

Use of Zinc Ferrite for Photocatalytic Treatment of Water Contaminated with Organic Dye

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Abstract. The present work aims to test the use of zinc ferrite as a photocatalytic agent for the discoloration of water contaminated by organic dyes. The zinc ferrite used is an industrial waste that comes from an industrial plant destined for the extraction of zinc. The organic dye studied was the Blue Patent V. The photocatalytic tests were prepared using aqueous solutions contaminated by the organic dye to which predetermined quantities of zinc ferrite were added and were subsequently exposed to sunlight for programmed times. Furthermore, systems in the presence of hydrogen peroxide have also been studied. After the exposure time, the systems were filtered and the concentrations of the solutions were measured with UV spectrophotometry. The ferrite after the photocatalytic tests was characterized by thermal analysis (DSC). The data obtained were analyzed according to the experimental parameters used. Zinc ferrite showed photodegradative abilities respect to the analyzed dye.

1. Introduction

Water pollution is an increasingly current problem. There are many causes that contribute to threatening the state of rivers and seas, which are almost always the major receptors of pollutants that are released into the environment. Increased sensitivity is driving research to act on several fronts [1-3]. The first important action is surely that of avoiding the production of harmful substances itself by production of materials and life cycles eco-sustainable [4-9]. Unfortunately, this is not always possible and therefore it is fundamental to seek new and adequate methods of treatment for the abatement of pollutants. Particularly important is the purification of contaminated water which is addressed using new materials such as molecular sieves [10-16], carbon nanotubes [17-20], geopolymers [21, 22], photo catalytic materials [23-26]. Zinc ferrite is an industrial waste and comes from industrial plants destined to extract zinc. Many studies have shown that it contains many metals [15, 27, 28]. Precisely this great abundance of metals led us to suppose that zinc ferrite could be a potential photochemical agent. In this work, therefore, we wanted to consider ferrite not only as a problem but as a potentially useful waste, giving it a new function. In particular, in this work, zinc ferrite has been tested as a photocatalytic agent for the discoloration of water contaminated by the organic dye.



2. Materials and Methods

The materials used in the experiments were Blue Patent V dye, Zinc Ferrite and hydrogen peroxide. Blue Patent V, or E131, in the European code for food additives, is a dark blue synthetic dye. It is a salt that can be in the sodium (CAS: 20262-76-4) or calcium (CAS: 3536-49-0) form. The appearance is of a violet powder very soluble in water. In this research the sodium form was used.



Figure 1. (a) Structure and (b) powder of Blue Patent V; (c) Zinc ferrite.

The Blue Patent V raises concern when it is spilled in an abusive manner, and not treated according to the existing standards in the environmental field, in natural water courses from the various industries that use it both in the food industry and in the textile, tanning, etc. Zinc ferrite is an industrial waste derived from the treatment of zinc extraction from blende, a mineral that includes zinc sulfide. This waste is presented as a dark colored powder (figure 1c). The hydrogen peroxide solution used has a concentration of 30% (w/w). The experimental procedure initially involved the preparation of the aqueous solution of Blue Patent V with a concentration of 0.1 g / L. Subsequently different systems were prepared by adding predetermined quantities of zinc ferrite to established volumes of the initial solution. Other systems have been prepared also by adding hydrogen peroxide. In order to have a reference, zinc ferrite-free systems have also been considered. The following table 1 summarizes the composition of the different systems considered.

Table 1. System composition.

System	Composition
0	15 mL Blue Patent solution [0.1g/L]
1	15 mL Blue Patent solution [0.1g/L] + 0.1g Zinc Ferrite
2	15 mL Blue Patent solution [0.1g/L] + 1 mL H ₂ O ₂ [30%w/w]
3	15 mL Blue Patent solution [0.1g/L] + 1 mL H ₂ O ₂ [30%w/w] + 0.1g Zinc Ferrite

Subsequently all systems were exposed to sunlight for 4, 8, 16, 16, 20 days. The reason for exposing them only to sunlight and avoiding other types of radiation was motivated by the choice of studying the most natural and economic methods possible. Once the predetermined exposure times had elapsed, the systems were filtered by a vacuum pump and the solution obtained was analyzed by UV spectrophotometry to search for the residual concentration of the dye. Furthermore, on the solid residue, that is the zinc ferrite after the test, thermal analyzes (DSC) were carried out in order to verify also possible adsorption phenomena.

3. Results and discussions

The first phase of the research was to verify the photostability of Blue Patent V in the experimental conditions used. The following figure 2 shows the concentration of the dye solutions after the photocatalytic tests at different times of exposure to sunlight.

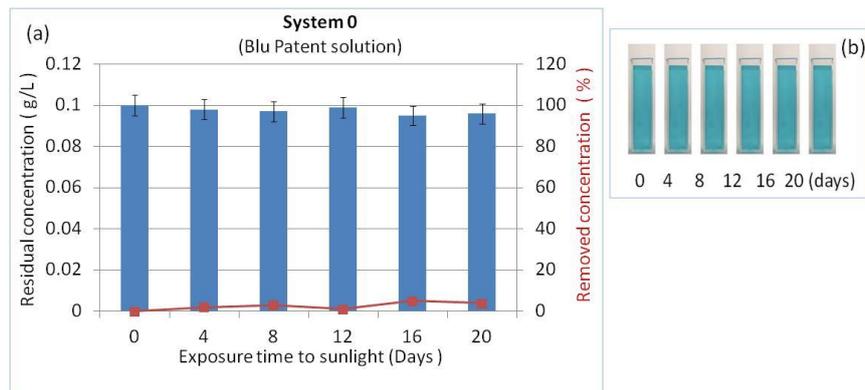


Figure 2. (a) Concentration and percentage of abatement of the system 0 and (b) respective images of the solutions as a function of the time of exposure to sunlight.

The data show that the Blue Patent V dye, in the experimental conditions used, presents a strong photostability in fact after 20 days of exposure to sunlight the concentration has remained almost unchanged. The following figure 3 shows the variation of the concentration of the dye solutions in the presence of zinc ferrite (system 1). The data obtained show that zinc ferrite accelerates dye degradation.

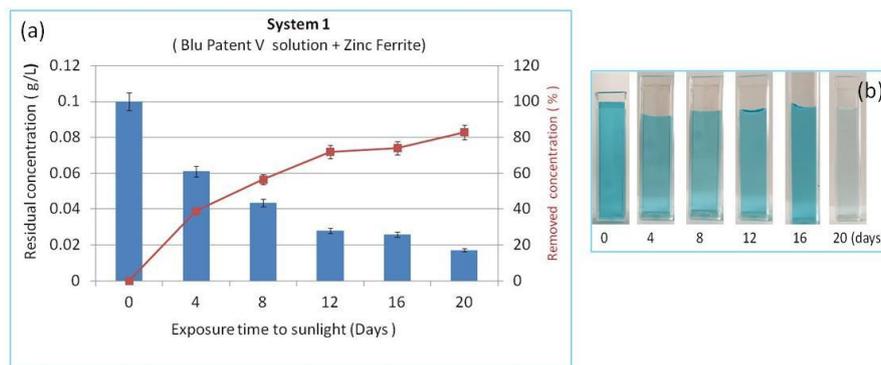


Figure 3. (a) Concentration and percentage of abatement of the system 1 and (b) respective images of the solutions the function of the time of exposure to sunlight.

The following figure 4 shows the variation of the concentration of the dye solutions in the presence of hydrogen peroxide but in the absence of zinc ferrite (system 2).

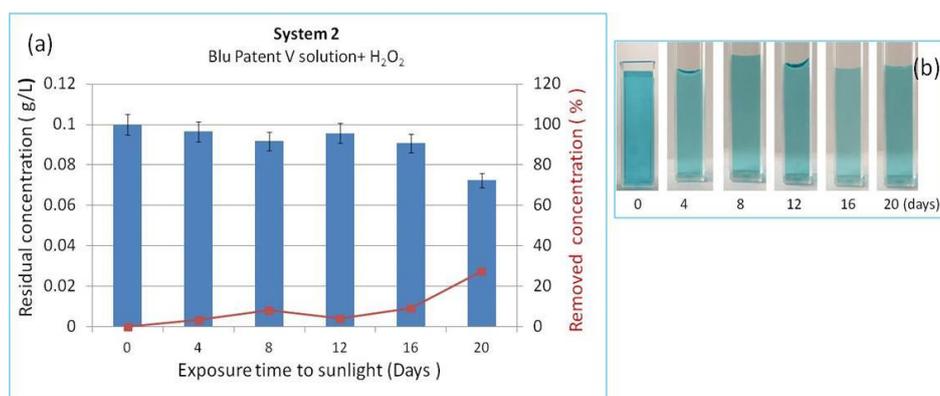


Figure 4. (a) Concentration and percentage of abatement of system 2 and (b) respective images of the solutions the function of exposure time to sunlight.

This test was carried out to verify the influence of hydrogen peroxide on the photostability of the dye. The data reported in figure 4 show that the dye is photostable even in the presence of hydrogen peroxide in fact a more significant decrease in concentrations is recorded only on the 20th day of exposure to sunlight. The following figure 5 shows the data obtained in the presence of zinc ferrite and hydrogen peroxide.

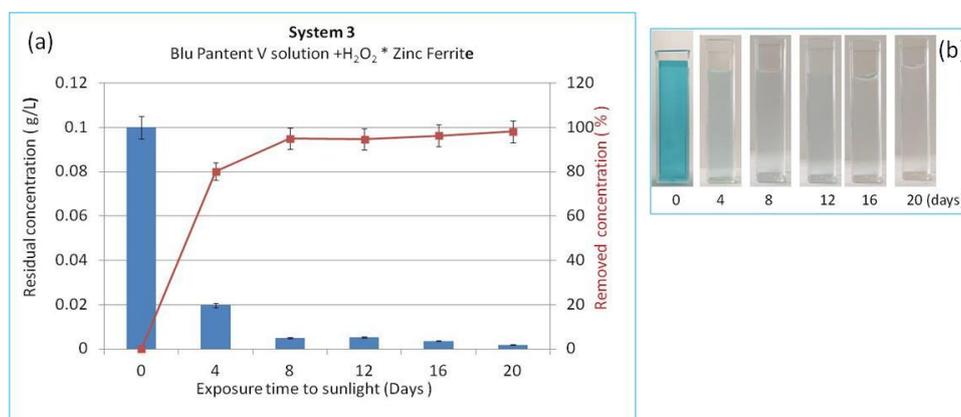


Figure 5. (a) Concentration and percentage of abatement of system 1 and (b) respective images of the solutions the function of exposure time to sunlight.

The addition of hydrogen peroxide to the system containing zinc ferrite increases the photodegradative action. In fact, even after only four days of exposure to sunlight there is a significant reduction in dye concentrations. From the thermal analysis (DSC) (figure 5) carried out it emerged that there was no adsorption action, in fact on the zinc ferrite samples (curves b and c) there are no peaks attributable to the dye. The degradation of the contaminant can be attributed exclusively to a photodegradative action.

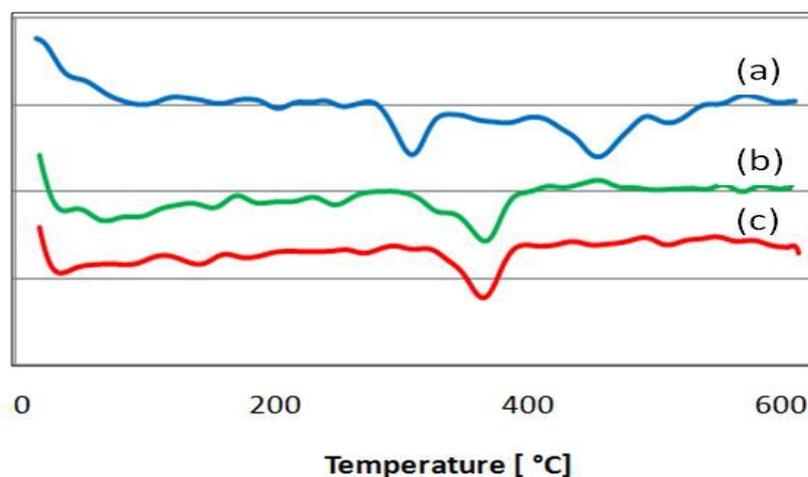


Figure 5. Thermal Analysis (DSC): (a) Blue Pantent V; Zinc Ferrite after test (b) of system 1 (b) and system 2 (c).

4. Conclusions

The results obtained showed that zinc ferrite showed photocatalytic capacities that are improved in the presence of hydrogen peroxide. Although this compound has metals in it, it has been used experimentally to see if it has a degradation action and surprisingly showed a high photodegradative behaviour.

Reference

- [1] Aiello D, Cardiano P, Cigala R. M, Gans P, Giacobello F, Giuffrè, O, Napoli A, Sammartano S 2017 Sequestering ability of oligophosphate ligands toward Al³⁺ in aqueous solution *J. Chem. Eng. Data* **62**(11) 3981-90.
- [2] Aiello D, Furia E, Siciliano C, Bongiorno D, Napoli A 2018 Study of the coordination of ortho-tyrosine and trans-4-hydroxyproline with aluminum (III) and iron (III) *J. Molec. Liq.* **269** 387-97.
- [3] Siciliano C, De Marco R, Guidi L. E, Spinella M, Liguori A 2012 A one-pot procedure for the preparation of N-9-Fluorenylmethoxycarbonyl- α -amino diazoketones from α -Amino Acids *J. Org. Chem.* **77**(23) 10575-82.
- [4] Ljungberg L. Y. 2007 Materials selection and design for development of sustainable products *Mater. Desig.* **28**(2) 466-79.
- [5] De Luca P; Carbone I, Nagy J. B 2017 Green building materials: A review of state of the art studies of innovative materials *J. Green Build.* **12**(4) 141-61.
- [6] Guigo N, Mija A, Vincent L, Sbirrazzuoli N 2010 Eco-friendly composite resins based on renewable biomass resources: Polyfurfuryl alcohol/lignin thermosets *Eur. Polym. J.* **46**(5) 1016-23.
- [7] De Luca P, Pane L, Vuono D, Siciliano C, Candamano S, Nagy J. B 2017 Preparation And Characterization of Natural Glues with Carbon Nanotubes *Environ. Eng. Manag. J.* **16**(8).
- [8] De Luca P, Roberto B, Vuono D, Siciliano C, Nagy J. B 2018 Preparation and optimization of natural glues based on Laricio pine resin *IOP conf. Ser. Mater. Sci. Eng.* **374**(1) 012071.
- [9] Cheung H. Y, Ho M. P, Lau K. T, Cardona F, Hui D 2009 Natural fibre-reinforced composites for bioengineering and environmental engineering applications *Comp. Part B Eng.* **4**(7) 655-63.
- [10] Barakat M. A 2011 New trends in removing heavy metals from industrial wastewater *Arab. J. Chem.* **4**(4) 361-77.
- [11] Lopes C B, Coimbra J, Otero M, Pereira E, Duarte A. C, Lin Z, Rocha J 2008 Uptake of Hg²⁺ from aqueous solutions by microporous titano-and zircono-silicates *Quimica Nova* **31**(2) 321-5.
- [12] Motsi T, Rowson N. A, Simmons M. J. H 2009 Adsorption of heavy metals from acid mine drainage by natural zeolite *Int. J. Miner. Process.* **92**(1-2) 42-8.
- [13] De Luca P, Mastroianni C, Nagy J. B 2018 Synthesis of self-bonded pellets of ETS-4 phase by new methodology of preparation *IOP conf. Ser. Mater. Sci. Eng.* **347**(1) 012003.
- [14] Kang S. Y, Lee J. U, Moon S. H, Kim K. W 2004 Competitive adsorption characteristics of Co²⁺, Ni²⁺, and Cr³⁺ by IRN-77 cation exchange resin in synthesized wastewater *Chemosphere* **56**(2) 141-7.
- [15] De Luca P, Bernaudo I, Elliani R, Tagarelli A, Nagy J. B, Macario A 2018 Industrial Waste Treatment by ETS-10 Ion Exchanger Material *Mater.* **11**(11) 2316.
- [16] Huang C. P, Blankenship D. W 1984 The removal of mercury (II) from dilute aqueous solution by activated carbon *Water Res.* **18**(1) 37-46.
- [17] Logar N. Z, Kaucic V 2006 Nanoporous materials: from catalysis and hydrogen storage to wastewater treatment *Acta Chim. Slov.* **53**(2) 117.
- [18] De Luca P, Nappo G, Siciliano C, Nagy J. B 2018 J. The role of carbon nanotubes and cobalt in the synthesis of pellets of titanium silicates *Porous Mater.* **25**(1) 283-96.
- [19] Lico D, Vuono D, Siciliano C, Nagy J. B, De Luca P 2019 Removal of unleaded gasoline from water by multi-walled carbon nanotubes *J. Environ. Manag.* **237** 636-43.
- [20] Sebastiano C, De Luca P, Frontera P, Crea F 2017 Production of geopolymeric mortars containing forest biomass ash as partial replacement of metakaolin *Environ.* **4**(4) 74.
- [21] Davidovits J 2015 *Geopolymer Chemistry & Application 4th Ed. Institute Geopolymere Saint-Quentin France* ISBN 9782951482098.
- [22] Al-Harashneh M. S, Al Zboon K, Al-Makhadmeh, L, Hararah M, Mahasneh M 2015 Fly ash based geopolymer for heavy metal removal: A case study on copper removal *J. Environ. Chem. Eng.* **3**(3) 1669-77.
- [23] De Luca P, Foglia P, Siciliano C, Nagy J. B, Macario A 2019 Water Contaminated by Industrial Textile Dye: Study on Decolorization Process *Environ.* **6**(9) 101.

- [24] De Luca P, Chiodo A, Nagy J. B 2011 Activated ceramic materials with deposition of photocatalytic titano-silicate micro-crystals *WIT Trans. Ecol. Environ.* **154** 155-65.
- [25] Di Paola A, Garcia-Lopez E, Marci G, Palmisano L 2012 A survey of photocatalytic materials for environmental remediation *J. Hazard. Mater.* **211** 3-29.
- [26] De Luca P, De Luca P, Candamano S, Macario A, Crea F, Nagy J. B 2018 Preparation and Characterization of Plasters with Photodegradative Action *Build.* **8(9)** 122.
- [27] De Luca P, Bernaudo I, Candamano S, Siciliano C, Macario A. 2019 Treatment of industrial slag zinc ferrite by zeolitic sludge *IOP conf. Ser. Mater. Sci. Eng.* **572(1)** 012046.
- [28] De Luca P, Bernaudo I, Tagarelli A, Candamano S, Nagy J. B 2018 Study on the Release Conditions of the Metals Present in the Zinc Ferrite *Proce. Environ. Sci. Eng. Manage.* **5(1)** 29.