

TOTAL MINERALIZATION OF MALACHITE GREEN DYE BY ADVANCED OXIDATION PROCESSES

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Abstract: In this work, the advanced decomposition of organic dyestuffs used in food and textile industry, such as Malachite Green (MG), was investigated in the presence of a cationic catalyst montmorillonite (P1-PILCs) prepared by ion-exchange method. The obtained material was characterized by BET, FTIR and XRD. The effects of different variables such as: catalyst dose, catalyst/ozone dose, ozonation time and the pH on the mineralization of the synthetic dye were studied and optimal experimental conditions were ascertained. Compared with simple ozonation, the introduction of the catalyst greatly reduces the duration of the process to reach over 95% yield from 110 minutes to some seconds.

Keywords: catalytic ozonation, Malachite Green, cationic clay, catalyst, dyestuff

Introduction

The organic dyes from the environment cause major problems worldwide because of their acute and chronic toxicity. Dyes are widely used in large quantities in different industries including textile, leather, food, cosmetics, paper, printing, plastic, pharmaceuticals etc. The textile industry

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alone represents two third of the total dyestuff production.¹ The discharge of coloured wastes into streams affects their aesthetic nature and interferes with the transmission of sunlight into streams, reducing the photosynthetic action. Some dyes are poorly biodegradable, therefore the conventional biological processes are not very effective in their removal.² Malachite Green (nature = basic green), classified in the dyestuff industry as a triarylmethane dye, was used in this study. The structure of MG is illustrated in Figure 1. It is usually used as a dyestuff³ for materials such as paper, leather, silk and controversially as a strong anti-bacterial, anti-fungal and antiparasitic agent in fish farming.⁴ Effects due to its presence in the environment by the accumulation of sediments in the aquatic environment can cause the disappearance of fish species or even aquatic life in time due to its toxicity. It is highly cytotoxic to mammalian cells and acts as a tumor enhancing agent.⁵ On humans, it possibly causes carcinogenic, mutagenic and teratogenic effects, if it may enters in the food chain.⁶ Through, the use of MG has been banned in several countries and is not approved by the US Food and Drug Administration, it is still being used due to its low cost, easy availability and efficacy.⁷⁻⁸ In solution, the dye exists as a mixture of the cationic form and its carbinol base, with the ratio depending on the pH of the solution. It can also can undergo chemical and metabolic reduction to a leuco derivative. In addition to these inconveniences, this dye is very dangerous to health, because its stability to light, oxidizing agents and heat, and its presence in wastewaters offers considerable resistance to the biodegradation.

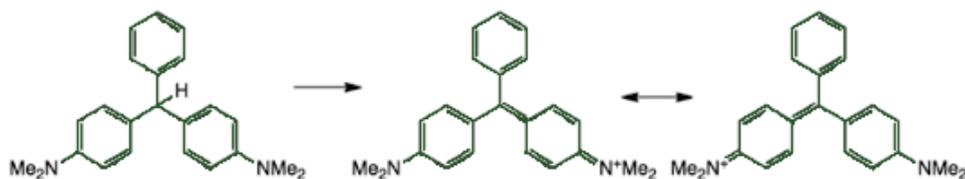


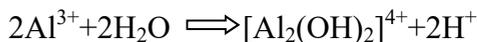
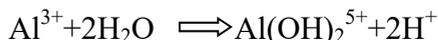
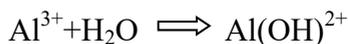
Figure 1. Malachite Green resonance structure.

Different methods of MG removal from textile effluents have been reported:⁹⁻¹¹ chemical oxidation, adsorption, froth flotation, coagulation, electro-dialysis etc. but the removal yield was not satisfying. All oxidation techniques have a common feature, which is their biggest disadvantage - the unavoidable formation of harmful byproducts. The oxidative water treatments were found to be essential for complete remediation without any impact on the biodiversity and human health. Compared to the Advanced Oxidation Processes (AOPs), the biological and physical water decontamination tests have been found to be unsatisfactory.¹²⁻¹³ As a consequence of the large amount and diversity of industrial textile dyes, the need for assessing the impact of these dyes on the environment, and especially on pollution, has grown more and more. In order to total mineralization of dyes from various industries, the art proposes the use of catalytic oxidation processes. These processes are sensitive to variations of: pH, temperature, ozone concentration, dye concentration, amount of catalyst and procedure duration.¹⁴ In order to combat these disadvantages of the oxidation methods, this paper proposes the use of heterogeneous catalysts based on chemically modified cationic clays, obtained by the pillaring method.

The pillaring process originates in the works by Brindle&Semples¹⁵ and Vaughan&Lussier¹⁶ for smectite minerals, who proposed and described mechanism of this kind by ion exchange. The first work on the synthesis

and textural properties of inorganic and zeolite-like interspersed smectites has been carried out by some pioneering laboratories.¹⁷⁻²⁴ Pillaring is the process in which lamellar compounds are transformed into more stable micro-, meso- and nanoporous materials, which maintain their lamellar structure and exhibit thermal stability. The obtained product is called lamellar compound, pillared clay, or pillared nanomaterial.²⁵ Intercalation refers to the insertion of different species into the interlamellar space of the clays while maintaining its structure, obtaining an intercalated clay.²⁶ By intercalation, the porosity of the obtained materials can be guided by the nature and characteristics of the cation which will act as a pillar in the pillaring process. From the literature, it comes to the idea that by intercalating the clays with Al the cations, they are inserted as polycations. Pillaring is an enlightening example of the concept of transforming solids with lamellar structure into materials with porous structure. The pillaring agent is a compound that can be interposed between adjacent structural lamellas, creating and maintaining the space between them and which, after the removal of the solvent, creates a porous interlayer structure. The maturation step supposes also polymerization reactions to occur.

The basicity during the hydrolysis step is given by the $\text{OH}^-/\text{Al}^{3+}$ ratio which reveals the nature of Al species. The Al polymeric cation is called Keggin ion and has the chemical formula: $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, abbreviated Al_{13} .²⁷ It presents a pseudospheric structure, as deduced by X-ray diffraction.²⁸ Other examples of polyoxocations are: $\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}^{8+}$, $(\text{TiO}_2)_8(\text{OH})_{12}^{4+}$, $\text{Cr}_n(\text{OH}_m)^{(3n-m)+}$.^{25,29} The formation of polyhydroxy-aluminium cations (Keggin agent) takes place according to the following reaction scheme:³⁰



The process of inserting the Keggin ion in the clay has a decisive influence on the drying and calcination steps. Swelling and loosening of the clay layers allows a good interference of the cations introduced into its structure, which requires magnetic stirring for 2 hours before adding of the pillaring agent.³¹ In order to form the pillaring agents, the solutions containing simple cations, mixed cations or different organic or inorganic mixed compounds are required.²⁵ Nowadays, Al is one of the most used cations, but others are used, such as: Fe³², Cr, Ni, Zr, Mg, Bi, Be, Ta, Mo, Ti, Cu³³, Ga^{25, 34-35} etc.

Materials and methods

All chemical reagents used were of analytical grade. Double distilled water was used throughout this work. All reagents used were purchased from Merck (NaOH, AlCl₃, Montmorillonite, MG, MW: 463.50).

X-ray powder diffraction patterns were obtained in a Rigaku Geigerflex diffractometer operating at 50 kV and 40 mA and using CuK α radiation ($\lambda = 0.157$ nm) from 6 to 40°(2 θ). Nitrogen adsorption isotherms was made by using a equipment Micromeritics ASAP 2020. FTIR spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrometer.

A laboratory ozone generator (OZONFIX, Romania) was used to produce different concentrations of ozone from ambient air. Ozonation was

carried out in a cylindrical glass reactor of 0.1 mL capacity, by bubbling ozone-air mixtures with different ozone concentrations. The experiments were run at ambient temperature (298-300 K).

Samples of dye solutions (25 mL) were taken at regular time intervals, centrifuged to remove the solid (2000 rpm) and measured on the basis of the maximum absorbance value in the UV-Vis by spectrophotometry (Perkin-Elmer Spectrum GX apparatus with a standard mid-IR DTGS detector). Quartz cuvettes of 1 cm optical length were used. The calibration curve of the dye in distilled water and the extinction coefficient from Lambert-Beer equation was obtained using 10 dye solutions with different concentrations (Figure 2a).

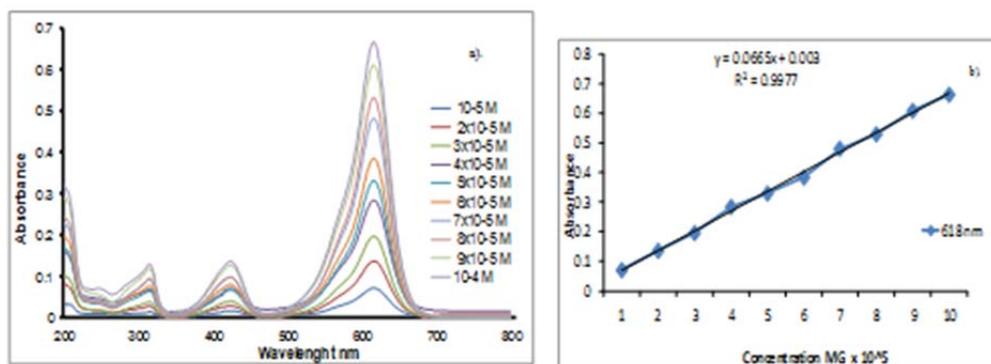


Figure 2. a) UV-Vis spectra of MG at different concentrations MG;
b) Calibration curve for MG (concentrations between 10⁻⁵M - 10⁻⁴M in distilled water, T = 22 °C, quartz cell of 1 cm pathlength).

The calibration curve for MG is well fitted by a straight line with a high regression coefficient value. The molar extinction coefficient was also calculated (Table 1).

Table 1. Molar extinction coefficient (ϵ) for 618 nm UV-Vis band for MG.

Max wavelength (nm)	Molar extinction coefficient (ϵ): (L.mmol ⁻¹ .cm ⁻¹)*	Correlation coefficient (R ²)
618	2.706	0.9977

* These coefficients were assessed from the slope of the linear part of the calibration curve fulfilling the Beer-Lambert's Law.

The decolorization extent was determined from the changes of the absorbance values at the characteristic wavelength of the dye in the UV/VIS absorption spectrum, using the relation:

$$Rcolor(\%) = \frac{Abs\ max,t_0 - Abs\ max,t}{Abs\ max,t_0} \times 100 \quad (1)$$

where Abs max,t₀ – absorbance at the dye main peak wavelength at reaction time zero, Abs max, t - absorbance of the main peak at time t.

The adsorption isotherms of the dye were obtained in a series of batch equilibrium experiments mixing 10 mg of clay in 50 mL of standard solutions containing respectively 150, 300, 450 and 600 mg/L of MG. All the solutions were prior kept overnight at 300 K in a temperature-controlled bath and pH 4.5 adjusted with HCl solution.

Preparation of chemically modified clays (P1-PILCs)

Montmorillonite was intercalated with AlCl₃, as described in our earlier study.³² Ion exchange step was achieved by contacting the clay with a freshly prepared solution of 1 M NaCl, under magnetic stirring for 4 hours at 353 K. The contact time does not have considerable influence, provided that this factor is combined with the other factors and a total ionic substitution is achieved.³⁶ After the homoionization operation, the clay was washed three times with double distilled water, until the chlorine ions were

totally removed (checked with AgNO_3 0.1 N). The intercalation with aluminium polyhydroxyl cationic solutions have been prepared at an OH / Al molar ratio of 2.2. The solution was added dropwise over the 2% clay slurry. Aging of the solution was done under microwaves for 15 minutes. The intercalated clay was calcined for 5 hours at 793 K; the literature data indicate that at temperatures above 473 K, the chemical pillaring and non-reversible of the clay occurs, because chemical bonds of Si-O-Al type are formed between the clay and the aluminum pillars.³⁷ After calcination, the intercalated polycations, turning into resistant metal oxide clusters, give solids with high thermal stability, microporous surface and high acidity.¹⁵ If the intercalated material is not calcined, the pillar structure can be hydrolyzed and destroyed. Depending on the temperature and humidity conditions, the decomposition can occur within a few weeks due to the hydrolysis of the Al polyhydroxylation. Therefore, calcination is an important step in the production of pillared clays, which is stable for storage for a long period of time under environmental conditions.³⁰

For the obtained catalyst, the content of each component can be determined by the intensity of the maximum absorption. This was possible because phosphate can maintain Lewis surface sites on catalyst, water chemisorption would be prevented causing less catalytic activity. Tabel 2 present the FT-IR band assignments for raw montmorillonite clay.

Results and discussions

The P1-PILCs sample was characterized by FTIR, BET and XRD.

Figure 3 illustrates the infrared spectra of montmorillonite and P1-PILC. Montmorillonite is made up of two layers of tetrahedra and one of octahedra, packed as a sandwich (T:O:T). The absorption band at

3633 cm^{-1} corresponds to the stretching of cations and hydroxyls groups from the octahedral sheet. The band from 3432 cm^{-1} is due to the water adsorbed on the clay surface, confirmed by the deformation band at 1642 cm^{-1} . Tyagi et al.³⁸ assigned in detail the bands from IR spectrum for a similar material. The bands from 524 cm^{-1} and 433 cm^{-1} correspond to deformation vibrations of Si–O–Al and Al–OH (Table 2).

Table 2. FT-IR band assignments for raw montmorillonite clay³⁸.

Maxima (cm^{-1})	Assignments
3697	-OH stretching
3623	-OH stretching
3440	-OH stretching, hydration
1639	-OH stretching, hydration
1113	Si-O stretching, out-of-plane
1035	Si-O stretching, in-plane
915	AlAlOH bending
875	AlFeOH bending
836	AlMgOH bending
793	Platy form of tridymite
692	Quartz
529	Si-O bending

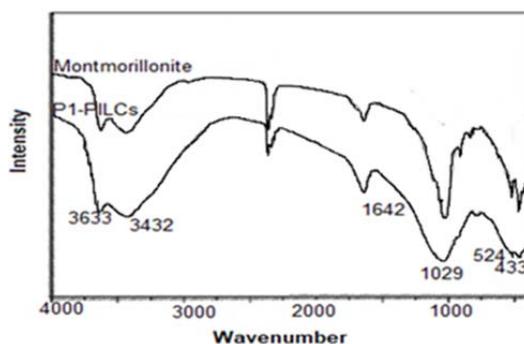


Figure 3. FTIR spectra of Montmorillonite and pillared Montmorillonite (P1-PILCs).

The BET pure nitrogen adsorption at 77 K allowed calculating the specific surface area and the total pore volume from the amount of nitrogen

adsorbed at $P/P_0 = 0.95$. The sample was activated before the nitrogen adsorption by degassing at 623 K for 6 hours.

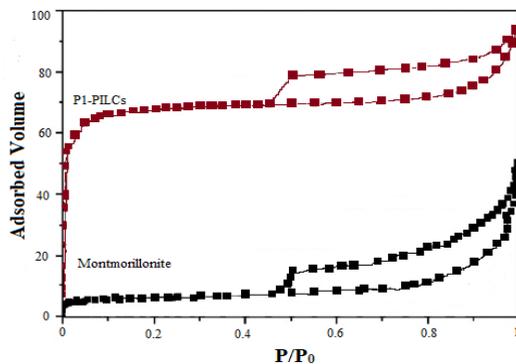


Figure 4. Adsorption/desorption isotherms of N_2 at 77 K .

The adsorption/desorption isotherms of N_2 at 77 K are displayed in Figure 4. According to the BET adsorption model, the specific surface of pillared montmorillonite (P1-PILCs) increased (220 to 290 m^2/g) and so did the pore volume (from 0.015 to 0.086 $cm^3 g^{-1}$). The sudden increase of the adsorbed amount of nitrogen at low P/P_0 values on the pillared sample indicates the generation of ordered micropores in the solid due to the pillaring procedure.

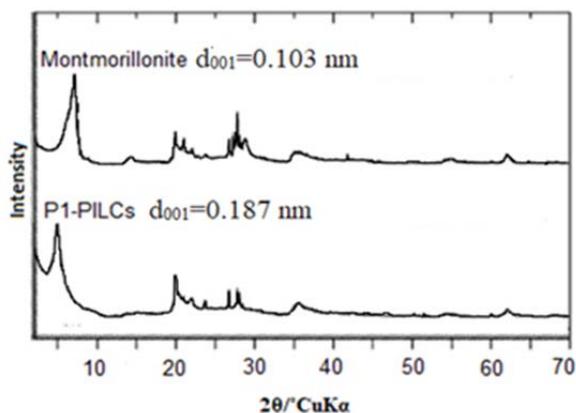


Figure 5. XRD patterns of Montmorillonite and pillared Montmorillonite (P1-PILCs).

The pillaring processes efficiency was also confirmed by XRD. Figure 5 represent the XRD patterns of Montmorillonite and catalyst

P1-PILCs. The typical basal spacing of montmorillonite 0.103 nm increased to 0.187 nm after pillaring.

pH and ozone effects

pH of the solution defines the surface charge of the catalyst and the ionization degree of the materials from the solution. The hydronium ion H_3O^+ and hydroxyl ions HO^- are strongly adsorbed, so the adsorption of other ions is influenced by the pH of the solution, inclusive in terms of reaction kinetics and equilibrium characteristics. It had been reported³⁹ that the surface adsorbs anions better at lower pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH, due to the presence of HO^- ions. The pH value affects the structural stability of MG and its colour intensity. Therefore, the effect of pH on MG color intensity was studied using solutions of 10^{-4} M of MG with natural pH and solutions adjusted to pH values of 3, 5 and 7, while treated with 0.5 g/h ozone. After 2 h following the pH adjustment, the absorbance of the solution at the characteristic $\lambda = 618$ nm was measured. At pH = 3, 96.74% of the chromophore was removed, at pH = 5, the yield was 80.5% and at pH = 7, yield was 50.1%. The strong color removal due to pH modification is probably due to damaging of the molecule's chromophore.

The ozone effect on the dye stability at pH value of 3 (most sensitive to degradation as fore-mentioned) was determined by tracing the spectra of MG solutions (10^{-4} M) subjected to ozonation for different times: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 min (Figure 6a). The value of the absorbances at 618 nm and 580 nm are presented in Figure 6b).

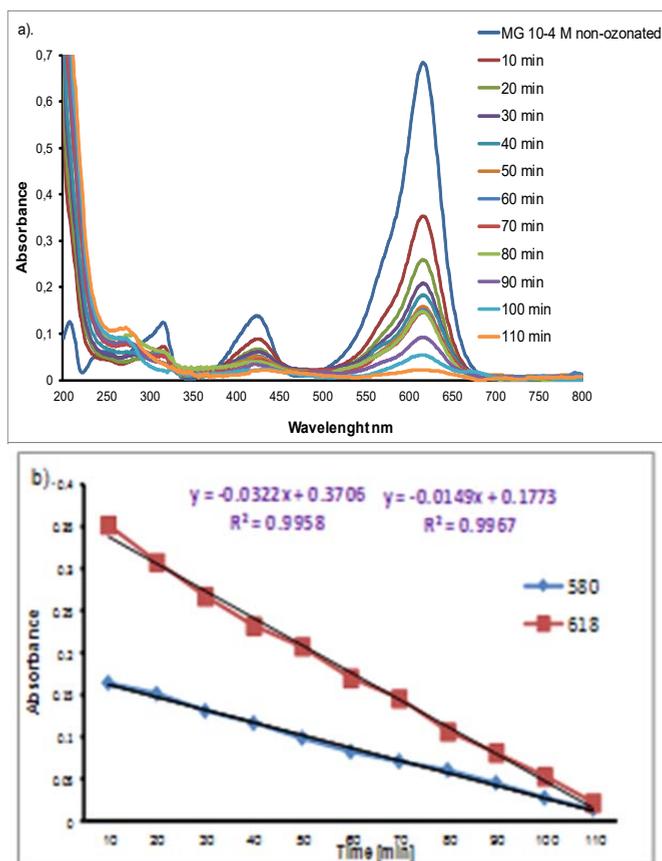


Figure 6. a) UV-Vis spectrum of ozonated MG 10^{-4} M in distilled water; **b)** Absorbance values of MG 10^{-4} M over time under O_3 (0.5 g/h) at pH = 3.

The excellent regression coefficient values ($R^2 = 0.9967$ for 618 nm and $R^2 = 0.9958$ for 580 nm) indicate that ozone is an effective oxidizer for MG in a time of less 2 hours, the dye being almost totally removed. Moreover, the secondary peak of MG from 589 nm also almost disappeared, indicating that the oxidation led mostly to dye mineralization.

Effect of catalyst dose

The chemically modified clay sample with Al^{3+} (P1-PILCs) was used as catalyst during the ozonation process. Various doses of P1-PILC catalyst: 25, 50, 100 and 150 mg/L were used and their effectiveness tested in the degradation of MG dye.

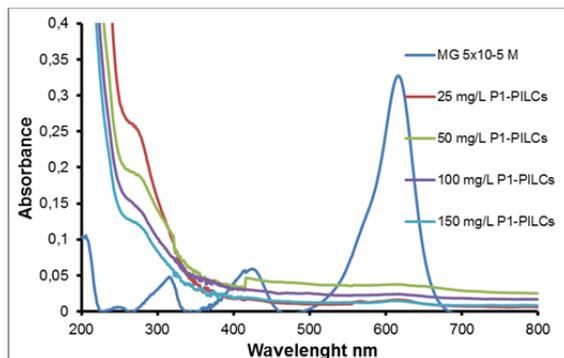


Figure 7. UV-Vis spectra after 5 seconds of catalytic ozonation of MG (5×10^{-5} M) with different catalyst doses (dye removal yields between 82-95.55%).

According to the data presented in Figure 7, the best yield in the degradation of MG dye (95.55%) was reached when using 150 mg/L of catalyst and 0.5 g/h of ozone. In the tested range, the higher amount of catalyst favorably influences the catalytic oxidation process. Compared with the simple ozonation, the introduction of the catalyst dramatically decreases the duration of reaction, from 110 minutes (yield of 96.74%) to some seconds (around 5 seconds, yield of 95.55%).

Effect of ozone:catalyst ratio

The catalytic ozonation of MG using different amounts of O_3 (0.5, 1, 1.5 and 2 g/h), and different amounts of catalyst (25, 50, 100 and 150 mg/L) were used and tested its effectiveness in dyestuff degradation, (Figure 8).

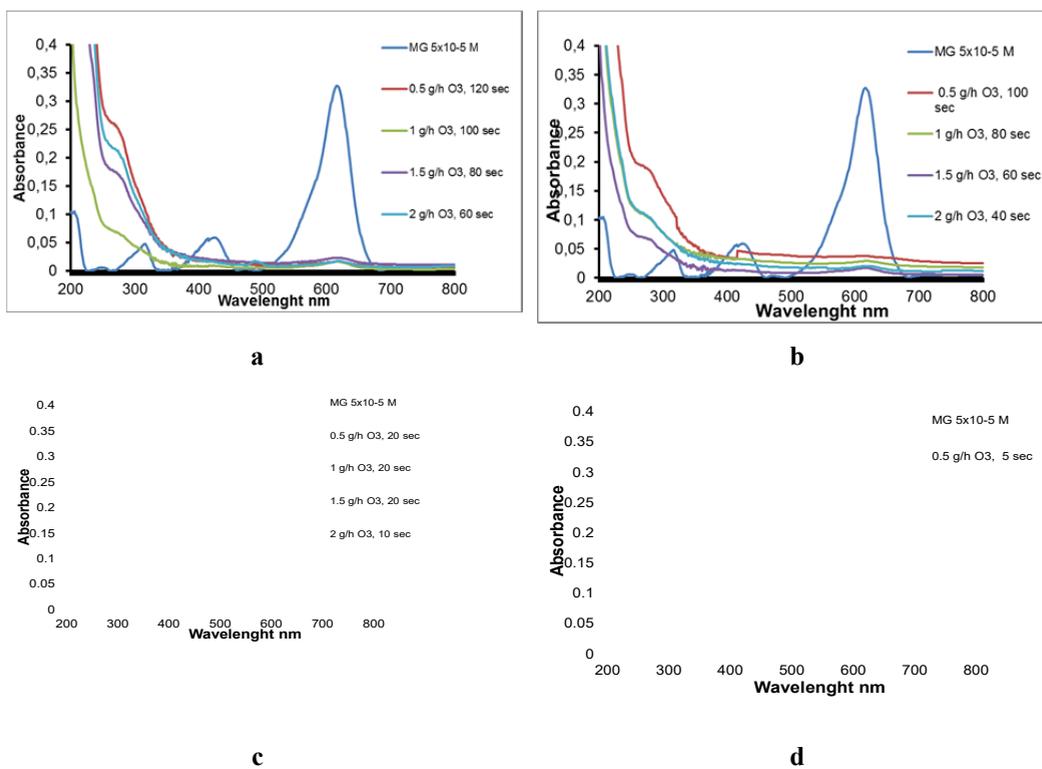


Figure 8. UV-Vis spectra of MG (5×10^{-5} M) during catalytic ozonation, Catalyst dose: a. 25 mg/L; b. 50 mg/L; c. 100 mg/L; d. 150 mg/L (time values mentioned in the legend).

According to the results displayed in Figures 8 a-d, the best result was obtained at 0.5 g/h ozone dose and 150 mg/L P1-PILCs, with the removal yield of 95.55%. The catalytic effect of aluminium is probably due to its capacity to define a porous surface and produce acidic sites. In conclusion, the catalyst addition produces the total disappearance of organic dye characteristic bands in the visible range.

Conclusion

The use of low-cost, abundantly available, highly efficient and eco-friendly adsorbent clay of smectite type (P1-PILC) were proved to be an advantageous alternative to the current expensive methods for removing the MG dye from aqueous solution by oxidation with low amounts of ozone.

According to BET analysis, the specific surface area of P1-PILC increased by pillaring from 220 to 290 m²/g and respectively the pore volumes grown from 0.015 to 0.086 cm³g⁻¹. The XRD analysis reveals that the basal distance changed from 0.103 nm to 0.187 nm, confirming the new spatioption between the clay layers. In consequence, the P1-PILC clay obtained by ion-exchange and intercalation of Keggin ions (Al₁₃⁷⁺) is a good candidate for MG removal from wastewaters.

By ozonation only (0.5 g/L), the MG (5x10⁻⁵ M) mineralization takes place in 110 minutes, with a removal yield of 96.74 %. Similar decolorization yields (over 95%) were obtained by adding the catalyst, at oxidation time of only some seconds. Due to the very short, almost instantaneous time of oxidation of the chromophore groups, the chemically modified clay obtained was judged as very suitable to be used as a good catalyst for the MG dye removal from wastewater.

Reference

1. Sharma, P.; Kaur, H.; Sharma, M.; Sahore, V. A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste. *Environ. Monit. Assess.* **2011**, *183* (1), 151-195.
2. ALzaydien, A.S. Adsorption of methylene blue from aqueous solution onto a low-cost natural Jordanian Tripoli. *Am. J. Appl. Sci.* **2009**, *6*(6), 1047-1058.
3. Rao, K. Inhibition of DNA synthesis in primary rat hepatocyte cultures by malachite green: a new liver tumor promoter. *Toxicol. Lett.* **1995**, *81*(2-3), 107-113.
4. Foster, F.J.; Woodbury, L. The use of malachite green as a fish fungicide and antiseptic. *Prog. fish-cult.* **1936**, *3*(18), 7-9.
5. Culp, S.J.; Beland, F.A. Malachite green: a toxicological review. *J. Am. Coll. Toxicol.* **1996**, *15* (3), 219-238.
6. Klein, E.; Edelhaeuser, M.; Lippold, R. Bestimmung von Malachitgrün-Rückständen in Speisefischen. III: Gesamtmalachitgrün einschließlich der Leucoform. *Deut. Lebensm.-Rundsch.* **1991**, *87*(11), 350-353.

7. Hameed, B.; El-Khaiary, M. Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: equilibrium isotherms and kinetic studies. *J. Hazard. Mater.* **2008**, *154(1-3)*, 237-244.
8. Papinutti, L.; Mouso, N.; Forchiassin, F. Removal and degradation of the fungicide dye malachite green from aqueous solution using the system wheat bran–*Fomes sclerodermeus*. *Enzyme Microb. Tech.* **2006**, *39(4)*, 848-853.
9. Pourreza, N.; Elhami, S. Removal of malachite green from water samples by cloud point extraction using Triton X-100 as non-ionic surfactant. *Environ. Chem. Lett.* **2010**, *8(1)*, 53-57.
10. Gupta, V.K.; Srivastava, S.K.; Mohan, D. Equilibrium uptake, sorption dynamics, process optimization, and column operations for the removal and recovery of malachite green from wastewater using activated carbon and activated slag. *Ind. Eng. Chem. Res.* **1997**, *36(6)*, 2207-2218.
11. Sartape, A.S.; Mandhare, A.M.; Jadhav, V.V.; Raut, P.D.; Anuse, M.A.; Kolekar, S.S. Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. *Arab. J. Chem.* **2017**, *10*, S3229-S3238.
12. Diez, M. Biological aspects involved in the degradation of organic pollutants. *J. Soil Sci. Plant Nut.* **2010**, *10(3)*, 244-267.
13. Ren, L.; Li, G.; Han, Y.C.; Jiang, D.H.; Huang, H.-C. Degradation of oxalic acid by *Coniothyrium minitans* and its effects on production and activity of β -1, 3-glucanase of this mycoparasite. *Biol. Control* **2007**, *43(1)*, 1-11.
14. Azzouz, A.; Mirila, D.C.; Nistor, D.I.; Boudissa, F.; Roy, R. Advances in the oxidative degradation of organic pollutants: Prospects for catalyzed oxidation processes targeting total mineralization. In *Catalytic Oxidation: Types, Catalysts and Applications*, Nova Science: New York, 2018.
15. Schoonheydt, R.A.; Pinnavaia, T.; Lagaly, G.; Gangas, N. Pillared clays and pillared layered solids. *Pure Appl. Chem.* **1999**, *71(12)*, 2367-2371.
16. Fenelonov, B.; Derevyankin, A.Y.; Sadykov, V. The characterization of the structure and texture of pillared interlayer materials. *Micropor. Mesopor. Mat.* **2001**, *47(2)*, 359-368.
17. Brindley, G.; Ray, S. Complexes of Ca-Montmorillonite with primary monohydric alcohols (Clay-organic studies-8). *Am. Mineral.* **1964**, *49(1-2)*, 106-115.
18. Brindley, G.; Sempels, R. Preparation and properties of some hydroxy-aluminium beidellites. *Clay Miner.* **1977**, *12(3)*, 229-237.

19. Brindley, G.; Yamanaka, S. A study of hydroxy-chromium montmorillonites and the form of the hydroxy-chromium polymers. *Am. Miner.* **1979**, *64*(7-8), 830-835.
20. Lahav, N.; Shani, U.; Shabtai, J. Cross-linked smectites. I. Synthesis and properties of hydroxy-aluminum-montmorillonite. *Clays Clay Miner.* **1978**, *26*(2), 107-115.
21. Vaughan, D.; Lussier, R. Preparation of molecular sieves based on pillared interlayered clays (PILC). *Proceedings of the 5th International Conference on Zeolites*, Heyden: London, 1980; pp 94-101.
22. Occelli, M.; Tindwa, R. Physicochemical properties of montmorillonite interlayered with cationic oxyaluminum pillars. *Clays Clay Miner.* **1983**, *31*(1), 22-28.
23. Perrott, K. Surface charge characteristics of amorphous aluminosilicates. *Clays Clay Miner.* **1977**, *25*(6), 417-421.
24. Lahodny-Sarc, O.; Khalaf, H. Some considerations of the influence of source clay material and synthesis conditions on the properties of Al-pillared clays. *Appl. Clay Sci.* **1994**, *8*(6), 405-415.
25. Cool, P.; Vansant, E.F. Pillared clays: preparation, characterization and applications. *Synthesis* **1998**, 265-288.
26. Molina, C.; Casas, J.; Zazo, J.; Rodriguez, J. A comparison of Al-Fe and Zr-Fe pillared clays for catalytic wet peroxide oxidation. *Chem. Eng. J.* **2006**, *118*(1), 29-35.
27. Ursu, A.V.; Gros, F.; Nistor, D.I.; Djelveh, G. Characterization and Utilization of a Commercial Clay for Ammonia Adsorption. *Rev. Chim.(Bucharest)* **2008**, *59*, 1067-1072.
28. Bergaya, F.; Aouad, A.; Mandalia, T. Pillared clays and clay minerals. In *Handbook of clay science*; F. Bergaya, B.K.G. Theng, G. Lagaly, Eds.; Elsevier Science, **2006**, pp 393-421.
29. Muntianu, G.; Platon, N.; Jinescu, G.; Siminiceanu, I.; Mardaru, A.; Zavada, R.M.; Miron, D.N.; Nistor, I.D. Preparation and characterization of nanostructured materials used for the retention of gaseous pollutants, *Annals of the University Dunarea de Jos of Galati: Mathematics, Physics, Theoretical Mechanics* **2011**, *2*(special issue), 115-122.
30. Nistor, D.; Miron, N.; Surpateanu, G.; Azzouz, A. Etude par desorption thermique programme des proprietes des argiles modifiees. *J. Therm. Anal. Calorim.* **2004**, *76*(3), 913-920.

31. Kiš, E.E.; Ranogajec, J.G.; Marinković-Nedučin, R.P.; Dimić, E.B.; Vulić, T.J. Soybean oil bleaching by Al-pillared montmorillonite. *Acta Period. Technol.* **2002**, *33*, 27-34.
32. Platon, N.; Siminiceanu, I.; Miron, N.D.; Muntianu, G.; Zavada, R.M.; Isopencu, G.; Nistor, I.D.; Preparation and characterization of new products obtained by pillaring process. *Rev. Chim. (Bucharest)* **2011**, *62*, 799-805.
33. Georgescu, A.-M.; Arus, V.-A.; Nardou, F.; Nistor, I.D.; Limoges Cedex, F. Preparation and characterization of Al(III) pillared interlayered clays based on indigenous bentonite. *Bull. Rom. Chem. Eng. Soc.* **2016**, *3(1-2)*, 94-99.
34. Chávez-García, M.L.; de Pablo-Galán, L.; Saucedo-Ramírez, M.P. Synthesis of intercalated Al-hydroxy-montmorillonite. *J. Mex. Chem. Soc.* **2006**, *50(1)*, 36-41.
35. Klopogge, J.T.; Duong, L.V.; Frost, R.L. A review of the synthesis and characterisation of pillared clays and related porous materials for cracking of vegetable oils to produce biofuels. *Environ. Geol.* **2005**, *47(7)*, 967-981.
36. Azzouz, A.; Dumitriu, E.; Hulea, V.; Catrinescu, C.; Carja, G. Pillared clays as catalysts for the condensation reaction of aldehydes. *Prog. Catal.* **1996**, *5(1)*, 9-18.
37. Azzouz, A.; Siminiceanu, I.; Nistor, D. Pontage des argiles type montmorillonite avec des polycations de type Al13, In *Proceedings of Colloque Franco-Roumain de Chimie Appliqué*, 2002; pp 289-292.
38. Tyagi, B.; Chudasama, C.D.; Jasra, R.V. Determination of structural modification in acid activated montmorillonite clay by FT-IR spectroscopy. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2006**, *64(2)*, 273-278.
39. Mall, I.D.; Srivastava, V.C.; Agarwal, N.K.; Mishra, I.M. Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses. *Colloids Surf. A Physicochem. Eng. Asp.* **2005**, *264(1-3)*, 17-28.