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Synthesis, characterization and application of Clinoptilolite-based catalysts for the degradation of Reactive Blue dye via photo-Fenton process

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INTRODUCTION

Water is the most important natural resource for society, being essential to meet the basic and industrial needs of the population. However, the pollution of water bodies by the enormous amount of chemicals released each year into rivers, lakes, and oceans poses a serious risk to this valuable resource, with the primary cause of this being the inadequate disposal of wastewater from industrial processes (Adam et al., 2022). As a result, there is a continuous effort by the scientific community, especially in the area of engineering, to propose ways to treat such pollutants in an attempt to curb the growing contamination of water bodies.

Pollution by heavy metals, pesticides or urban waste are the most commented sources of water contamination, but one that is often unnoticed by the eyes of others is the improper disposal of industrial effluents. In this scenario, the waste from the textile industry stands out, which is characterized by the presence of dyes. The presence of these in water bodies is worrisome, as they compromise water quality due to visual pollution due to the presence of color, interfering with the photosynthesis process of plants and algae, which leads to considerable damage to the aquatic ecosystem (Macedo, Lima & Silva, 2020; Romualdo et al., 2019). In addition, dyes correspond to a series of aromatic compounds, many of which are strongly reactive, which have mutagenic and carcinogenic behavior, causing serious health problems (Romualdo et al., 2019).

Such contaminants make up the class of emerging pollutants, whose degradation by usual methods is highly difficult due to their structural complexity. As a result, in the case of dyes, techniques such as ultrafiltration and waste adsorption membranes are chosen, but they are only efficient in separating them from the water and not removing them definitively (Torres & Carvalho, 2019; Silva, Martins & Sena et. al., 2018). For this reason, in recent years, as presented by Guaratini and Zanoni (2000), the development of technologies capable of degrading them by photochemical, electrochemical or biological processes has gained prominence.

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In this context, the use of advanced oxidative processes (AOPs) is pointed out as a solution for the contamination of water bodies by the presence of dyes from textile effluents. Based on this, it is clear that for the Reactive Blue dye, one of the most used in the textile industry, a class of POA's that has been showing satisfactory degradation results is photocatalysis, especially the photo-Fenton process (Santana, Nascimento & Napoleão et. al., 2017; Araújo, 2002).

The photocatalytic process is characterized by the release of highly reactive radicals, namely hydroxy radicals (OH), through the use, for example, of a semiconductor metal oxide acting as a catalyst by the action of light. The most used compound in this application is titanium dioxide (TiO2), however, according to Daghrir (2013), it has some disadvantages, such as the rapid recombination of electron/gap pairs, reducing the efficiency of the process, and also the high energy of *Band Gap*, restricting its application to the use of highly powerful light sources in the UV range and, consequently, artificial.

An alternative is the use of natural zeolites, such as Clinoptilolite. As described by Jewur (1985), in terms of heterogeneous catalysis, zeolites occupy a prominent place due to the fact that they promote selective chemical reactions in relation to molecular size in their uniform pores and well-defined channels, even presenting the capacity for ion exchange due to the crystalline structure formed by tetrahedra of AlO4 and SiO4, which makes practical and cost-effective modification possible.

OBJECTIVE

Synthesize Clinoptilolite-based catalysts impregnated with different iron mass fractions (2.5 and 5% w/w), characterizing them by microwave-assisted acid digestion techniques followed by atomic absorption spectrophotometry (AAS), X-ray diffraction (XRD), Mössbauer spectroscopy and photoacoustic spectroscopy (PAS), and perform a photocatalytic evaluation of their use for the degradation of the *Reactive Blue dye* via the photo-Fenton process.

METHODOLOGY

Two catalysts were prepared, all based on Clinoptilolite and impregnated with iron for the photo-Fenton process at different mass contents: 2.5 and 5% w/w, which were identified as shown in Table 1.

Table 1. Description of the catalytic converters.

IDENTIFICATION	COMPOSITION
2.5Fe-Clp	2.5% (w/w) of iron and clinoptilolite (Clp).
5Fe-CLP	5% (w/w) of iron and clinoptilolite (Clp).

Source: Prepared by the authors.

The following materials were used for the preparation: natural zeolite of the Clipnotilolite type (CELTABRASIL), ferric chloride P.A hexahydrate and deionized water. The synthesis route used is known as wet ion exchange (Sousa, 2007), which consisted of the addition of 10g of Clinoptilolite in FeCl3.6H2O solutions with the necessary mass for the contents of 2.5 and 5% w/w in magnetic stirring for 2 days. After that, it was followed by vacuum filtration in a common paper filter and drying in an oven at 60°C for 60min.

The catalysts were characterized by the following techniques: microwave-assisted acid digestion followed by atomic absorption spectrophotometry (AAS), X-ray diffraction (XRD), Mössbauer spectroscopy and photoacoustic spectroscopy (PAS). The first three were carried out to investigate the composition and structure, and the last to determine the Band *Gap* energy, thus allowing a greater understanding of the photo-Fenton process, which allowed the continuation of the work.

For the photocatalytic evaluation, 15 reactive tests were performed in duplicate following a Box-Behnken experimental design explained in Table 2 with three factors (pH, catalyst concentration and reaction time), whose levels were taken from the literature (Anchieta et al., 2016), with the dependent variable being the mean percentage yield (R) of the photo-Fenton process, given by Eq. (1). Each test consisted of shaking for two hours in the dark of 40mL of a 20ppm solution of *Reactive Blue* at the pH and with the concentration of catalyst specified for the adsorption step, followed by the addition of 2mL of hydrogen peroxide so that the lamp was lit, remaining on for the time also specified in the study with the system still in agitation.

Table 2. Experimental Planning.

REACTION TEST	pH	CONCENTRATION (mg/mL)	TIME (min)
1	2,0	100,0	60,0
2	4,0	100,0	60,0
3	2,0	400,0	60,0
4	4,0	400,0	60,0
5	2,0	250,0	30,0
6	4,0	250,0	30,0
7	2,0	250,0	90,0
8	3,0	250,0	90,0
9	3,0	100,0	30,0
10	3,0	400,0	30,0
11	3,0	100,0	90,0

12	3,0	400,0	90,0
13	3,0	250,0	60,0
14	3,0	250,0	60,0
15	3,0	250,0	60,0

Source: Prepared by the authors.

$$(1) R(\%) = \frac{(A_0 - A_t)}{A_0} . 100$$

Where A0 is the absorbance of the 20ppm dye solution, and Na is the absorbance after the reaction test, which is acquired after filtration by absorption spectroscopy in the UV-VIS region.

From the results obtained by the reactional tests, a mapping was carried out for the yield of the photo-Fenton process, with the highest values reproduced for the construction of kinetic curves, which were used to assess the photocatalytic study presented.

DEVELOPMENT

The execution of the present work was divided into two parts, the first being aimed at validating the use of catalysts prepared by means of characterization techniques to investigate the presence of Fe3+ ions and determine the Band Gap energy, because as illustrated in the Eq. (2) and Eq. (3), in which it refers to the energy provided by the light source used, which were presented by Souza, Figueira, Carvalho et al. (2021), such factors are essential to ensure the functioning of the photo-Fenton process, and the second part corresponded to the photocatalytic evaluation for the degradation of the Reactive Blue dye $h\upsilon$ following the Box-Behnken experimental design.

$$Fe^{3+} + H_2O + h\upsilon \rightarrow Fe^{2+} + \dot{O}H + H^- \quad (2)$$

$$H_2O_2 + h\upsilon \rightarrow 2\dot{O}H \quad (3)$$

DETERMINATION OF THE PRESENCE OF Fe3+

The presence of the trivalent form of iron ions is necessary for their reduction to the bivalent form to occur, so it was necessary to investigate the structure of the synthesized catalysts. For this, three characterization techniques were performed: Microwave-assisted acid digestion followed by atomic absorption spectrophotometry (AAS), X-ray diffraction (XRD) and Mössbauer spectroscopy.

Microwave-assisted Acid Digestion was performed for the two catalysts and also for Clinoptilolite (Clp) not modified for comparative purposes, and the methodology was adapted from a manual provided by the company Provecto Analítica. After execution, the samples were subjected to atomic absorption

spectrometry (AAS) analysis, providing a compositional analysis of which elements were present. From the results presented in Table 3, it is possible to affirm that in all catalysts there was iron impregnation, and that the values are not the same as those expected by the process of formation and mining of the natural zeolite.

Table 3. Reaction system.

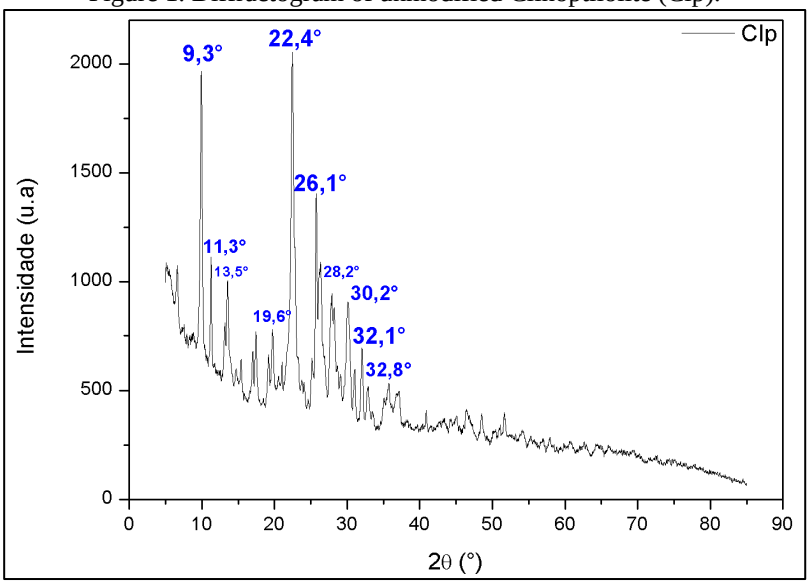
IDENTIFICATION	EXPECTED VALUE (ppm Fe)	READING IN AAS (ppm Fe)
Clp	-	64,39
2.5Fe-Clp	17,46	30,45
5Fe-CLP	34,92	56,68

Source: Prepared by the authors.

To complement this statement, the X-ray Diffraction (XRD) technique was used, mainly to provide a preliminary analysis of the structure acquired by the catalysts in comparison to Clinoptilolite and the occurrence of ion exchange.

According to Moradi, Karimzadeh and Moosavi (2018), the diffraction peaks characteristic of Clinoptilolite occur at 2θ = 9.8°, 12.2°, 13.3°, 17.3°, 19.1°, 22.7°, 26.1°, 28.2°, 28.5°, 30.2°, 31.9°, 32.8° (JCPDS File Card N. 25-1349), and, as illustrated in Figure 1, it can be seen that for natural zeolite (Clp) there was the presence of peaks at the following angles: 9.3°, 11.3°, 13.5°, 19.6°, 22.4°, 26.1°, 28.2°, 30.2°, 32.1° and 32.8°. Such values are close to and in many cases even equal to those present in the literature.

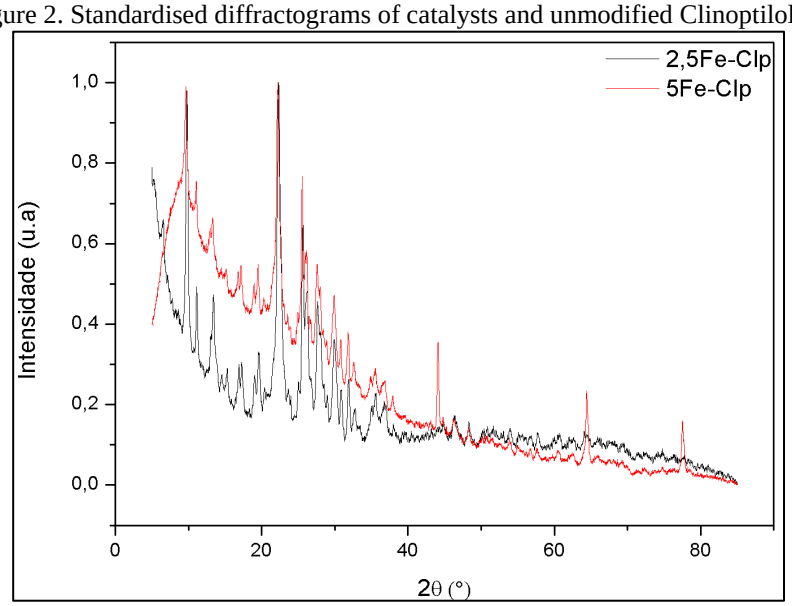
Figure 1. Diffractogram of unmodified Clinoptilolite (Clp).



Source: Prepared by the authors.

By comparing with the diffractograms of the catalysts, Figure 2, it is possible to perceive the absence, displacement or variation in the intensity of characteristic peaks, that is, there were changes in the crystal structure, being an initial indication of the occurrence of ion exchange.

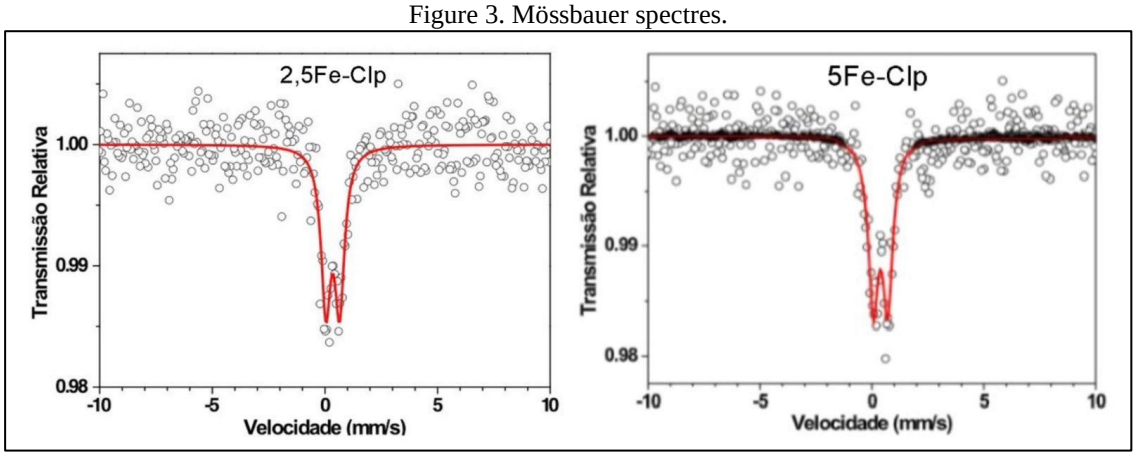
Figure 2. Standardised diffractograms of catalysts and unmodified Clinoptilolite.



Source: Prepared by the authors.

So, with the confirmation that the iron was impregnated, that is, the synthesis route used was efficient, it is necessary to evaluate in which ionic form it was able to stabilize. For this, the technique of Mössbauer spectroscopy was performed. As reported by Blanco and Andrés (2016), isomeric displacement (IS) values lower than 0.8mm/s indicate the stabilization of Fe3+, and with this characterization, values of 0.41 and 0.39mm/s were obtained for 2.5Fe-Clp and 5Fe-Clp, respectively. This can be observed in a preliminary way by the presence of a simple peak, and not a doublet, as described in Figure 3.

Figure 3. Mössbauer spectres.

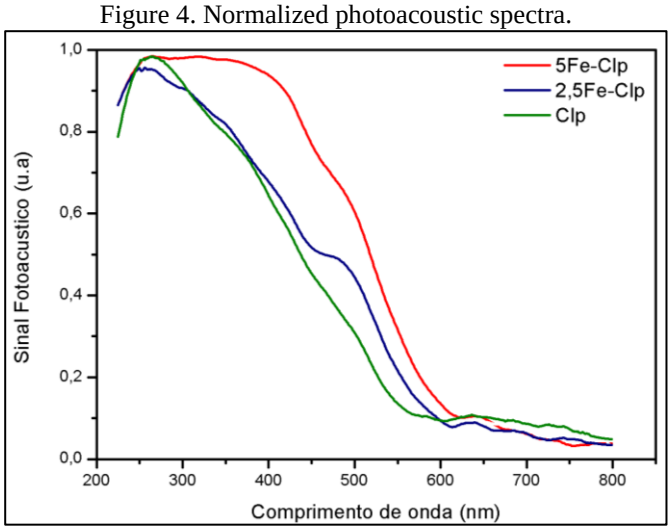


Source: Prepared by the authors.

DETERMINATION OF BAND GAP ENERGY

Photoacoustic Spectroscopy (PAS) was performed to determine the *Band Gap* energy of the catalysts in order to assist in the choice of the lamp for the photocatalytic process. The spectrum of the catalysts and natural Clinoptilolite are shown in Figure 4, and from them, it is possible to obtain the value of the *Band Gap* by the linear method reported by Frederichi (2019), whose values are shown in Table 4. With this, it can be seen that the catalysts have an optical transition range between 400 and 700nm, encompassing the visible spectrum and also that a higher iron mass content implies a lower value for the *Band Gap*. From this, the choice of lamp was limited to those that best fit this range, distancing itself from the conventional choices of UV-type lamps, and, for this reason and also for factors such as availability and cost, it was decided to use the 35W Xenon lamp.

Figure 4. Normalized photoacoustic spectra.



Source: Prepared by the authors.

Table 4. Band *Gap energy* by the linear method.

IDENTIFICATION	BAND GAP ENERGY (eV)
Clp	2,64
2.5Fe-Clp	2,38
5Fe-Clp	2

Source: Prepared by the authors.

PHOTOCALYTIC EVALUATION

The percentage yields obtained for each catalyst are shown in Table 5, and the conditions of each reaction test are described in Table 2. Thus, it is possible to state that both presented a better performance under conditions in which the pH of the solution containing the dye was more acidic and for longer reaction times, while in relation to the catalyst concentration for the one impregnated with 5% iron (5Fe-Clp) low concentrations presented good performances and for the one with 2.5% (2.5Fe-Clp), high

concentrations. This means that for a higher mass content of iron present in the catalyst, a lower amount of it is needed to ensure good degradation performance.

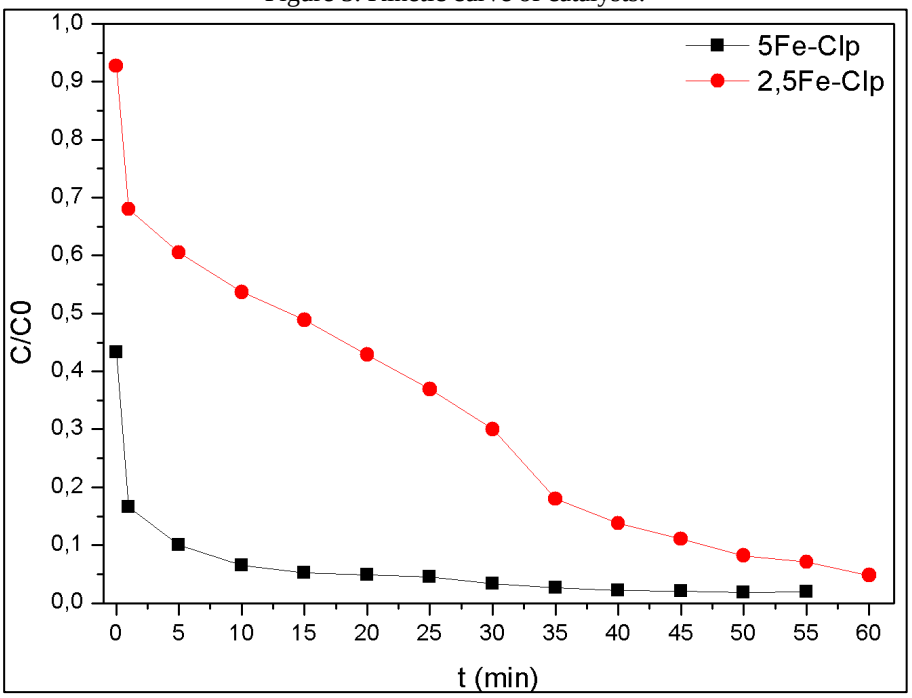
Table 5. Percentage returns obtained.

REACTION TEST	R2,5Fe-Clp (%)	R5Fe-Clp (%)
1	93,65	96,88
2	40,48	33,81
3	98,68	85,51
4	43,65	76,70
5	96,56	92,33
6	41,80	57,39
7	97,09	96,31
8	31,22	52,84
9	51,59	92,05
10	53,17	92,61
11	43,65	95,45
12	56,08	92,33
13	42,06	92,33
14	46,56	95,17
15	47,09	94,89

Source: Prepared by the authors.

From the Box-Behnken experimental design, a mapping for the yield of the photo-Fenton reaction was carried out, finding that for 2.5Fe-Clp the conditions with the highest yield were those of test 3, while for 5Fe-Clp they were those of test 1. Thus, the kinetic curves present in Figure 5 were constructed, illustrating the evolution of this process with the time in which the lamp was lit.

Figure 5. Kinetic curve of catalysts.



Source: Prepared by the authors.

It is possible to observe that both catalysts presented satisfactory results, with degradation rates equal to 95.21% for 2.5Fe-Clp and 98.06% for 5Fe-Clp in relation to the original concentration of the dye in solution. It is also worth noting that the difference between the initial points is due to the period of agitation for two hours in the dark, that is, before the beginning of the photo-Fenton reaction, this indicates that the catalyst 5Fe-Clp was able to remove more of the contaminant from the solution when compared to the other, this removal being due to the adsorption on the surface of the catalyst.

FINAL CONSIDERATIONS

It was proven that the synthesis route used was an economical, simple and efficient alternative for the impregnation of Fe3+ in Clinoptilolite and that the photo-Fenton process can be performed with lamps outside the UV range, bringing it closer to possible applications in natural light. In addition, with the factorial study carried out by the Box-Behnken planning, it was possible to map the best conditions of pH, catalyst concentration and reaction time necessary to ensure high degradation rates, optimizing the process, as illustrated by the kinetic curves constructed. Thus, the two catalysts represent a promising alternative for the degradation of the Reactive Blue dye, being a contribution to the fight against the pollution of water bodies by textile effluents.

As a suggestion for future work, it is valid to analyze the applicability of Clinoptilolite-based catalysts in processes powered by sunlight, due to the low Band Gap energy obtained by the impregnation of metals. In addition, it is also interesting to investigate the combination of iron with other compounds that have catalytic properties, such as ZnO and TiO2.

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