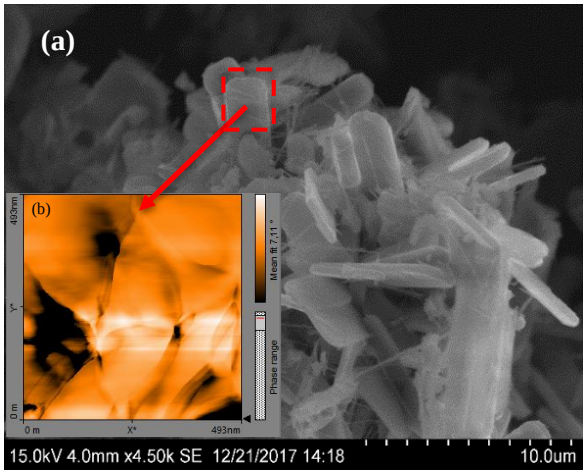

Figure 1: (a), SEM and (b) AFM images of α- $NiMoO_4$ nanosheets

2.2. Photocatalytic investigation

To carry out the photocatalytic experiments, we considered methylene blue (MB) as a model pollutant. Firstly, we ensured that there was no self-degradation of MB, either in the dark or under visible light irradiation. Then, 50 mg of α-$NiMoO_4$ catalyst was added to 100 mL of MB solution (1.56×10^{-5} M), and the mixture was kept under stirring in the dark throughout the experiment.
From t = 0 min to t = 60 min, 5 ml of the prepared solution was taken every 5 min, to measure the absorbance A_t using a UV–vis spectrophotometer.

The degradation rate η(t) of MB is estimated from absorbance values A_0 at t = 0 and A_t at given time t, according to the relation (1) [19]:

$$\eta(\%) = \left(1 - \frac{A_t}{A_0}\right) \times 100 \qquad (1)$$

This experiment, conducted in dark, give us information of the catalytic potential of the nickel molybdates, before considering photocatalytic experiments.

By considering one hour as a time reference, we obtained a degradation rate of $\eta_0(60)$ = 44%, in dark. This value confirms the high level of MB adsorption on the nickel molybdate nanosheets, due to their large active surface areas. This degradation rate also indicates that this synthesized material presents a catalytic effect that can be enhanced by visible irradiation

Finally, the same experiment was conducted under visible light irradiation. The mixture was thus illuminated with a low power lamp (8W, 370 nm) during 60 min. Every 5 minutes, 5 mL of the solution is taken to measure the absorbance A_t and to estimate the degradation rate η(t).

At the end of the experiment, the molybdate particles were recovered by centrifugation and rinsed several times with distilled water only, before being used again with a freshly prepared MB solution. This experiment was repeated 4 times to see the regeneration potential of the photocatalyst, before considering more efficient solvents for recovery.

The degradation rates $\eta_i(60)$ is estimated for each of the five successive catalytic experiments (i being the experiment rank, from 1 to 5). Then, the photocatalytic efficiency is estimated by comparing degradation rates $\eta_i(60)$ under irradiation against that in dark $\eta_0(60)$:

$$\text{Efficiency} = \left(\frac{\eta_i(60) - \eta_0(60)}{\eta_0(60)}\right) \times 100 \qquad (2)$$

The values obtained are gathered in figure 2 which shows a photocatalytic efficiency close to 100% (compared to the absence of irradiation) for the first experiment, and which decreases progressively until a value of 24% after the 4th regeneration. Besides the undeniable interest in using visible irradiation, this figure shows that rinsing only with distilled water, even abundantly, is not sufficient to completely regenerate the molybdates, because of their strong roughness. In the future, we plan to test different regeneration routes, including green solvents and the use of ultrasonic baths.

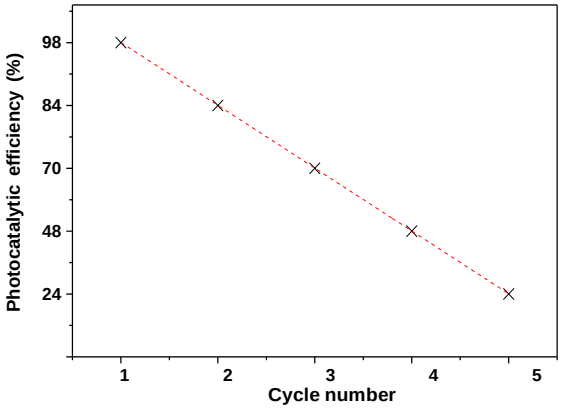

Figure 2: Photocatalytic efficiency and stability of NM nanosheets, after successive regenerations.

To study the adsorption kinetic during the photocatalytic process. The pseudo-second order model of Yoon–Nelson was applied to experimental data, according to equation (3) [20]:

$$\left(\frac{C_0}{C_t}\right) = 1 + \exp(-K_{YN}(t - \tau)) \qquad (3)$$

Where C_0 is the initial concentration of MB, C_t is the concentration of MB at time t, K_{YN} is the Yoon–Nelson rate constant (min^{-1}) and τ is the time required for reach 50% adsorbate breakthrough (min).
Experimental data, recorded in dark and under visible irradiation, and corresponding fits according to the considered model are gathered on figure 3.
Modified Yoon-Nelson model appears suitable to describe chemical adsorption mechanism of MB onto α-$NiMoO_4$, independently of lighting conditions. Compared to dark, illumination results in a 3.3-fold increase in the rate constant.

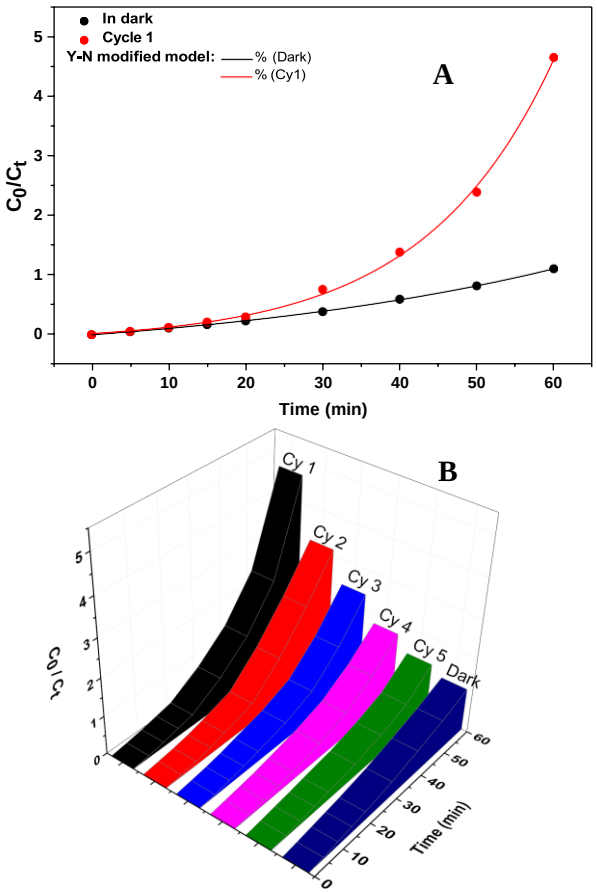

Figure 3: Modelling of MB degradation Kinetics, bymeans of Yoon-Nelson (Y-N) modified model, (A) in dark and under first cycle light illumination, (B) 3D representation for 5 consecutive cycles compared todark.

Modified Yoon-Nelson model is suitable to describe chemical adsorption mechanism of MB onto α-$NiMoO_4$. Compared to dark, illumination results in a 3.3-fold increase in the rate constant.
The estimated rate constants K_{YN} as well as reliability (correlation) factor R^2 are gathered in Table 1.

Table 1: Kinetic parameters estimated from the modified Yoon-Nelson model

Cycle number	K_{YN} 10^{-2} (min^{-1})	R^2
In dark	1.02±0.04	0.99
1	3.41±0.15	0.98
2	3.03±0.20	0.97
3	2.29±0.16	0.96
4	1.76±0.15	0.94
5	1.18±0.18	0.84

For the first experiment under illumination, the rate constant increases by about 230%, showing the photo-catalytic effect, compared to a purely catalytic one. Investigations on the parameters allowing to increase the value of this parameter should allow faster photo degradation of pollutants.

For successive experiments, the photocatalytic effect decreases to almost disappear from the fifth cycle. This highlights the second way of improvement, in addition to the increase of rate constant, That of efficient regeneration methods of the catalysts.

3. SUMMARY

Due to its shape and high roughness, nickel molybdate exhibited an important pollutant adsorption rate. This high level of adsorption leads to the degradation of pollutant molecules (MB), even in the absence of light. A degradation efficiency of 44% was observed in only one hour in the dark. Under visible radiation, this degradation efficiency reaches 87% in the same reference time (1 hour), which is an improvement of almost 100%. Attempts to regenerate and reuse nickel molybdate are quite encouraging, as the recoveryprocess, which consists of washing only with distilled water, is not yet optimized. Soon, other experiments using green solvents in ultrasonic baths will be considered. However, the current results are promising enough, to consider these oxides for efficient photocatalytic water remediation, especially for developing countries.

4. REFERENCES

[1] Pollution and health: a progress update, R. Fuller, P.J Landrigan, K. Balakrishnan, G. Bathan, S. Bose-O'Reilly, M. Brauer, J. Caravanos, T. Chiles, A. Cohen, L. Corra, M. Cropper, G. Ferraro, J. Hanna, D. Hanrahan, H. Hu, D. Hunter, G. Janata, R. Kupka, B. Lanphear, M. Lichtveld, K. Martin, A. Mustapha, E. Sanchez-Triana, K. Sandilya, L. Schaefli, J. Shaw, J. Seddon, W. Suk, M. María Téllez-Rojo, C. Yan. www.thelancet.com/planetary-health Published online May 17, 2022. https://doi.org/10.1016/S2542-5196(22)00090-0

[2] https://www.eea.europa.eu/highlights/soer2020-europes-environment-state-and-outlook-report

[3] OECD ENVIRONMENTAL OUTLOOK TO 2030 ISBN 978-92-64 04048-9 © OECD 2008

[4] C. Byrne, G. Subramanian, S.C. Pillai, Recent advances in photocatalysis for environmental applications, Journal of Environmental Chemical Engineering 6 (2018) 3531–3555. http://dx.doi.org/10.1016/j.jece.2017.07.080

[5] E. Pramauro and M. Vincenti, Photocatalytic Degradation of Monuron in Aqueous Ti02 Dispersions, Environ. Sci. Technol. 1993, 27, 1790-1795.

[6] Biljana Abramovic, Sanja Kler, Daniela Sojic, Mila Lausevic, Tanja Radovic, Davide Vione, Photocatalytic degradation of metoprolol tartrate in suspensions of two TiO2-based photocatalysts with different surface area. Identification of intermediates and proposal of degradation pathways, Journal of Hazardous Materials, 198 (2011) 123-132. doi:10.1016/j.jhazmat.2011.10.017

[7] T.J. Al-Musawi, N. Mengelizadeh, M. Taghavi, Z. Shehu, D. Balarak, Capability of copper–nickel ferrite nanoparticles loaded onto multi-walled carbon nanotubes to degrade acid blue 113 dye in the sonophotocatalytic treatment process, Environ Sci Pollut Res (2022). https://doi.org/10.1007/s11356-022-19460-z

[8] S. Hamid Ud Din, M. H. Arshed, S. Ullah, P. O. Agboola, I. Shakir, A. Irshad, M. Shahid, Ag-doped nickel ferrites and their composite with rGO: Synthesis, characterization, and solar light induced degradation of coloured and colourless effluents, Ceramics International 48 (2022) 15629–15639. https://doi.org/10.1016/j.ceramint.2022.02.097

[9] R. Kumar, A. Sudhaik, P. Raizada, A. Hosseini-Bandegharaei, V.K. Thakur, A. Saini, V. Saini, P. Singh, An overview on bismuth molybdate based photocatalytic systems: Controlled morphology and enhancement strategies for photocatalytic water purification, Journal of Environmental Chemical Engineering 8 (2020) 104291. https://doi.org/10.1016/j.jece.2020.104291

[10] Y. Qiu, J. Lu, Y. Yan, J. Niu, Y. Duan, Bismuth molybdate photocatalyst for the efficient photocatalytic degradation of tetracycline in water under visible-light irradiation, Surfaces and Interfaces 31 (2022) 102009. https://doi.org/10.1016/j.surfin.2022.102009

[11] H.Y. Chung, X. Wu, R. Amal, Y. H. Ng, Balancing the crystallinity and specific surface area of bismuth tungstate for photocatalytic water oxidation, Molecular Catalysis 487 (2020) 110887. https://doi.org/10.1016/j.mcat.2020.110887

[12] P. Taneja, S. Sharma, A. Umar, S.K. Mehta, A.O. Ibhadon, S. K. Kansal, Visible-light driven photocatalytic degradation of brilliant green dye based on cobalt tungstate (CoWO4) nanoparticles, Materials Chemistry and Physics 211 (2018) 335e342. https://doi.org/10.1016/j.matchemphys.2018.02.041

[13] A. Iqbal, A. Ul Haq, G. A. Cerrón-Calle, S. A. Raza Naqvi, P. Westerhoff, S. Garcia-Segura, Green Synthesis of Flower-Shaped Copper Oxide and Nickel Oxide Nanoparticles via Capparis decidua Leaf Extract for Synergic Adsorption-Photocatalytic Degradation of Pesticides, Catalysts, 2021, 11, 806. https://doi.org/10.3390/catal11070806

[14] A. Sagadevan Ethiraj, P. Uttam, K. Vunkumar, K. F. Chong, A. Gomaa,M. Ali, Photocatalytic performance of a novel semiconductor nanocatalyst: Copper doped nickel oxide for phenol degradation, Materials Chemistry and Physics 242 (2020) 122520. https://doi.org/10.1016/j.matchemphys.2019.122520

[15] B. Bashir, M. U Khalid, M. Aadil, S. Zulfiqar, M.F. Warsi, P.O. Agboola, I. Shakir, CuxNi1-xO nanostructures and their nanocomposites with reduced graphene oxide: Synthesis, characterization, and photocatalytic applications, Ceramics International 47 (2021) 3603–3613. https://doi.org/10.1016/j.ceramint.2020.09.209

[16] S. Swathi, R. Yuvakkumar, P. S. Kumar, G. Ravi, D. Nanthini, D. Velauthapillai, "Flower like strontium molybdate for efficient energyconversion applications", Fuel, vol 308, pp. 122051, January 2022. DOI:org/10.1016/j.fuel.2021.122051

[17] Q. Tian, C. Han, Z. Lin, Y. Y. Li, Y. Zheng, J. Zhuang, "One-Dimensional Core Shell $Cd_{0.85}Zn_{0.15}S$@$Cd_{0.85}Zn_{0.15}MoO_4$ Binary Solid Solution Composite: In Situ Construction and Photocatalytic H_2 Evolution Performance", The Journal of Physical Chemistry C, vol 126, no. 8, pp.3881-3890, February 2022. DOI:10.1021/acs.jpcc.2c00214

[18] T. Aloui, H. Guermazi, N. Fourati, C. Zerrouki, S. Guermazi "Synthesis and characterization of nanosheet $NiMoO_4$ powder as a highly efficient and reusable catalyst for environmental remediation" J Nanopart Res (2022) 24: 35. DOI: 10.1007/s11051-022-05417-3.

[19] M. Dhanasekar, S. Ratha, C. S. Rout, S. V. Bhat, "Efficient sono-photocatalytic degradation of methylene blue using nickel molybdate nanosheets under diffused sunlight," Journal of Environmental Chemical Engineering, vol. 5, no. 3, pp. 2997–3004, Jun. 2017. DOI: 10.1016/j.jece.2017.05.054

[20] S. K. Ray, D. Dhakal, J. Hur, and S. W. Lee, "Visible light driven MoS_2/α-$NiMoO_4$ ultra-thin nanoneedle composite for efficient Staphylococcus aureus inactivation," Journal of Hazardous Materials, vol. 385, pp. 121553, Mar. 2020. DOI: 10.1016/j.jhazmat.2019.121553