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Regeneration and reuse of magnetic particles for contaminant degradation in water

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ABSTRACT

Fenton reaction is an oxidation process of interest in wastewater treatment because of its ability to degrade organic compounds. Iron-based magnetic particles can be a very useful catalyst when using heterogeneous Fenton process. The major problem of this heterogeneous process is the saturation of the Fe^{3+} on the surface, which limits the process. In this study, the possibility of using magnetite particles as a substrate is presented, increasing its degradation efficiency by Fenton reaction through a regeneration process that achieves the electronic reduction of its surface using reducing agents. The results indicate that the regeneration process is quite effective, increasing the efficiency of the degradation of Methylene Blue up to 99%. The concentration of magnetite is the most influential factor in the efficiency of the reaction, while the regeneration time and the concentration of reducing agent do not significantly affect the results considering the range used. The presence of mechanical stirring may adversely affect the reaction in the long term. Increasing the oxidant agent concentration reduces the initial speed of the reaction but not the long-term efficiency. The use of hydrazine in this process allows the successive reuse of these particles maintaining a high percentage of elimination of methylene blue, above 70% even after 10 uses, compared to an elimination below 20% for particles not regenerated after the second use and for particles regenerated with ascorbic acid after the eighth use.

1. Introduction

Wastewater treatment is a problem that still requires attention (Castelo-Grande et al., 2010). The increasing presence of organic compounds and other emerging contaminants (Gogoi et al., 2018), including pharmaceuticals, which are not easily removed in traditional water treatment plants due to their complexity, make it necessary to search for new processes and materials capable of removing these compounds (Arzate et al., 2020).

One of the materials with greater potential are iron-based magnetic particles, their application in other fields is being investigated (Alvaro et al., 2007; Augusto et al. 2004, 2005, 2017, 2019, 2020a; Chen et al., 2020; Gao et al., 2020; Shi et al., 2020; Wu et al., 2020), and they have several advantages. Their main advantage is the magnetic character that allows them to be oriented/manipulated without direct contact; in addition they also present a low cost of production and easiness of modification for different purposes (Augusto et al. 2002, 2007a, 2007b, 2007c, 2007d, 2020a; Li et al., 2006; Rowntree et al., 2017). The use of iron-based magnetic particles for the elimination of pollutants through physical processes such as adsorption is being more intensively investigated in the last decade (Ali et al., 2019; Almomani et al., 2020; Augusto et al. 2019, 2020a, 2020b; Cardona et al., 2019; Cunha et al., 2020; Debs et al., 2019; Estevez et al., 2008; Gupta et al., 2009; Yang et al., 2020), and its application as advanced oxidation in chemical processes for decontamination has being increasingly studied in the last years.

Advanced oxidation processes are generally based on the generation of oxidizing radicals, such as the hydroxyl radical or the persulfate radical, which are very effective for the complete degradation of organic compounds (Pignatello et al., 2006; Wacławek et al., 2017; Wang and Xu 2012). The Fenton reaction is one of such processes, and one of the mostly used (Augusto et al., 2020a; Koppenol 1994).

The Fenton process generates radicals from the reaction of ionic iron with hydrogen peroxide (Koppenol 1994):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + OH^- \tag{1}$$

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$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot + H^+ \quad (2)$$

$$2\,H_2O_2 \rightarrow HO\cdot + HOO\cdot + H_2O \quad (3)$$

The homogeneous Fenton process uses iron ions in solution to produce the reaction (Ma et al., 2020; Van et al., 2020), although alternatives are possible (Pignatello et al., 2006). This process has the disadvantage that an iron containing residue is generated. Heterogeneous processes use solid catalysts (Van et al., 2020; Zárate-Guzmán et al., 2016) and are cleaner processes. The main disadvantage of the heterogeneous process is that the surface iron starts losing its electrons, converting to the 3+ valence, what leads to a point where all the surface iron has been converted into Fe^{3+}, and the Fenton reaction stops (Avetta et al., 2015). Two methods have been developed to try to solve this problem: the photo-Fenton method, which uses light to produce radicals and regenerate the surface iron (Poblete and Pérez 2020; Sharmila et al., 2019) and the electro-Fenton method, which uses electrical currents for this purpose (Anotai et al., 2006; Gholizadeh et al., 2020). However, these two methods highly increase the degree of technological complexity.

In this work we seek to use magnetite particles in a heterogeneous process. The application of magnetic particles in heterogeneous Fenton processes is an important issue in the scientific community today (Augusto et al. 2020a, 2020b; Bhaskar et al., 2019; Costa et al., 2006). In our study, we use particles obtained directly by crushing natural magnetite mixed with others obtained by coprecipitation, and we innovate by using a simple but effective activation process to activate and regenerate the particles, so that they are effective in successive applications. This eliminates the problem of electronic exhaustion of the magnetic particles (which would make the Fenton reaction to stop at a certain point) and also achieves a continuous reuse of the particles. As contaminant, we have used methylene blue.

2. Materials and methods

2.1. Reagents

In our study we used: Hydrogen peroxide (H_2O_2 30% w/v) from PanReac, pure L (+) ascorbic acid, pharmaceutical grade from PanReac, hydrazine (N_2H_4 anhydrous, 98%) from Sigma-Aldrich. Methylene blue hydrate (>97%) from Panreac, 25–63 μm particles of magnetite obtained by crushing natural magnetite and by chemical coprecipitation (Augusto et al., 2019) and Nitrogen gas (99%) from Air Liquide. All solutions are made with distilled water.

2.2. General experimental methodology

2.2.1. Methylene blue degradation

In the tests for Fenton Degradation, the particles are first washed (through a magnetic sedimentation process (Augusto et al., 2019)) before being introduced in a beaker with a methylene blue and hydrogen peroxide solution of a predetermined concentration. The solution is stirred with a mechanical overhead stirrer during all, or part, of the test. A sample for analysis is taken at certain intervals and returned to the solution afterwards. In the majority of the cases, particles were first regenerated in order to present reduced iron at its surface.

2.2.2. Regeneration of particles

For the regeneration of particles, the non-regenerated/exhausted magnetic particles are washed before being introduced into a spherical reactor with three outlets containing a solution of the regenerating reagent, with a predetermined concentration and for a predefined period of time. Nitrogen gas is added to provide an inert atmosphere during regeneration. After the regeneration, the particles are washed again - being the supernatant discarded.

a) Using Ascorbic acid:

Ascorbic acid (also known as vitamin C) is a potent non-toxic reducing agent. In this test we used ascorbic acid to reduce Fe^{3+} ions from the surface of the particles to Fe^{2+}, as described. In this case we regenerated 3g/l of magnetite particles with 5g/l of an ascorbic acid solution for 2 hours.

b) Using Hydrazine:

Hydrazine is another powerful reducing agent, and could be used as an alternative to ascorbic acid. In this test the same regeneration process was used as with ascorbic acid, regenerating 3g/l of particles in a solution of 1.58 M of hydrazine, for 10 minutes. These 3g/l of particles were used to compare the elimination in two solutions, one without peroxide and the other with 0.18 M of peroxide.

2.2.3. Adsorption of methylene blue

For the adsorption tests, the particles are first washed. Then they are inserted in a beaker with a solution containing a predetermined methylene blue concentration, which is stirred mechanically during all, or part, of the test. A sample for analysis is taken at certain intervals and returned to the solution afterwards.

2.2.4. Determination of methylene blue concentration

To determine the methylene blue concentrations in the initial, final and intermediate samples, the absorbance of the samples is analyzed with a spectrophotometer. The absorption peak of dissolved methylene blue is around 660 nm (Cenens and Schoonheydt 1988). We have used relative absorbance in the resulting graphics and thus divided the values obtained in this method by the initial (and highest) value.

2.2.5. Reuse of particles

In the experiments concerning the reuse of particles, the particles after each degradation step were regenerated and then inserted in a fresh Methylene Blue solution for another degradation step. The resulting treated water was analyzed at the end of each step. No stirring was applied during these experiments.

2.2.6. Determination of the influence of the main variables

For all these experiments the default options are: regenerating reagent – ascorbic acid; concentration of magnetite particles – 5 g/l; concentration of hydrogen peroxide (when Fenton reaction is expected) – 0.18M; stirring: from 0 until 2 h; regeneration time (when regeneration was applied): for ascorbic acid the regeneration time is 2 h, and for hydrazine 10 min. The analyzed variables were:

a) Effect of Mechanical Stirring

In these experiments we have used two options: no stirring and stirring from 0 until 120 min.

b) Effect of catalyst concentration

In this test, the concentrations of magnetite used were 1 g/l, 2 g/l, 4 g/l and 5 g/l.

c) Effect of concentration of regenerating reagents

In this test, the concentration of ascorbic acid and hydrazine used in the regeneration process is varied: 1.25 g/l, 2.5 g/l, 7.5 g/l, 10 g/l, and 0.32M, 0.63M, 0.95M, 1.26M, respectively.

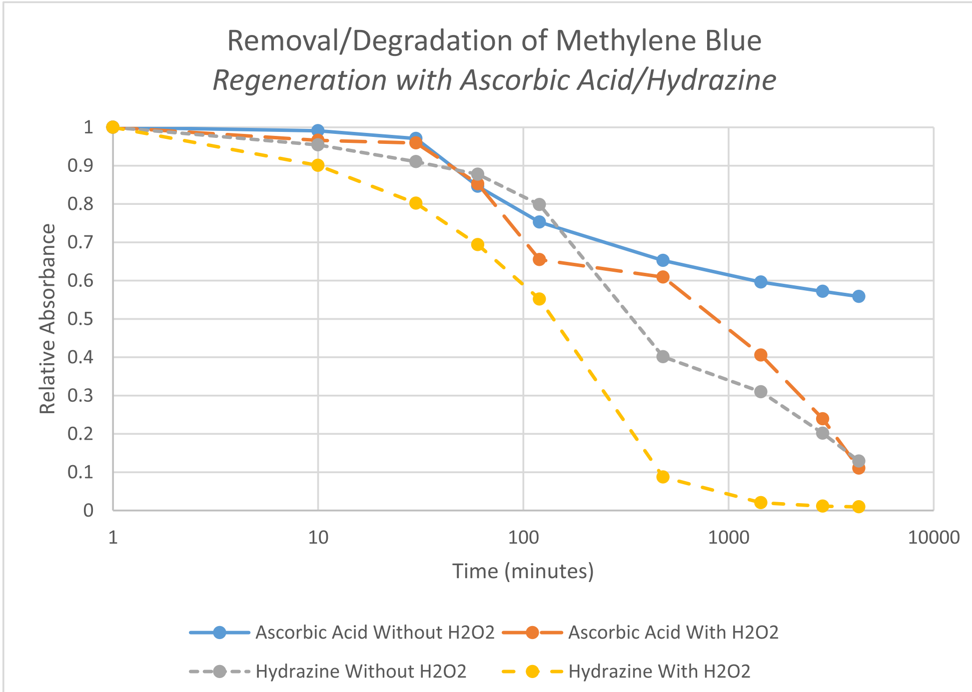

Fig. 1. Relative absorbance as a function of time on a logarithmic scale during the removal/degradation of methylene blue using particles regenerated with ascorbic acid/hydrazine (with/without addition of H_2O_2). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

d) Regenerating time

In this process the time of actuation of the ascorbic acid during regeneration was varied: 24h, 1h, 30min, 10min.

e) Hydrogen Peroxide concentration

In this case, the concentration of H_2O_2 added was varied: 44 mM, 88 mM, 0.44M and 0.88M.

2.3. Instrumentation

The main instrumentation that we have used was: RSLAB-13 mechanical overhead stirrer from RS-Lab, Spectrophotometer Helios Alpha from Unicam/Thermo Fisher, spherical reactor with three outlets, besides regular laboratory glass material.

3. Experimental results and discussion

One of the problems encountered when using magnetite particles for the Fenton heterogeneous reaction is that the surface of the particles becomes gradually oxidized, by contact with air or by repeated use. The Fenton reaction requires Fe^{2+} and Fe^{3+} ions, which are present in the magnetite, whereas if the surface becomes fully oxidized, only Fe^{3+} ions will be present and the reaction speed will be drastically reduced (until it completely stops) (Van et al., 2020; Avetta et al., 2015).

We have done some preliminary experiments with the magnetite particles in order to determine their natural efficiency for the Fenton process, without any regeneration process being applied previously. However, almost no degradation due to the Fenton process was achieved by these particles in several of these experiments. The most plausible reason for this behavior is that in most of the cases the surface of the particles was already oxidized when the Fenton process was tested. In those cases, regeneration was needed in order to achieve any kind of efficiency.

The results are organized in three sub-sections. In the first sub-section we present the results of the efficiency for the particles that are subject to a first regeneration cycle by using two reducing agents: ascorbic acid and hydrazine. In the second sub-section we present the study of the influence of the main variables (mechanical agitation, decontamination mechanism, concentration of magnetic particles, concentration of regenerating reagents, regeneration time, peroxide concentration). In the last sub-section we present the results obtained regarding the reuse of successively regenerated particles.

3.1. - Efficiency tests

3.1.1. - Regeneration with ascorbic acid

The magnetite particles can adsorb on their surface the dissolved methylene blue (thus reducing the observed absorbance of the solution) in parallel to the effect of the Fenton reaction. In this test we compared the removal of methylene blue from solution when no hydrogen peroxide is added to the solution (causing the dye to be removed by adsorption only) with the removal when 0.18M of hydrogen peroxide is added - to give rise to the reaction. In both studies we used 3 g/l of regenerated particles. The mechanical stirring was turned on 30 min after starting the experiment till its end (i.e., during 8 h).

Fig. 1 shows the obtained results (values in Supplementary Material) and it may be noticed a clear difference, where the particles subjected to the Fenton reaction (i.e., when hydrogen peroxide is added to the solution) show a higher removal of methylene blue. This difference increases with time (Zárate-Guzmán et al., 2016; Son et al., 2018), which is due to the fact that while the adsorption centers become saturated, Fe^{2+} is still available for Fenton reaction.

3.1.2. Regeneration with hydrazine

Fig. 1 shows also similar results for hydrazine (values in Supplementary Material) as to those obtained with ascorbic acid, but the particles regenerated with hydrazine outperform the ones regenerated with ascorbic acid, and above all, they do so requiring less time (24 times less). This is as expected, as hydrazine is a more powerful reducing agent than ascorbic acid (Lesiak et al., 2021). It is also important to notice that there is a relevant difference between the decrease in relative adsorption without H_2O_2 between ascorbic acid and

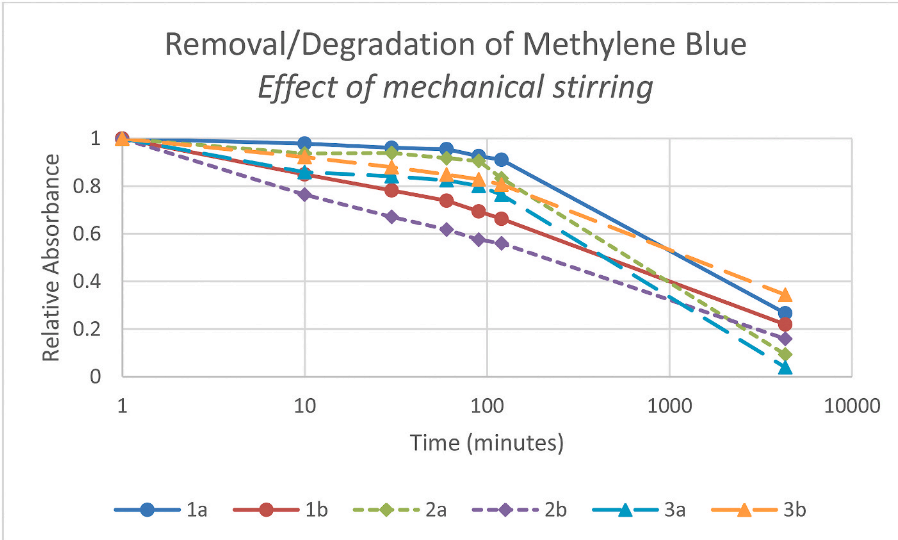

Fig. 2. Relative absorbance as a function of time on a logarithmic scale during the removal/degradation of methylene blue under various conditions: 1a: Relative absorbance with non-regenerated particles, no peroxide, no stirring; 1b: Relative absorbance with non-regenerated particles, no peroxide, stirred from 0 to 120 min; 2a: Relative absorbance with non-regenerated particles, with 0.18M peroxide, no stirring; 2b: Relative absorbance with non-regenerated particles, with 0.18 M peroxide, stirred from 0 to 120 min; 3a: Relative absorbance with regenerated particles, with 0.18 M peroxide, no stirring; 3b: Relative absorbance with regenerated particles, with 0.18 M peroxide, stirred from 0 to 120 min. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

hydrazine (for hydrazine experiments without hydrogen peroxide the decrease in absorbance is in same cases even higher than for ascorbic acid regenerated particles with H_20_2); this is thought to be caused by the difference on reducing strength of both reagents, allied with their common ability to reduce the sorbed species, namely Methylene Blue (El-Aila 2012; Mowry et al., 1999), and thus besides regenerating Fe^{2+} these reagents also regenerate sorption active sites (hydrazine being more powerful in both reductions than ascorbic acid).

3.2. *Effect of the main variables*

In order to evaluate the effect of the different main variables we have used the default values described in section 2, and then changed the variables under study (Rodríguez et al., 2020). It is important to refer that we have used the ascorbic acid as default reagent for the regeneration of particles, because being a weaker reducing agent than hydrazine, it allows the behavior of the modified variables to be smoother and thus better to follow and to explore.

3.2.1. *Effect of mechanical stirring*

Mechanical stirring or similar (Pirsahe et al., 2019) can benefit one mechanism over the other (adsorption versus Fenton), so in this test we analyze the removal/degradation of methylene blue with non-regenerated magnetite without peroxide (when adsorption occurs), non-regenerated magnetite with peroxide, and magnetite regenerated with ascorbic acid.

During this test it was observed that maintaining stirring for too long causes considerable evaporation of water from the solution, increasing the concentration of methylene blue, and thus the measured absorbance. Therefore, the stirring is limited from the beginning of the test to 2 h later.

In Fig. 2 (values in Supplementary Material) it can be seen that agitation benefits short-term elimination in non-regenerated particles, whereas in the long term only the peroxide-free solution, where no Fenton reaction took place, shows more elimination in the test with stirring. This indicates that stirring enhances the adsorption mechanism, which is in accordance with published literature for other type of sorbers (Kuśmierek et al., 2015). On the other hand, stirring reduces the efficiency of the particles to react with hydrogen peroxide; the reason may be that stirring tends to accumulate the particles in a small area at the bottom of the vessel, reducing the available surface for the reaction, while without stirring the particles are distributed over the entire bottom, so the surface available for the Fenton process is higher; the other reason may be the strong sensitivity that Fenton reaction shows to the type and level of stirring,

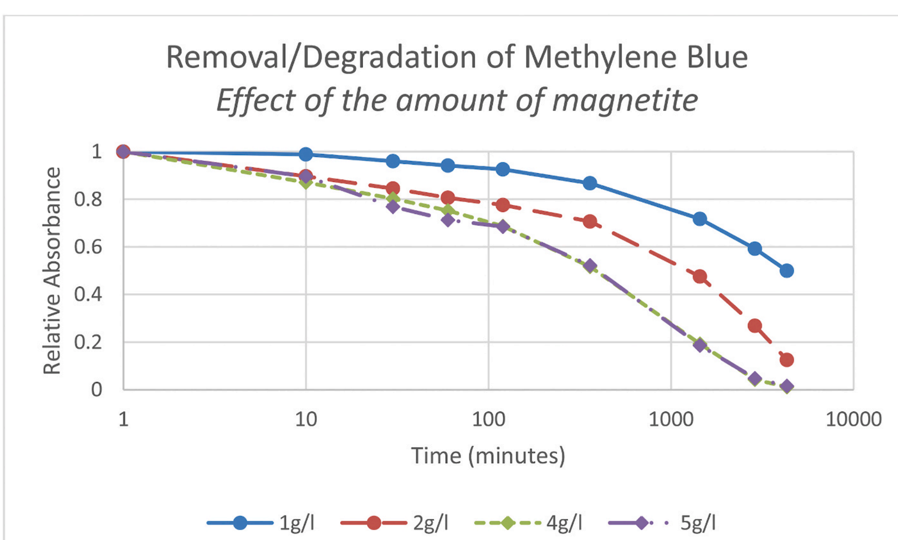

Fig. 3. Relative absorbance as a function of time on a logarithmic scale during the removal/degradation of methylene blue while adding different amounts of magnetite particles. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

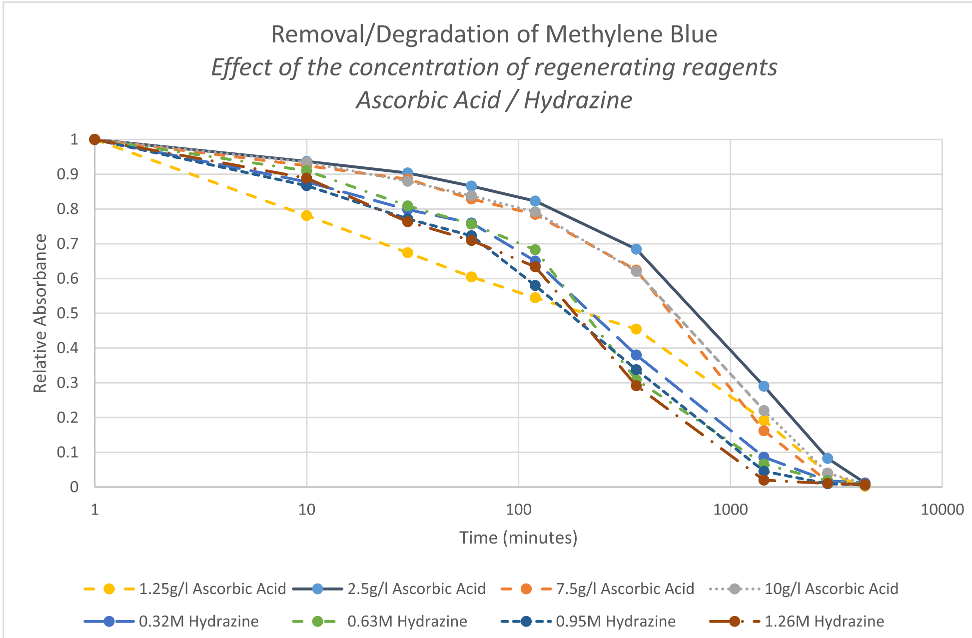

Fig. 4. Relative absorbance as a function of time on a logarithmic scale during the removal/degradation of methylene blue while regenerating the magnetite particles with different amounts of ascorbic acid/hydrazine. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

which may show a negative effect when stirring is applied and OH· radicals are consumed in parallel reactions (Zhou et al., 2016).

These results also show the difference between non-regenerated and regenerated particles. In the tests with peroxide and without stirring, the regenerated particles removed more dye than the non-regenerated ones, while the opposite is true in the tests with agitation. This may be because the regeneration process makes adsorption less efficient compared to non-regenerated particles, as stirring benefits adsorption over the Fenton reaction.

3.2.2. *Effect of the concentration of magnetite*

From the results obtained and presented in Fig. 3 (values in Supplementary Material), it can be deduced that there is an optimum amount of magnetite required, above which no significant difference is observed, but below which elimination is considerably reduced (Gonçalves et al., 2020; Minero et al., 2015). Similar tendency has been observed previously in other coated magnetite particles (Nadejde et al., 2015). This leads to the conclusion that an increase in the amount of magnetite increases the number of iron centers available for the Fenton process, until the amount is too high and either the reaction is not fast enough to keep up with the increase in active iron centers, or the maximum surface area available for the Fenton reaction is reached for the reaction volume used.

3.2.3. *Effect of the concentration of regenerating reagents*

From the results obtained and presented in Fig. 4 (values in Supplementary Material), it can be seen that in both cases and within the tests of the same regenerating reagent, no significant differences are observed, because the ions to be reduced are only present on the surface of the particles, so that a much smaller amount of reducing reagent would probably be needed than that used in these tests in order to

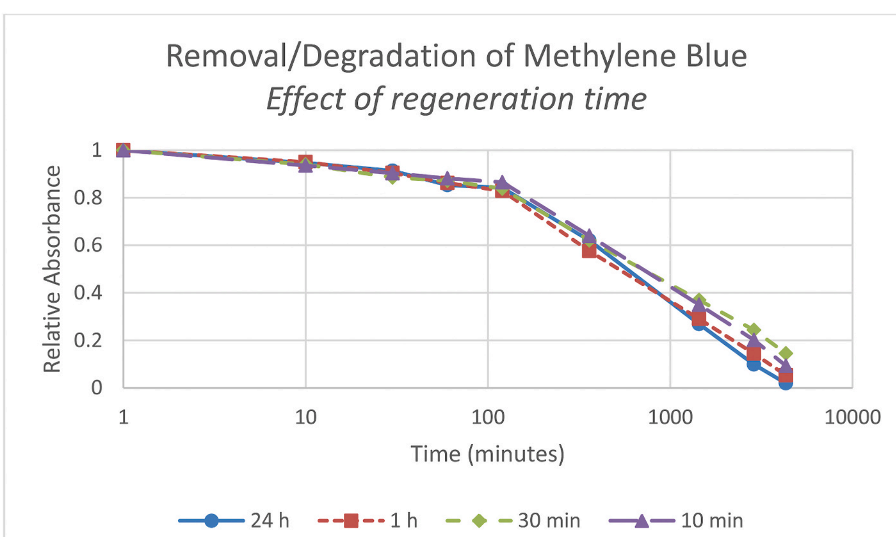

Fig. 5. Relative absorbance as a function of time on a logarithmic scale during the removal/degradation of methylene blue while regenerating the magnetite particles with ascorbic acid for different times. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

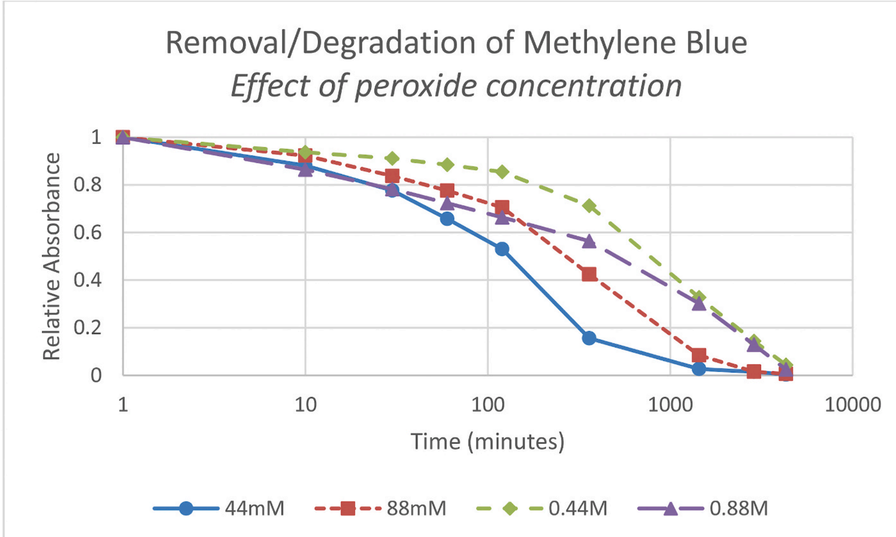

Fig. 6. Relative absorbance as a function of time on a logarithmic scale during the removal/degradation of methylene blue while regenerating the magnetite particles with ascorbic acid and adding different amounts of H_2O_2. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

observe any significant detrimental effect on the efficiency. The lack of difference in behavior is due to the strong regenerative efficiency of ascorbic acid and hydrazine which reaches complete particle regeneration in all situations tested.

It is also clear that, as expected, in terms of the time needed to obtain the same level of degradation, hydrazine regenerated particles behave better than ascorbic acid regenerated ones (hydrazine is a stronger reduction reagent than ascorbic acid, as detailed previously).

3.2.4. Effect of regeneration time

It can be seen, from the results presented in Fig. 5 (values in Supplementary Material), that a shorter regeneration time has a slight negative effect on the elimination of methylene blue, but the effect is not as pronounced as other factors, meaning that the first moments of regeneration are the most decisive.

It is not useful to test for hydrazine regeneration time, as 10 min are already sufficient to achieve very high removal efficiencies.

3.2.5. Effect of peroxide concentration

From the results obtained and presented in Fig. 6 (values in Supplementary Material), it can be noticed that higher concentrations of peroxide slow down the reaction, and with lower concentration the same proportion of elimination is reached in less time. However, it is possible that smaller quantities do not produce enough radicals to completely oxidize the dye (Wan et al., 2016, Wu et al., 2020b,c), making it necessary to find an optimal point, like usually described in literature (Arie Wibowo et al., 2019; Nadejde et al., 2015; Khandarkhaeva et al., 2019).

3.3. Reuse testing

The easiness of recovery is one of the advantages of using magnetic particles, so the ability to reuse these particles is an important factor in choosing the most appropriate method (Leifeld et al., 2018; Wang et al., 2020).

In this test, the removal capacity of the particles in successive uses is determined. We compare the efficiency results for Methylene Blue

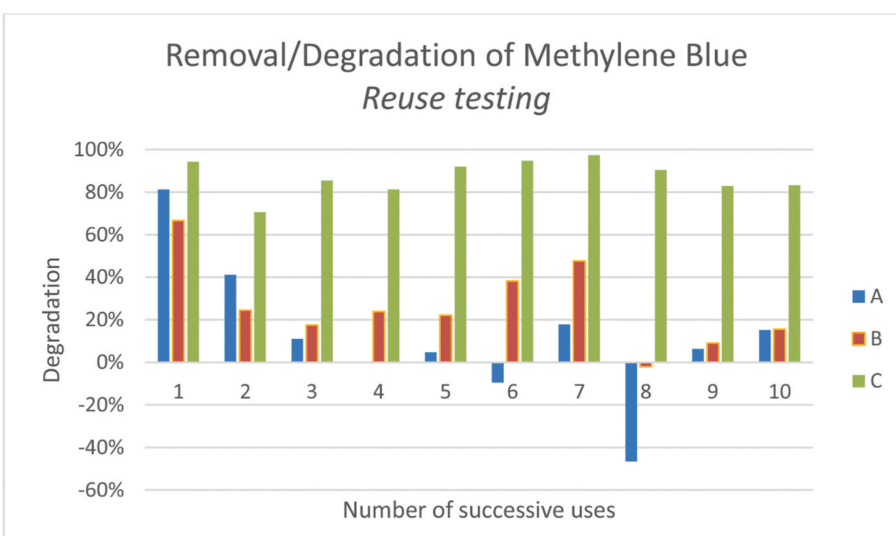

Fig. 7. Percentage of degradation according to the number of successive uses of the magnetite particles during the removal/degradation of methylene blue. (A: Non-regenerated particles; B: Particles regenerated with ascorbic acid; C: Hydrazine regenerated particles). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

degradation for the following cases: a) when the particles are not regenerated between uses; b) when they are regenerated with 5 g/l of ascorbic acid for 2 h; c) when they are regenerated with 0.63M of hydrazine for 10 min.

From Fig. 7 (values and extra information in Supplementary Material), it can be concluded that the reuse of particles without further regeneration is only 40% effective after the first reuse, becoming ineffective from that first reuse forward. In relation to the particles regenerated with ascorbic acid, the reuse becomes ineffective from the eighth regeneration onwards, the efficiency in each reuse being moderately to low. The particles successively regenerated with hydrazine always remain effective until the end of the batch of reuses tested in this work; moreover, they always present very effective values of degradation via Fenton. In the case of non-regenerated particles negative values appear in some of the experiments, because of desorption of methylene blue in the particles (sorption and desorption cycles like the ones reported in Augusto et al., 2019, Castelo-Grande et al., 2021a and Castelo-Grande et al., 2021b).

4. Conclusions

The regeneration process, which electronically reduces the total charge existing at the surface area of the particles, increases the efficiency of the particles in catalyzing the Fenton reaction, for both regeneration reagents (ascorbic acid and hydrazine), increasing degradation, when compared to the Fenton reaction without regeneration, by as much as 99%.

As for the main variables studied: stirring is useful at the beginning of the reaction to bring the particles into contact with the reagents, but in the long term it is unfavorable to the Fenton reaction. The concentration of magnetite has a great influence, with the greatest reduction in absorbance being achieved for the 4 g/l case. The concentration of regenerating reagents does not have a significant influence, but it is possible that this is due to the fact that all the amounts added have been in excess to that required to electronically reduce the total charge existing at the surface area of the particles. The regeneration time has a slight influence on the efficiency, but is not very significant. Adding a high concentration of peroxide causes the reaction to occur slower, but does not reduce its long-term efficiency.

The use of hydrazine in the regeneration process not only increases efficiency, but also allows the reuse of the particles repeatedly with a very high percentage of degradation (70–97%) compared to non-regenerated particles (less than 20% after the 2nd use) or particles regenerated with ascorbic acid (less than 20% after the 8th use).

Credit author statement

Lorenzo Hernández: Formal analysis, Investigation; Methodology; Writing - Original Draft; Paulo A Augusto: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration, Funding acquisition; Teresa Castelo-Grande: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration, Funding acquisition; Domingos Barbosa: Conceptualization, Methodology, Writing - Original Draft, Writing - Review & Editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.112155.

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