chemistry proceedings

MDPI

Proceedings

Ag@ZnO-saponite nanocomposite for photodegradation of ciprofloxacin†

Dihêgo H. L. Damacena[1], Victor H. Macedo[1], Albert S. Silva[1], Luzia M. C. Honorio[1], Edson C. Silva-Filho[1], Pollyana Trigueiro[1,*], Josy A. Osajima[1,*]

[1] Interdisciplinary Laboratory for Advanced Materials (LIMAV), UFPI, 64049-550, Teresina, PI, Brazil
* Correspondence: *pollyanatrigueiro@gmail.com*; *josyosajima@ufpi.edu.br*
† Presented at the title, place, and date.

Abstract: Unregulated disposal of antibiotics has become a global concern for the pollution of water bodies. Photocatalysis appears as an efficient method for removing these emerging contaminants. Clay minerals are used as supports for semiconductors in order to improve their photocatalytic activity. This study aimed to obtain new photocatalysts by incorporation of the Ag and ZnO nanoparticles in saponite to be used in the photodegradation of ciprofloxacin in aqueous solution. The results showed a good incorporation of nanoparticles onto support surface. Ag@ZnO-saponite nanocomposite corresponds at low band gap energy, showing high ability under visible light. The nanocomposite showed efficiency about to 90% of degradation of antibiotic after 120 min of reaction.

Keywords: Saponite; Ag nanoparticles, ZnO, nanocomposite, photocatalysis, residual antibiotic.

Citation: Damacena, D. H. L.; Macedo, V. H.; Silva, A. S.; Honorio, L. M. C.; Silva-Filho, E. C.; Trigueiro, P.; Osajima, J. A.; Ag@ZnO-saponite nanocomposite for ciprofloxacin photodegradation. *Chem. Proc.* **2021**, *3*, x. https://doi.org/10.3390/xxxxx

Published: date

1. Introduction

The adverse effects caused by so-called emerging contaminants in water pollution have become a global concern [1]. Conventional treatments do not efficiently remove drugs for example the ciprofloxacin from contaminated water due to its resistance, high solubility and recalcitrant nature. The technologies such as heterogeneous photocatalysis become more efficient for the degradation of this pollutant [2].

ZnO is an example of a n-type semiconductor widely used in photocatalysis studies mainly because has high efficiency, non-toxicity and chemical stability [3]. Noble metal nanoparticles such as Ag NPs have attracted great interest due to their surface plasmonic resonance (SPR), which in the photocatalytic process accelerates the separation of photogenerated charges when irradiated under visible light [4].

Clay minerals have been used as support for semiconductor oxides due to their attractive physicochemical properties: high surface area, surface chemistry, cation exchange capacity and high mechanical/chemical stability [5,6]. The incorporation of semiconductors in the structure of clay minerals promotes an increase in the surface area of the catalyst, an increase in active sites and facilitates the recovery of the catalyst from the reaction medium [7], becoming an interesting strategy for improving photocatalytic performance.

This study aimed to obtain a new catalyst from the incorporation of Ag and ZnO nanoparticles on the saponite clay mineral structure. The photocatalytic efficiency of the nanocomposite was monitored in the photodegradation of ciprofloxacin antibiotic under visible light irradiation.

2. Materials and Methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) (≥ 99%), $ZnCl_2$ (≥ 98%), NaOH (≥ 99%), isopropanol (≥ 70%) were purchased from Sigma Aldrich and used without prior purification.

2.2. Synthesis of nanocomposite

For incorporation of Zn^{2+} in saponite, the method reported by Fatimah et al [8] was used. Firstly, a dispersion of Na-saponite (previously synthesized) [9] was prepared by adding 5% by weight of clay mineral in distilled water with subsequent dropwise addition of a CTAB solution (2.5 mmol CTAB g-1 saponite) and the resulting solution it was left under stirring for 24 h. Separately, a zinc chloride solution was prepared by mixing $ZnCl_2.2H_2O$ and NaOH (1:1 molar ratio) mixed with a solution H_2O:isopropanol (50:50 v/v) with stirring for 4 h. The Zn^{2+} precursor solution was slowly added to the saponite dispersion. The mixture was stirred for 24 h and the, it was filtered and washed. The solid was recovered and calcined at 500 °C for 4 h. The deposition of the nanoparticles was carried out by adding 0.5 g of ZnO-saponite in 5 mL of the Ag NPs solution (previously prepared) [10] and left stirring for 48 h. The material was recovered and dried at 50 °C for 24 h. The nanocomposite obtained was called Ag@ZnO-saponite.

2.3. Photocatalysis tests

Prior to the photodegradation experiments, a known amount of catalyst (0.5 g L^{-1}) and contaminant solution was placed in 100 mL of the desired concentration. The ciprofloxacin solution was left under dark conditions for adsorption on the solid surface until saturation (equilibrium). After reaching equilibrium (30 min) the lamp was turned on to irradiate the reaction system. To carry out the photocatalysis tests, a radiation chamber with a borosilicate reactor coupled to a thermostatic bath were used and 160 W Hg vapor lamp was used as a visible light source. Aliquots were taken at predefined times of 5, 10, 15, 30, 45, 60, 90 and 120 minutes, and the, was centrifuged and the supernatant was analyzed by UV-Vis spectrophotometer. The band at 272 nm was used to monitor the drug concentration.

3. Results and discussion

The X-ray diffraction patterns of pure saponite and nanocomposite samples are depicted in Figure 1. XRD profiles showed the (001), (110), (201) and (060) reticular planes of the saponite characteristic reflections. The presence of (060) reflection suggests obtaining a clay-like trioctahedral structure [11]. After incorporation of ZnO nanoparticles were observed (010), (002), (011), (012), (110), (013), (112) and (021) planes for zinc structure [12]. With the deposition of Ag NPs, no significant changes were observed in the crystal structure of the nanocomposite. These results indicate a good incorporation of nanoparticles onto clay mineral surface without destruction the matrix structure.

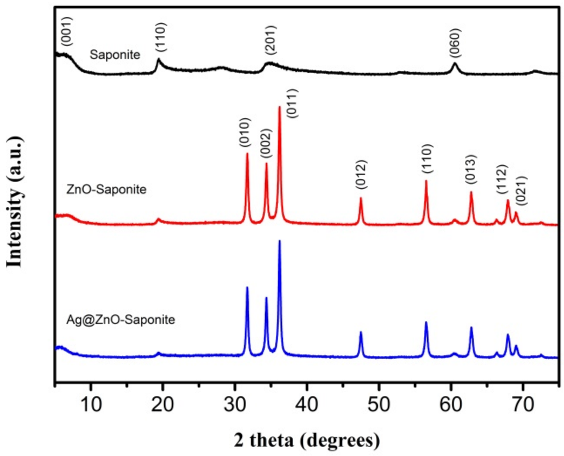


Figure 1. XRD patterns of saponite clay mineral, ZnO-saponite and Ag@ZnO-saponite nanocomposites.

The optical band gap of the nanocomposite was calculated using the Kubelka–Munk function and the Talc-plot was showed in Figure 2. ZnO has a known band gap energy (Eg) value of 3.37 eV [12]. The Ag@ZnO-saponite nanocomposite presents a major contribution at 3.15 eV and a minor contribution at 2.22 eV. The shift in the band gap value suggests the influence of ZnO confinement in the clay mineral matrix. Probably the optical gap at 3.15 corresponds to ZnO and the presence of Ag NPs corresponds to the optical gap at 2.22 eV. In this case, the photocatalyst absorbs light in the visible region by the presence of Ag components producing the electron/hole pairs induced by plasmon [4]. Electrons are excited from the valence band for the conduction band of the semiconductor. Photogenerated holes and electrons react with H_2O or OH^- ions and oxygen to produce oxidizing species that gradually break down organic pollutant molecule.

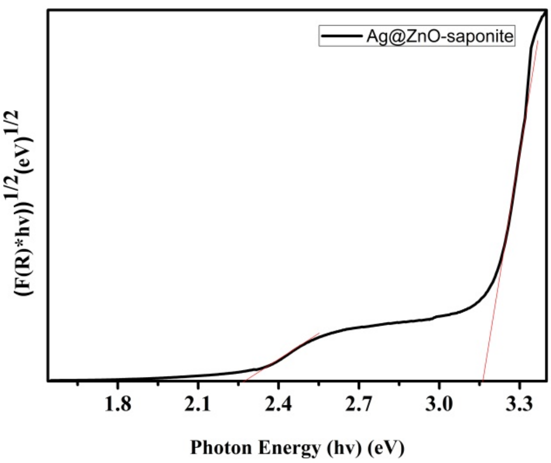
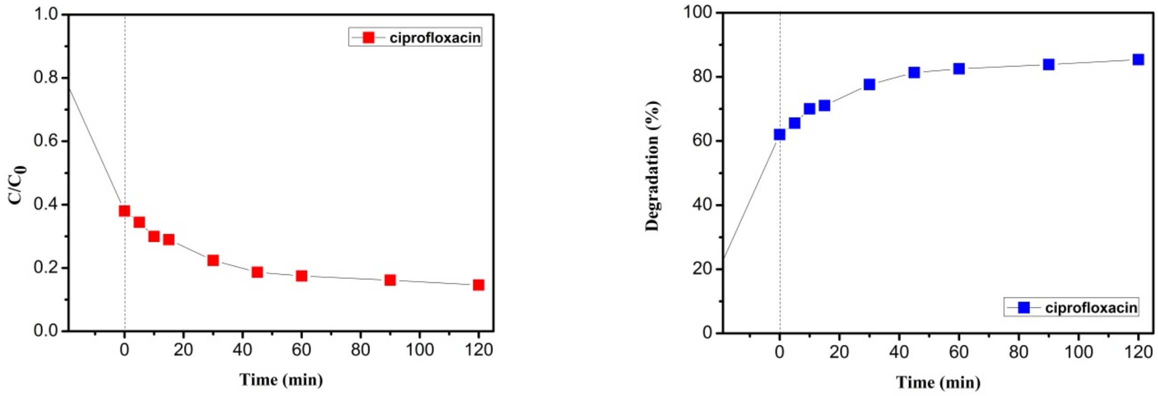


Figure 2. Band gap value (Eg) of Ag@ZnO-saponite determined according to the Kubelka–Munk method by using the Tauc equation.

The photocatalytic performance of the Ag@ZnO-saponite nanocomposite was evaluated for degradation of ciprofloxacin drug under visible light. C/C_0 ratio and degradation performance in function of irradiation time were showed in Figure 3. Photocatalytic efficiency of about 90% was archieved after 120 min of reaction, this result is similar to studies involving the photodegradation of ciprofloxacin using other catalysts [13,14]. The adsorption of ciprofloxacin on the surface of the support reached value close to 60% at saturation (30 min) and after irradiation it was observed that the drug degradation archieved a value of around 90%. In this study, the synergistic effect between adsorption and photocatalysis processes for degradation of ciprofloxacin can be suggested. The results demonstrated a high photocatalytic activity for the synthesized nanocomposite.



(**a**) (**b**)

Figure 3. C/C_0 ration as a function of irradiation time (**a**) and ciprofloxacin degradation from photocatalysis using Ag@ZnO-saponite nanocomposite under visible light.

3. Conclusions

The XRD results confirmed the successful incorporation of nanoparticles in the saponite structure. The optical gap of the Ag@ZnO-saponite nanocomposite was adequate for an efficient reaction under visible light. The photocatalytic experiments showed high performance of the material and the combination of adsorption and photocatalysis properties promoted notable removal of ciprofloxacin in aqueous solution. Therefore, the obtained nanocomposite can be a promising material for studies involving photochemical degradation of other organic pollutants.

Author Contributions: D.H.L.D.: methodology, investigation and writing—original draft preparation; V.H.M.: methodology and investigation; A.S.S.: investigation; L.M.C.H.: investigation; E.C.S.F.: writing—review and editing; P.T.: conceptualization and writing—review and editing; J.A.O.: supervision, project administration and writing—review and editing.

Funding: This research was funded by the CAPES and CNPq agencies, the authors are grateful for the financial support for the research.

Institutional Review Board Statement: Not applicable

Informed Consent Statement: Not applicable

Conflicts of Interest: The authors declare no conflict of interest

References

1. Taheran, M.; Naghdi, M.; Brar, S.K.; Verma, M.; Surampalli, R.Y. Emerging contaminants: Here today, there tomorrow! *Environ. Nanotechnology, Monit. Manag.* **2018**, *10*, 122–126.
2. Gupta, B.; Gupta, A.K.; Tiwary, C.S.; Ghosal, P.S. A multivariate modeling and experimental realization of photocatalytic system of engineered S–C_3N_4/ZnO hybrid for ciprofloxacin removal: Influencing factors and degradation pathways. *Environ. Res.* **2021**, *196*, 110390.
3. Araujo, F.P.; Trigueiro, P.; Honório, L.M.C.; Oliveira, D.M.; Almeida, L.C.; Garcia, R.P.; Lobo, A.O.; Cantanhêde, W.; Silva-Filho, E.C.; Osajima, J.A. Eco-friendly synthesis and photocatalytic application of flowers-like ZnO structures using

Arabic and Karaya Gums. *Int. J. Biol. Macromol.***2020**, *165*, 2813-2822.

4. Sohrabnezhad, S.; Seifi, A. The green synthesis of Ag/ZnO in montmorillonite with enhanced photocatalytic activity. *Appl. Surf. Sci.***2016**, *386*, 33–40.
5. Akkari, M.; Aranda, P.; Belver, C.; Bedia, J.; Ben Haj Amara, A.; Ruiz-Hitzky, E. ZnO/sepiolite heterostructured materials for solar photocatalytic degradation of pharmaceuticals in wastewater. *Appl. Clay Sci.***2018**, *156*, 104–109.
6. Osajima, J.A.; Sá, A.S.; Honorio, L.M.C.; Trigueiro, P.; Pinto, L.I.F.; Oliveira, J.A.; Furtini, M.B.; Bezerra, R.D.S.; Alcantara, A.C.S.; Silva-Filho, E.C. Au@Ag bimetallic nanoparticles deposited on palygorskite in the presence of TiO_2 for enhanced photodegradation activity through synergistic effect. *Environ. Sci. Pollut. Res.***2021**, *28*, 23995–24007.
7. Zyoud, A.; Jondi, W.; AlDaqqah, N.; Asaad, S.; Qamhieh, N.; Hajamohideen, A.R.; Helal, M.H.S.; Kwon, H.; Hilal, H.S. Self-sensitization of tetracycline degradation with simulated solar light catalyzed by ZnO@montmorillonite. *Solid State Sci.***2017**, *74*, 131–143.
8. Fatimah, I.; Wang, S.; Wulandari, D. ZnO/montmorillonite for photocatalytic and photochemical degradation of methylene blue. *Appl. Clay Sci.***2011**, *53*, 553–560.
9. Tangaraj, V.; Janot, J.; Jaber, M.; Bechelany, M.; Balme, S. Adsorption and photophysical properties of fluorescent dyes over montmorillonite and saponite modified by surfactant. *Chemosphere.***2017**, *184*, 1355-1361.
10. Oliveira, A.C. de J.; Araújo, A.R. de; Quelemes, P.V.; Nadvorny, D.; Soares-Sobrinho, J.L.; Leite, J.R.S. de A.; da Silva-Filho, E.C.; Silva, D.A. da Solvent-free production of phthalated cashew gum for green synthesis of antimicrobial silver nanoparticles. *Carbohydr. Polym.***2019**, *213*, 176–183.
11. Bisio, C.; Gatti, G.; Boccaleri, E.; Marchese, L.; Superti, G.B.; Pastore, H.O.; Thommes, M. Understanding physico-chemical properties of saponite synthetic clays. *Microporous Mesoporous Mater.***2008**, *107*, 90–101.
12. Araujo, F.P.; Trigueiro, P.; Honório, L.M.C.; Furtini, M.B.; Oliveira, D.M.; Almeida, L.C.; Garcia, R.R.P.; Viana, B.C.; Silva-Filho, E.C.; Osajima, J.A. A novel green approach based on ZnO nanoparticles and polysaccharides for photocatalytic performance. *Dalt. Trans.***2020**, *45*, 1–12.
13. Su, X.; Wu, D. Facile construction of the phase junction of BiOBr and $Bi_4O_5Br_2$ nanoplates for ciprofloxacin photodegradation. *Mater. Sci. Semicond. Process.***2018**, *80*, 123–130.
14. Li, Z.; Chen, M.; Hu, H.; Zhang, Q.; Tao, D. Mechanochemical synthesis of novel Pt modified ZnAl-LDH for effective ciprofloxacin photodegradation. *J. Solid State Chem.***2020**, *290*, 121594.