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Chemistry

Preparation of the highly efficient $CoFe_2O_4/TiO_2$ composite in the degradation of organic pollutant through photo-Fenton under visible and solar radiation

Preparação do compósito $CoFe_2O_4/TiO_2$ altamente eficiente na degradação de poluente orgânico através de foto-Fenton sob irradiação solar e visível

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ABSTRACT

Due to globalization and society growth, dyes began to be used daily in various industrial sectors These are often dumped directly into water bodies without any prior treatment. One solution for dye removal/degradation is through photo-Fenton, in which its technological advancement is linked to the development and improvement of catalysts. In this work, cobalt ferrite ($CoFe_2O_4$) was synthesized on titanium dioxide (TiO_2), and its catalytic activity was evaluated in the photo-Fenton reaction aiming at the decomposition of an organic pollutant in aqueous solution. Cobalt ferrite was synthesized with the support of the solvothermal route. The magnetic materials were characterized by X-ray diffraction (XRD) and nitrogen adsorption/desorption. Diffraction patterns indicated that cobalt ferrite was added to the titanium dioxide surface sparsely. Regarding the surface area, a value of 149.4 $m^2\ g^{-1}$ and a pore volume equivalent to 0.291 $cm^3\ g^{-1}$ were determined. The catalysts were evaluated in the degradation of amaranth dye under artificial visible light and solar irradiation. The produced $CoFe_2O_4/TiO_2$ composite showed satisfactory catalytic activity, being superior compared to pure cobalt ferrite. The catalytic activities for both materials were higher when using solar irradiation, reaching 89% ($CoFe_2O_4$) and 100% ($CoFe_2O_4/TiO_2$) of discoloration in 30 min of reaction, respectively. Therefore, the $CoFe_2O_4/TiO_2$ composite presents itself as a promising material for the degradation of organic pollutants in aqueous solutions through the heterogeneous photo-Fenton reaction, under solar irradiation.

Keywords: Catalyst development; Solvothermal route; Photocatalytic reaction

RESUMO

Devido à globalização e crescimento da sociedade, os corantes passaram a ser utilizados diariamente em diversos setores industriais. Estes sendo muitas vezes despejados diretamente em corpos hídricos sem nenhum tratamento prévio. Uma solução para remoção/degradação de corantes é através do foto-Fenton, na qual seu avanço tecnológico está ligado ao desenvolvimento e melhoria de catalisadores. Neste trabalho, ferrita de cobalto (CoFe2O4) foi sintetizada sobre dióxido de titânio (TiO2) e sua atividade catalítica foi avaliada na reação foto-Fenton visando a decomposição de um poluente orgânico em solução aquosa. Ferrita de cobalto foi sintetizada sobre o suporte pela rota solvotérmica. Os materiais magnéticos foram caracterizados por difração de raios-X (XRD) e adsorção/dessorção de nitrogênio. Os padrões de difração indicaram que a ferrita de cobalto foi adicionada a superfície do dióxido de titânio de maneira esparsa. Em relação a área superficial foi determinado um valor de 149.4 $m^2\,g^{-1}$ e um volume de poros equivalente a 0.291 $cm^3\,g^{-1}$. Os catalisadores foram avaliados na degradação de corante amaranto, sob luz visível artificial e irradiação solar. O compósito produzido $CoFe_2O_4/TiO_2$ apresentou satisfatória atividade catalítica, sendo superior comparado a ferrita de cobalto pura. As atividades catalíticas para ambos os materiais foram superiores, quando do uso de irradiação solar, atingindo 89% ($CoFe_2O_4$) e 100% ($CoFe_2O_4/TiO_2$) de descoloração em 30 min de reação, respectivamente. Portanto, o compósito $CoFe_2O_4/TiO_2$ apresenta-se como material promissor para a degradação de poluentes orgânicos em soluções aquosas por meio da reação foto-Fenton heterogênea, sob irradiação solar.

Palavras-chave: Desenvolvimento de catalisadores; Rota solvotérmica; Reação fotocatalítica

1 INTRODUCTION

The increase in industrial activity in recent times, associated with the growing scarcity of natural resources, has significantly increased environmental awareness and the search for sustainable development (J. Wang & Azam, 2024). Therefore, there is a need for actions that reduce the impact of anthropogenic activity on nature. Much of the problem comes from industrial processes that are aggressive to the environment, in which there is a high generation of liquid effluents, in addition to solid waste, which has a major impact on nature. The greatest difficulty in treating these effluents is due to the presence of high quantities of organic compounds with low biodegradability. The latter makes it difficult to remove and obtain satisfactory results for the treatment of these effluents, using traditional processes such as conventional biological and physical/chemical processes. In line with these facts, associated with the stricter requirements for effluent discharge standards, recent efforts have been sought by researchers in the environmental field for more efficient treatment methods (Eremeeva, Savoskina, Poddymkina, Abdulmazhidov, & Gamidov, 2023).

Advanced oxidative processes (AOPs) are currently known to be used efficiently in the degradation of organic pollutants (Dwyer & Lant, 2008; Oliveira, Halmenschlager, Jahn, & Foletto, 2019). These processes are based on the generation of hydroxyl radicals (HO●.), which are highly oxidizing substances that can quickly and non-selectively degrade numerous organic compounds (Rayaroth, Boczkaj, Aubry, Aravind, & Aravindakumar, 2023). Among the various existing AOP methodologies/routes, we can mention some that have been demonstrated to be highly efficient in the degradation of various organic pollutants, such as ozonation, heterogeneous photocatalysis, Fenton and photo-Fenton (homogeneous and heterogeneous) (Foletto et al., 2013; Oliveira, Mazutti, Urquieta-González, Foletto, & Jahn, 2016; Oturan & Aaron, 2014).

The Fenton and photo-Fenton processes are strong oxidation systems between POAs, being an efficient way to remove organic pollutants from wastewater (Dwyer & Lant, 2008; Oliveira et al., 2019). The most valuable feature of the Fenton process for environmental remediation is its general applicability regardless of the nature and functional groups present in organic pollutants, justifying its non-selectivity. The heterogeneous Fenton reaction with supported catalysts is one of the most well-regarded POAs, as it presents good efficiency, and operation advantages and facilitates the recovery and reuse of the catalyst after the treatment process (Munhoz, Zazycki, Silva, & Oliveira, 2023).

Iron-based materials, such as ferrites with a general formula of MFe_2O_4 (where M represents the cation of a metal), have been widely used as potential heterogeneous photo-Fenton catalysts, due to their high catalytic activity, stable crystalline structure, extremely high solubility, and, especially, magnetic property for the separation of the reaction system by a magnetic field (Dom, Subasri, Radha, & Borse, 2011; Du, Ma, Liu, Zou, & Ma, 2016; Tezuka, Kogure, & Shan, 2014). Due to their low band gap (around

2.0 eV), ferrites can absorb visible light, in addition to UV light, making them highly efficient in a broad spectrum of light (Casbeer, Sharma, & Li, 2012; Dom et al., 2011).

Several studies have demonstrated that the use of different supports to anchor and disperse an active phase promotes greater catalyst efficiency. Due to the higher surface area which leads to the increments of radicals generated (HO•), resulting in higher reaction rates (Gao, Wang, & Zhang, 2015; Yuan, Zhang, Guo, & Wan, 2016). Several metal oxides are reported as possible catalysts for AOPs aiming at the degradation of several polluting organic molecules, such as Al_2O_3 (Ernst, Lurot, & Schrotter, 2004), MnO_2 (Tong, Liu, Leng, & Zhang, 2003), SnO_2 (Zheng, Li, Dou, & Li, 2009), in addition to supported catalysts (Chen, Dai, Wang, & Chen, 2014; Pocostales, Álvarez, & Beltrán, 2011).

However, few studies report the use of cobalt ferrite ($CoFe_2O_4$) supported on semiconductor materials such as titanium dioxide (TiO_2) due to the photoactive phase called anatase to obtain a magnetic composite with application in systems of solar photo-Fenton (Kovačič, Likozar, & Huš, 2022). In this context, the main objective of this work was to prepare and characterize the magnetic composite of cobalt ferrite ($CoFe_2O_4$) supported on titanium dioxide (TiO_2), and to evaluate its catalytic activity in the degradation of organic pollutants through the heterogeneous photo-Fenton reaction under visible and sunlight.

2 MATERIALS AND METHODS

2.1 Catalyst development

For the synthesis of cobalt ferrite ($CoFe_2O_4$), the solvothermal route was used (de Oliveira et al., 2018). Cobalt chloride ($CoCl_2.6H_2O$, Sigma-Aldrich, 97%) and ferric chloride ($FeCl_3.6H_2O$, Nuclear, 97%) as the precursor, and ethylene glycol ($C_2H_4O_2$, Synth, 99%) was used as the solvent. The stoichiometric ratio of salts used was 1:2 = Co: Fe. Thus, 4 mmol of cobalt chloride and 8 mmol of ferric chloride were dissolved in 120 mL of ethylene glycol, under magnetic stirring (30 min and 350 rpm), followed by the addition of 60 mmol of sodium acetate ($NaC_2H_3O_2.3H_2O$, Synth, 98%), resulting in solution 1. The solution was transferred into Teflon cups coupled to stainless steel autoclaves and then subjected to a temperature of 200 ºC for a period of 10 hours. Afterward, it was washed and dried at 80 ºC for 12 h, the $CoFe_2O_4$ was used as a reference catalyst.

For the synthesis of TiO_2, the solvothermal methodology was also employed, detailed description can be found elsewhere (Police et al., 2014). In this case, ethylenediamine ($C_2H_8N_2$, Êxodo Cientifica, 99%) was used as a stabilizing agent, and isopropyl alcohol (C_3H_8O, Synth, 99.5%) as a solvent to dissolve titanium dioxide isopropoxide (IV) ($C_{12}H_{28}O_4Ti$, Sigma-Aldrich, 99%). The mixture was added to Teflon cups coupled to stainless steel autoclaves (TCSSA), after that, it was heated at the temperature of 200 ºC for 24 h. Then the material was washed, dried at 80 ºC, and calcined at 400 ºC for 2 h.

For the $CoFe_2O_4/TiO_2$ it was employed impregnation method (de Oliveira et al., 2018). Solid TiO_2 was added to solution 1, aiming to obtain 10 % W/W of the final catalyst. First, the suspension was ultrasonified for 30 min, to ensure that the solution was well mixed. Second, the mixture was added to TCSSA, where it was subjected to 200 ºC for 10 h. Last, the formed catalyst was washed and dried at 80 ºC for 12 hours.

2.2 Catalyst characterization

The materials formed were characterized by X-ray diffraction (XRD) and N_2 adsorption/desorption isotherms. A diffractometer (model Miniflex 300, brand: Rigaku) was used to obtain the XRD for the ferrite, titanium dioxide, and catalyst. The diffractometer is equipped with a Cu-Kα anode ($\lambda = 1.5418$ Å), an energy source with 30 kV and 10 mA. The resolution employed was 0.03° with an acquisition time of 0.9 s. The N_2 adsorption/desorption isotherms were obtained by employing a porosimeter (model: ASAP 2020, brand: Micrometrics). The samples were previously treated at 300 ºC under vacuum, with dimensionless pressure ranging from 0.05 to 1. The specific surface area, the pore volume, and the average pore diameters were determined through the application of the Brunauer, Emmet, Teller (BET) and the Barret, Joyner, and Halenda (BJH) methods.

2.3 Photocatalytic assays

The photocatalytic potential was evaluated by employing the Amaranth dye, (CAS n. 915-67-3, $C_{20}H_{11}N_2Na_3O_{10}S_3$, molecular mass: 604.47 $g.mol^{-1}$), which is widely used in pharmaceutical industries. For the photo-Fenton assays, a glass container of 250 mL, with a magnetic stirrer, was irradiated under artificial visible and solar light. For tests under visible light, a commercial fluorescent lamp (85 W, Empalux) was located 10 cm above the surface of the aqueous dye solution. For the experiments under sunlight, the solution was exposed outdoors on a cloudless day. The tests under solar irradiation were carried out between 1:30 pm and 2:30 pm on March 28, 2024, in Santa Maria, Brazil (29º 41’ 3.725” S and 53º 48’ 46.732” W). The average intensity of solar irradiation was 734.633 $kJ.m^{-2}$ (INMET, 2024).

The experiments were carried out using a ratio of 0.5 g of catalyst per liter of dye solution, while, for the test with the reference catalyst $CoFe_2O_4$, 0.05 g per liter of solution was used, as this quantity corresponds to the content of $CoFe_2O_4$ (10% by mass) contained in the $CoFe_2O_4/TiO_2$ composite. The dye concentration in the solution was 75 mg. L^{-1}. The solution was adjusted to pH = 3.0 with sulfuric acid diluted in distilled water (0.1 mol L^{-1}). Before starting the photo-Fenton reaction, the solution (100 mL) was stirred in the presence of the catalyst until adsorption equilibrium was reached for 60 min. Therefore, 8 mmol. L^{-1} of hydrogen peroxide (H_2O_2) was added to the solution, and it was exposed to irradiation (visible or solar), starting the photo-Fenton reaction. Samples were taken during the reaction using a syringe and centrifuged to separate the catalyst from the solution. The discoloration of the solution was determined by reading the color on a UV-vis spectrophotometer (Bel Photonics, SP1105), at the maximum absorbance wavelength of 525 nm. The discoloration kinetics of the solution were expressed by the ratio $C/C_0 = (A/A_0)$ as a function of time, where: A_0 and A are the absorbances of the initial dye solution and at reaction time t, respectively. The tests were carried out in triplicate and an experimental error of a maximum of 4% was observed for dye decolorization.

3 RESULTS AND DISCUSSION

3.1 Characterization results

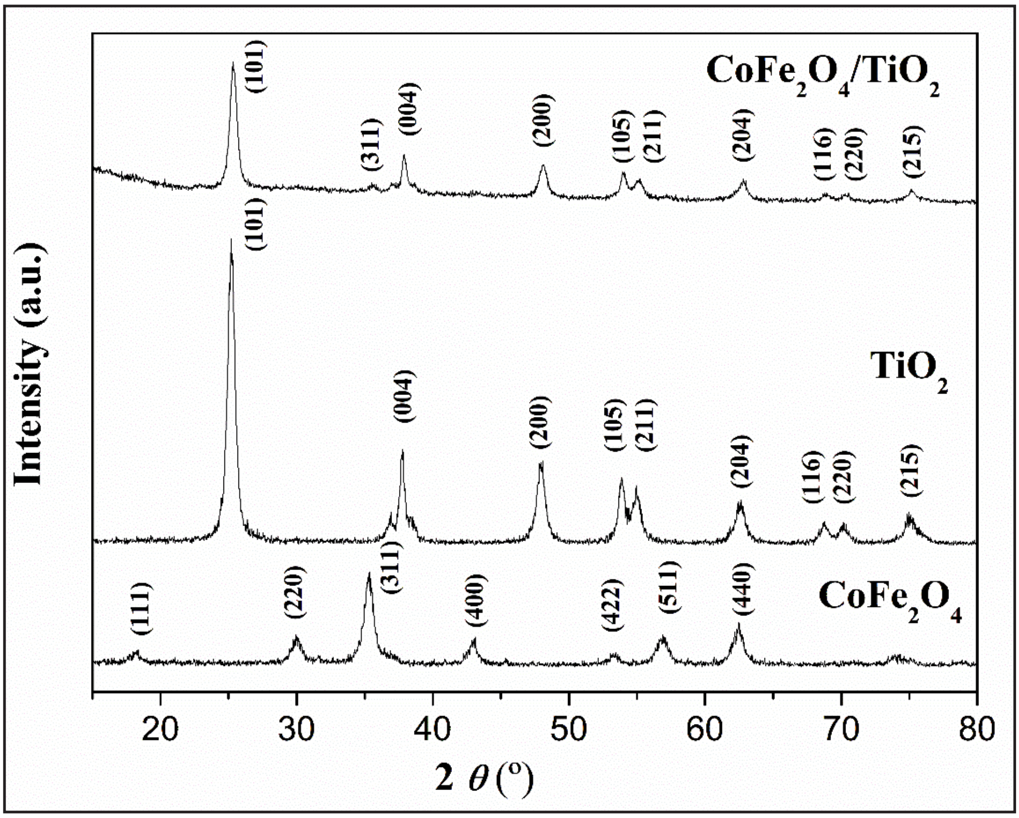
Figure 1 shows the X-ray diffractograms of $CoFe_2O_4$, pure TiO_2, and the $CoFe_2O_4/TiO_2$ composite. First, it was found that $CoFe_2O_4$ presented single phase, with diffraction peaks located at 18.29º; 30.08º; 35.44º; 37.06º; 43.06º; 53.45º; 56.97º and 62.59º. According to the JCPDS (number 22-1086), it was possible to correlate those 2θ values corresponds to the reflection planes of (111), (220), (311), (222), (400), (422), (511) and (440). For the catalyst ($CoFe_2O_4/TiO_2$) it was identified the diffraction peaks corresponding to 25.0°; 38.7°; 48.9°; 54.9°; 55°; 63.6°;69.8°;70.7°; 75.4°. From the JCPDS (number 89-4921), it was identified that the degrees correspond to reflection planes of (101), (004), (200), (105), (211), (204), (116), (220) and (215). In addition, it was found a low peak at 35.5°, which corresponds to the plane (311) of the $CoFe_2O_4$. This indicates that the $CoFe_2O_4$ has been dispersed at the surface of the TiO_2 (Costa, Vilar, Lira, Kiminami, & Gama, 2006; Police et al., 2014). From the Sherrer Equation, is possible to obtain the average crystallite size, according to the peak with the highest intensity.

$$\overline{D}_p = \frac{K\lambda}{\beta cos(\theta)} \tag{1}$$

Where K is the shape factor (0.94), λ is the X-ray wavelength (0.15418 nm), β is the full width at maximum wavelength (°), and θ is the Bragg angle.

According to Eq. (1) it was found that the D_p is equivalent to 12.15, 11.6, and 10.25 nm for the $CoFe_2O_4/TiO_2$, TiO_2, and $CoFe_2O_4$, respectively. This indicates that the addition of the ferrite onto the titanium dioxide tends to increase the D_p. Comparison with other works is difficult due to the different conditions and reactants employed. However, in this case, the synthesized catalyst, wherein the range of the $CoFe_2O_4/TiO_2$ obtained by Rodríguez-Rodríguez et al., (2017). In their work, the catalyst presented an average crystallite size of 15.6 nm which was obtained through microemulsions and different reactants.

Figure 1 – $CoFe_2O_4$, TiO_2, and $CoFe_2O_4/TiO_2$ diffractogram

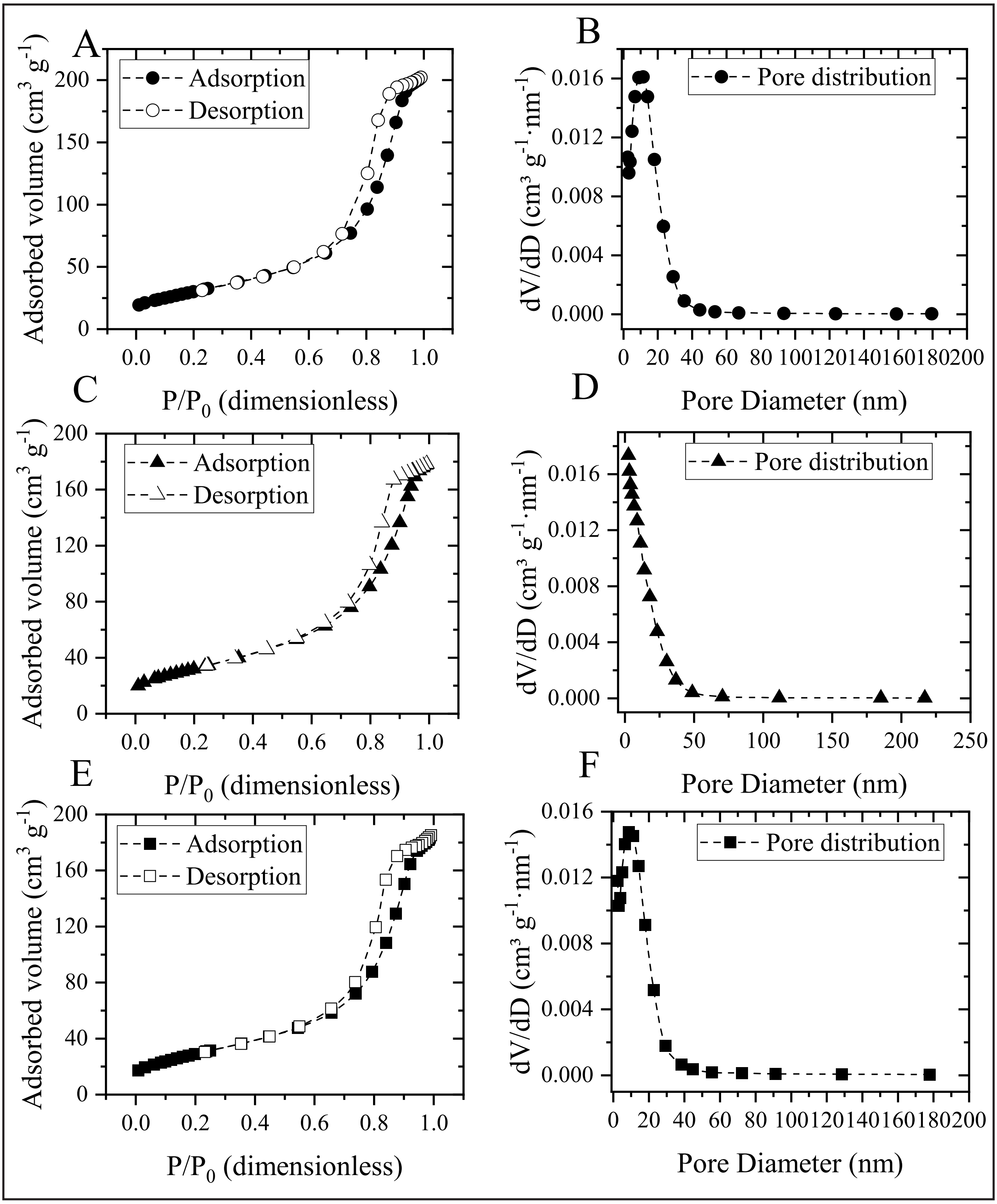


Source: Authors (2024)

The N_2 adsorption/desorption and the pore size distribution for the precursors and catalyst are given in Figure 2. According to the IUPAC classification, all isotherms can be classified as type IV, which corresponds to the mesoporous structure (Thommes et al., 2015). The hysteresis type corresponds to the H3, which is a narrow type with quick adsorption rate. This indicates that the pore shape is wedge-type, with openings at both sides, generally occurring in flaky-type particles (Chent et al., 2018). A similar isotherm was also reported by Rodríguez-Rodríguez et al., (2017) for the developed catalyst; however, the hysteresis is more compressed, indicating that their method fills the pores of the TiO_2 as well. Regarding the pore distribution, it was found that the catalyst ($CoFe_2O_4/TiO_2$) follows a similar distribution as titanium dioxide (TiO_2), being classified as mesoporous (2 nm <pore size <50 nm). In addition to that, these results are in agreement with the XRD results, which indicates that the $CoFe_2O_4$ was scattered at the surface since the pore distribution remained similar.

The estimated textural proprieties for the precursors and the catalyst are given in Table 1. Comparing the specific surface area of the titanium dioxide and the final catalyst, it is clear that the solvothermal method led to an increase in the specific surface area, from 109.8 to 149.3 $m^2\ g^{-1}$. On the other hand, the pore volume decreased with the addition of the $CoFe_2O_4$ from 0.315 to 0.291 $cm^3\ g^{-1}$ while the pore diameter increased from 8.63 to 9.57 nm. This may indicate that the $CoFe_2O_4$ is deposited at the edge of the TiO_2 pores without filling the pores of the support. Sun et al., (2020) have reported a specific surface area of 155.23 $m^2\ g^{-1}$ with a lower pore diameter of 3.15 nm and an average pore volume of 0.12 $m^3\ g^{-1}$, these values are directly related to the hydrolysis-hydrothermal method that the authors employed. The results reported by Rodríguez-Rodríguez et al., (2017) were 138.6 $m^2\ g^{-1}$, 9.58 nm; and 0.497 nm for the specific surface area, average pore, and pore volume. These reports indicate that the material developed in this work is in agreement, meaning that despite the method employed, similar textural proprieties are obtained.

Figure 2 – N_2 adsorption/desorption isotherms and pore size distribution for TiO_2 (A and B), $CoFe_2O_4$ (C and D), $CoFe_2O_4/TiO_4$ (E and F)



Source: Authors (2024)

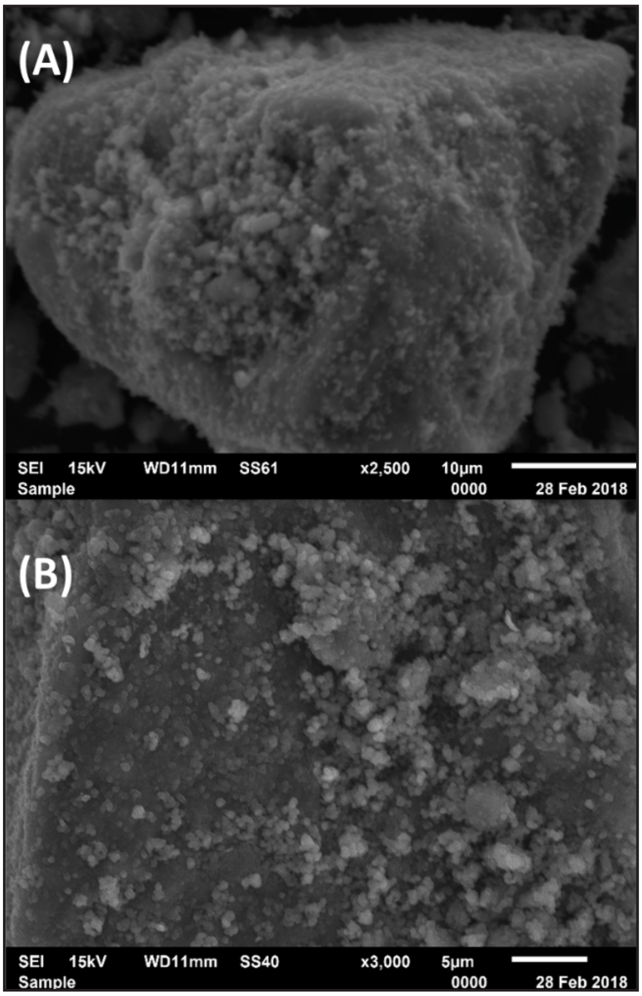
Table 1 – The table titles must be above it

Sample	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	D_p (mm)
TiO_2	109.8	0.315	8.636
$CoFe_2O_4$	116.0	0.282	8.889
$CoFe_2O_4/TiO_2$	149.4	0.291	9.574

Source: Authors (2024)

Figure 3 shows the SEM images of the $CoFe_2$O4/TiO_2 sample (2,500x Figure 3a), (3000x Figure 3b). The images show agglomerations of irregularly shaped particles with small spheres of $CoFe_2O_4$ highly dispersed on the surface of the TiO_2 support (De Oliveira et al., 2018).

Figure 3 – $CoFe_2O_4/TiO_2$ SEM images at magnifications 2.5 kx (A) and 3.0 kx (B)



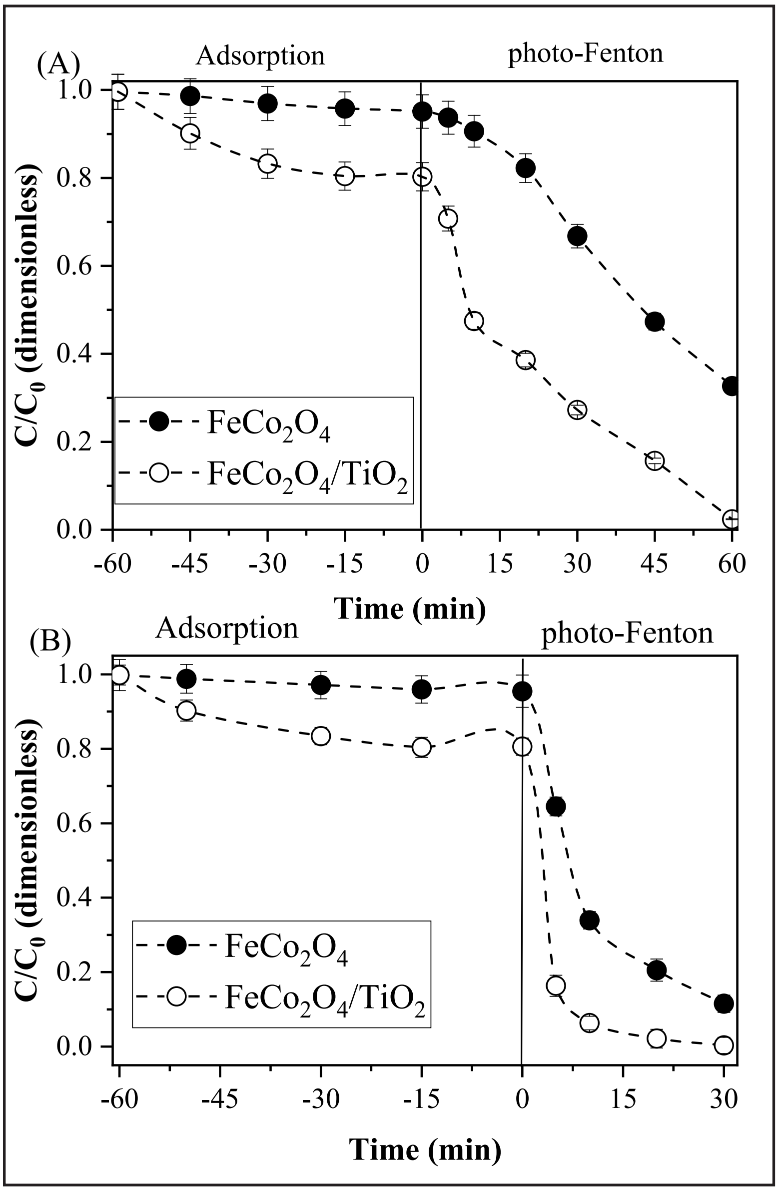
Source: Authors (2024)

3.2 Catalytic activity

Figure 4 presents the results of the decolorization efficiency for the amaranth dye solution, using $CoFe_2O_4$ and the $CoFe_2O_4/TiO_2$ composite, in the presence of visible artificial light and solar irradiation. It is worth noting that preliminary tests carried out under the Fenton condition (presence of catalyst and hydrogen peroxide and without irradiation) showed negligible decolorization efficiencies of the solution. Observing the efficiency of the catalysts, the $CoFe_2O_4/TiO_2$ composite showed significantly superior performance compared to pure ferrite ($CoFe_2O_4$), demonstrating that the use of supports is essential for obtaining greater discoloration of the solution. This result can be attributed to the large dispersion of ferrite over the surface of the support, consequently, leading to an increase in contact between the catalyst surface and polluting molecules, generating a rapid rate of degradation (Oliveira et al., 2019). The use of solar irradiation resulted in a surprising increase in catalytic activity compared to the configuration using visible light. The superiority of catalytic activity under sunlight may be related to the presence of around 5% irradiation in the ultraviolet wavelength (INMET, 2024).

It was found that $CoFe_2O_{4/}TiO_2$ has a high catalytic efficiency when compared to other catalysts mentioned in the literature for the degradation of the azo dye Amaranth (Oliveira et al., 2019, 2016; Omrani, Ahmadpour, Heravi, & Bastami, 2022; L. Wang et al., 2021). Besides that, Sun et al., (2020) employed the $CoFe_2O_4/TiO_2$ (1 g L^{-1}) on the degradation of Rhodamine B, achieving a 60% removal after 60 min. Santos et al., (2023) have employed the $CoFe_2O_4/TiO_2$ as a catalyst for the degradation of Erionyl Red A-3G, being 100% degradation at 60 min, at pH 2 and dosage of 1 g L^{-1}. $CoFe_2O_4$ were also employed in the catalytic degradation of acid blue 113, reaching around 85% of removal after 30 min, at pH 5 (Krishna et al., 2020). Overall, it is possible to confirm that the $CoFe_2O_4/TiO_2$ can be employed in the degradation of different dyes.

Figure 4 – Decolorization efficiency of the amaranth solution under visible (A) and solar light (B)



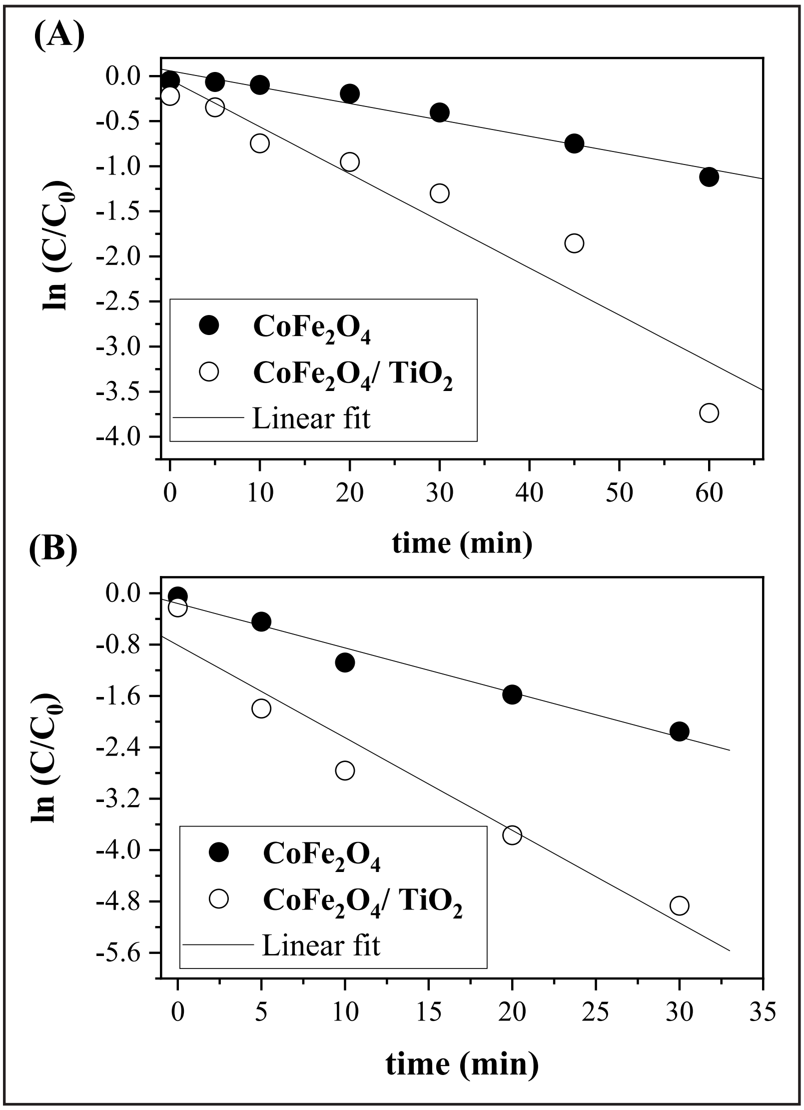
Source: Authors (2024)

The dye decolorization rate constants (K_d, min^{-1}) for the different catalysts were obtained through the slope of the straight line (Figure 4 a and b), according to Eq. (2), which followed the pseudo-first order kinetic model.

$$\ln\left(\frac{C}{C_0}\right)=K_d t \qquad (2)$$

Where: C is the concentration at any time (mg L^{-1}), C_0 is the initial concentration (mg L^{-1}), K_d is the rate of reaction constant (min^{-1}), t is the time (min).

Figure 4 – Fitted first order model onto the experimental data: visible light (A), and solar light (B)



Source: Authors (2024)

According to the results of the discoloration rate constants shown in Table 2, the highest values occurred for the composite ($CoFe_2O_4/TiO_2$), being almost three times faster compared to pure cobalt ferrite ($CoFe_2O_4$) in visible light and a little more than twice as fast when exposed to solar irradiation.

Table 2 – Rate constants for the decolorization of amaranth dye under visible light and solar irradiation

Catalyst	**Visible light**		**Solar irradiation**	
	K_d (m^2 g^{-1}) x10^3	**R^2**	**Kd (m^2 g^{-1}) x10^3**	**R^2**
CoFe2O4	18.15	0.98	0.282	0.8889
CoFe2O4/TiO2	52.22	0.95	0.291	0.9574

Source: Authors (2024)

4 CONCLUSION

The preparation of cobalt ferrite supported on titanium dioxide was successfully carried out, providing the magnetic catalytic composite $CoFe_2O_4$/TiO2. The system presented textural properties of S_{BET} of 149.4 m^2 g^{-1}, Vp of 0.291 cm^3 g^{-1}, Dp of 9.574 nm and structural (cubic phase of spinel and anatase) that culminated in relevant results for the effective degradation of the amaranth dye (52.22 x 10^{-3} min in visible light and 144.20 x 10^{-3} min in solar irradiation) in the photo-Fenton reaction. The results showed that the $CoFe_2O_4/TiO_2$ composite was considerably more efficient when compared to pure cobalt ferrite. Regarding the source of irradiation, solar proved to be much more effective. Therefore, the CoFe2O4/TiO2 magnetic composite presents attractive characteristics with high potential for application in the solar photo-Fenton process for treating liquid effluents containing the organic pollutant amaranth.

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