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Synthesis and application of metallic iron nanoparticles on the 4-Chorophenol degradation

Síntese e aplicação de nanopartículas de ferro metálico na degradação do 4-clorofenol

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RESUMO
Os herbicidas são uma classe importante de agroquímicos usados para o controle de plantas daninhas. Os herbicidas organoclorados apresentam alta toxicidade e persistência ambiental, aumentando o risco de contaminação do solo e da água. Os clorofenóis e seus derivados são contaminantes tóxicos do meio ambiente oriundos da degradação de agroquímicos. Nanopartículas de ferro metálico (Fe-NPs) têm sido utilizadas para a remoção e degradação de uma variedade de poluentes orgânicos, incluindo herbicidas e compostos organoclorados. O objetivo deste trabalho foi estudar a síntese de Fe-NPs e sua aplicação na degradação do 4-clorofenol (4-CP). Fe-NPs com tamanho médio de 113 nm compostas pela fase α-Fe foram obtidas através da redução de borohidreto. As Fe-NPs foram misturadas com 500 μM de 4-CP em vários valores de pH. A degradação do 4-CP foi confirmada pelo monitoramento da banda de absorção em 298 nm. Além disso, a produção de fenol foi seguida pela reação com monocloramina que produz uma solução de cor azul com absorção máxima a 680 nm. A diminuição da absorbância em 298 nm sugere degradação do 4-CP.

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Palavras-chave: Ferro zero valente, organoclorados, fenol, degradação.

ABSTRACT
Herbicides are an important class of agrochemicals used for weed control. Organochloride herbicides show high toxicity and environmental persistence increasing the risk of soil and water contamination. Chlorophenols and their derivatives are toxic contaminants in the environment originated from degradation of agrochemicals. Metallic iron nanoparticles (Fe-NPs) have been used for removal and degradation of a range of organic pollutants, including herbicides and organochlorides compounds. The aim of this work was to study the synthesis of Fe-NPs and their application in 4-chlorophenol (4-CP) degradation. Fe-NPs with average size of 113 nm composed of α-Fe phase were obtained through borohydride reduction. The Fe-NPs were mixed with 500 μM of 4-CP at several pH values. The degradation of 4-CP was confirmed by monitoring the absorption band at 298 nm. Additionally, the phenol production was followed by reaction with monochloramine which produces a blue colored solution with maximum absorption at 680 nm. The decrease in absorbance in 298 nm suggest degradation of 4-CP.

Keywords: Zero valent iron, organochlorides, phenol, degradation.

1 INTRODUCTION

The increasing number of human industrial and urban activities in the last decades led to accumulation of innumerous pollutants in natural hydric resources, such as pesticides, dyes and heavy metals (YONGLONG LU *et al*., 2015). As reported by Taghizade et al (TAGHIZADE et al., 2018) the residue of these pesticides may be dispersed on the soil, groundwater and drinking waters. This critical environmental impact has been subject in the development of new materials and protocols for water remediation. In this scenario, nanotechnology products have attracted the interest of researchers over the decades due to its distinctive physicochemical properties and applications (SADHASIVAM *et al*., 2020; FENGLIAN FU *et al*. 2014).

Nanomaterials have been successfully used in a variety of applications, such as environmental (YAN XU *et al*., 2017; FANG LUO *et al*. 2016), medicine (BINGJUN SUN *et al*., 2016) and agriculture (TOSCO *et al*., 2014). In particular, metallic nanomaterials, such as iron and nickel, are of interest for environmental remediation applications. In the nanoparticulate form, metallic iron displays high reactivity towards organic compounds reduction. These characteristics emerge from the small size and high surface to volume ratio. The metallic iron redox standard potential is about -0.44 V which renders this material excellent reduction power towards several classes of organic compounds, such as halogenated hydrocarbons. Several studies report on the dehalogenation of hidrocarbons by using Fe-NPs (RAYCHOUDHURY *et al*., 2013; O'CARROLL *et al*., 2013; YAN *et al*., 2010).

Organochlorides are classified as highly toxic pollutants and are persistent on soil and water. They are originated from synthetic chemical derivatives of industrial use. Among the chlorinated organic compounds, 4-chlorophenol (4-CP) is largely used in agrochemicals, dyes, and some drugs synthesis.

The 4-CP present high toxicity and low biodegradability, is potentially carcinogenic and biocumulative. The presence of 4-CP in the environment endangers human health (HWANG *et al*., 2015). The removal of chlorophenols is of great importance for the protection of natural resources and represents a technological challenge. In this context, the use of Fe-NP has demonstrating promising results for degradation of recalcitrant contaminants (DORATHI *et al*., 2012). Here, we studied the synthesis of Fe-NPs and their application in 4-CP degradation. It is an innovative and applied work with great potential in the agricultural area.

2 EXPERIMENTAL

2.1 MATERIALS

All chemicals were used as received. Iron (II) chloride tetrahydrate (99% Sigma), sodium borohydride (96% Fluka), 4-chlorophenol (98% Sigma), phenol (99% Synth), sodium hydroxide (Alfatec, 99%), ammonium chloride (Cromoline 99%), sodium hipochloride (12% Dinâmica), sodium nitroprusside (99% Sigma).

2.2 SYNTHESIS OF FE-NPS

The Fe-NPs were prepared by reduction of Fe^{2+} with sodium borohydride ($NaBH_4$). Briefly, 4 mmol of iron(II) chloride were dissolved with 40 mL of water purged with argon gas. Then, 12 mmol of $NaBH_4$ dispersed in 3 mL of triglyme was injected into the reaction vessel. The precipitate was magnetically decanted and washed three times with purged deionized water. The as-prepared Fe-NP were stocked in 20 mL of purged water for further experiments.

For characterization studies the Fe-NPs were dried under argon atmosphere. The X-ray diffractograms were recorded in a Siemens D5005 system using Cu Kα radiation, operating at 40 kV in the 2ɵ range between 20° and 90°. The size and morphology of the Fe-NPs were investigated by using a JEOL model JSM-7500F scanning electron microscope (SEM), operated at an accelerating voltage of 2 kV.

2.3 DEGRADATION EXPERIMENTS

For degradation experiments aliquots of 4-CP stock solution were taken and added to a 50 mL tube, diluted with water and the pH was adjusted with 1.0 $molL^{-1}$ HCl or NaOH solution to 2, 3, 4, 5, 6, 7, 8, 9 and 10. Each contaminant solution was sparged with argon gas and then 5 mL of Fe-NPs dispersion was added with. The final volume was adjusted to 25 mL with deionized water and the concentration of 4-CP was set at 500 $\mu molL^{-1}$. The system was thoroughly purged with argon gas, closed

and allowed to react during 6 and 24 h. After, the Fe-NPs was removed by magnetic separation and the supernatant collected for spectrophotometric analysis.

2.4 ANALYTICAL METHODS

The as-collected supernatants from the samples described above were used for measuring the UV-Visible spectra in the range of 200 to 400 nm in order to quantify the remaining 4-CP present in the sample solutions. The concentration was determined by the standard addition method using a calibration curve of 4-CP with concentrations ranging from 2 to 2000 $\mu molL^{-1}$ containing fixed volume of samples and measuring the absorption center at 298 nm.

The assay procedure used for phenol determination was based on studies developed by Hwang et al. (HWANG *et al*., 2015). In a typical analysis, reagent A is prepared by diluting 1 mL of 10% hypochlorite and 66 mL of 0.5 $molL^{-1}$ NaOH solution to 100 mL with deionized water. Reagent B was prepared so as to contain 4.78 gL^{-1} of NH_4Cl and 0.3 gL^{-1} of sodium nitroprusside ($Na_2[Fe(CN)_5NO] \cdot 2H_2O$) dissolved in deionized water. A solution namely reagent AB was prepared by mixing equal volumes of reagent A and B. The quantification procedure was as follow: 2.3 mL of sample supernatant and was completed with reagent AB to 5 mL, than allowed to react in the dark for 2 h. After the UV-VIS spectra was acquired in the range of 400 to 800 nm. A calibration curve was obtained by varying the concentration from 2 to 50 $\mu mol\ L^{-1}$ and measuring the absorbance at the center of the band (680 nm) and used for phenol quantification.

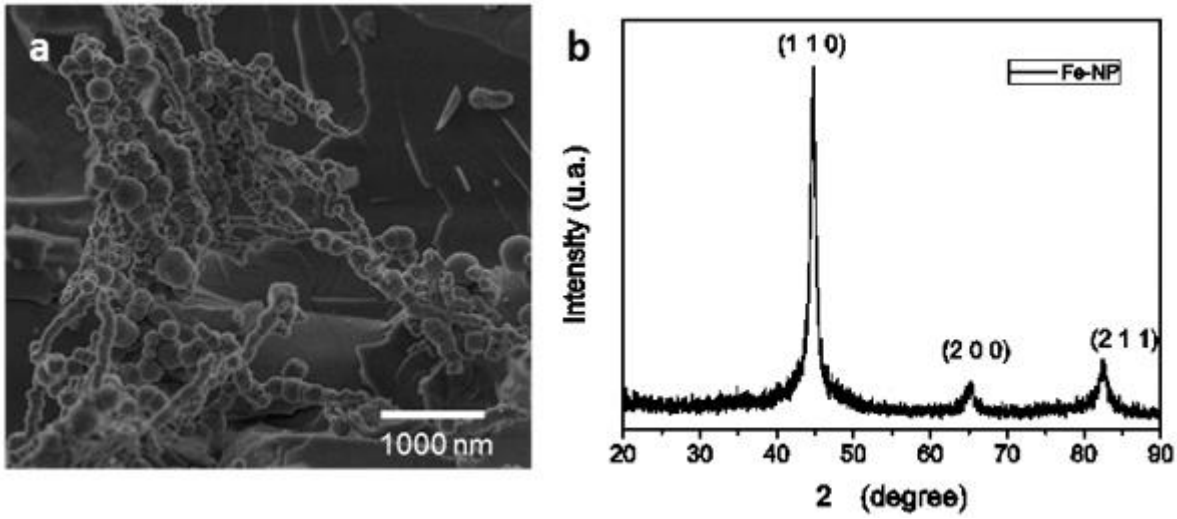
3 RESULTS AND DISCUSSION

3.1 FE-NPS CHARACTERIZATION

The Fe-NPs were prepared by chemical reduction of Fe^{2+} with sodium borohydride ($NaBH_4$) in aqueous solution. The as-produced solid presented black coloration and was highly magnetic in nature. **Figure 1 (a)** displays the SEM images of the Fe-NPs and **Figure 1 (b)** the XRD pattern of as-synthesized Fe-NPs. As shown by the SEM images, the most of particles were nanosized, presenting a roughly spherical morphology. The average size of 113 ± 66 nm was obtained, suggesting a high polydispersity in particle sizes.

The XRD pattern (see **Figure 1(b)**) agree with the α-Fe crystalline phase, and the diffracted peaks matched the interplanar distances marked by the Bragg indexes (110), (200) and (211). The broadening of the diffraction peaks is more likely due to low crystallinity of the particles as well due to the existence of small (around 10-20 nm) nanocrystals in the sample (NUNES *et al*., 2014).

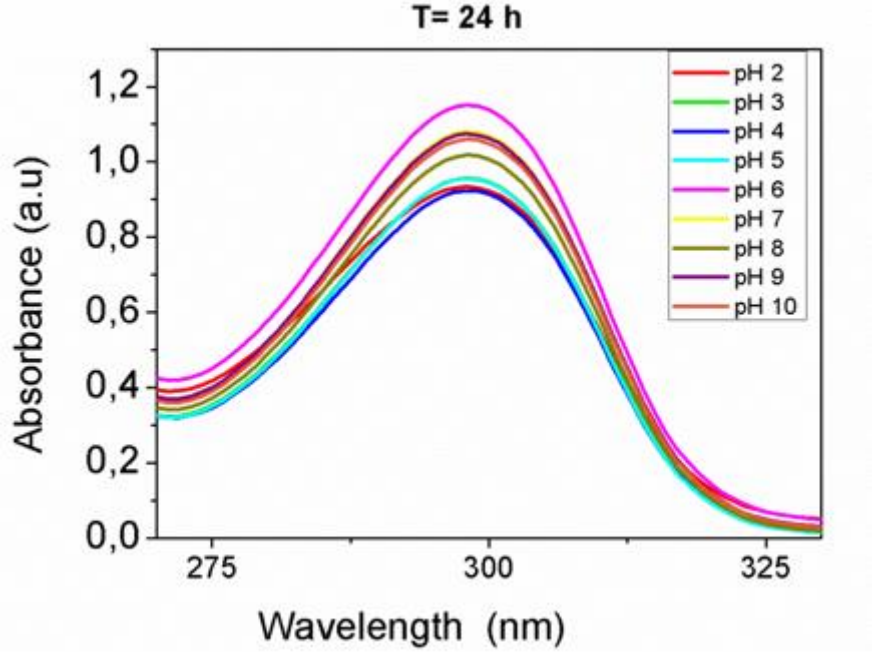
Figure 1. SEM image (a) and XRD pattern of as-synthesized Fe-NPs (b).



3.2 DEGRADATION OF 4-CHLOROPHENOL STUDY

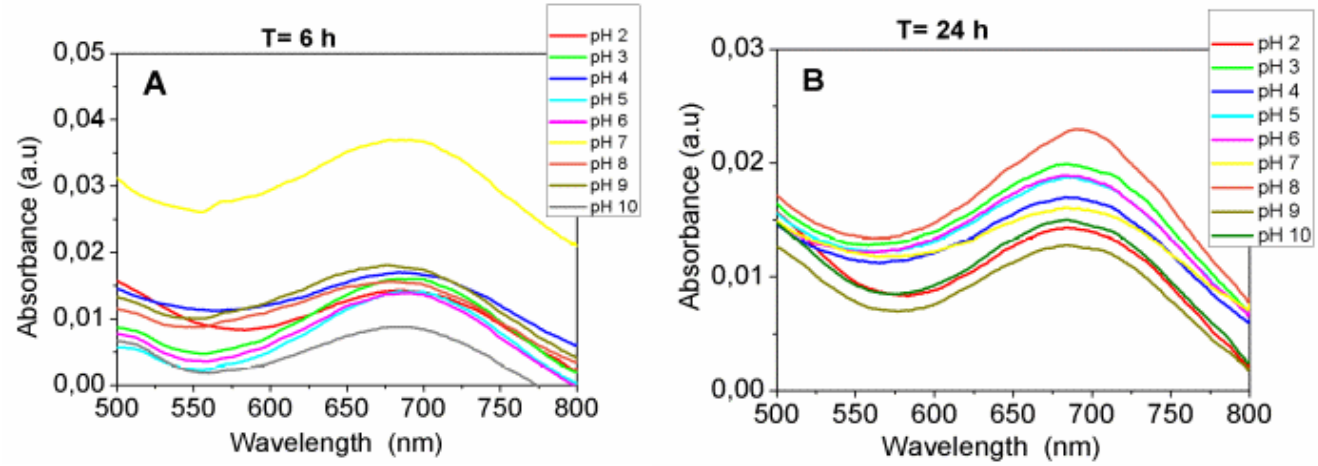
The degradation of 4-CP in presence of Fe-NP was evaluated for different pH and reaction time. **Figure 2** shows the UV-VIS spectra of samples supernatant at pH range of 2 to 10 taken after 24 h of incubation. The decrease of the absorbance in 298 nm suggests the 4-CP degradation was larger for acidic pH's. The pH 4 was optimum for 4-CP degradation and the remaining concentration in the sample supernatant was 86 $\mu molL^{-1}$. In the presence of proton donors, the reductive dehalogenation of chlorinated organic substances is favored (ARRUDA *et al*., 2020). According to Raja et al [16], the Fe-NP acts as an electron donor which reacts with 4-CP promoting a reductive dechlorination, since the process is thermodynamic favored (RAJA *et al*., 2005).

Figure 2. UV-VIS spectra of samples supernatant produced from 4-CP degradation for 24 h at different pH values.



The reduction of 4-CP with Fe-NP leads to phenol, driven by an electron transfer process. In order to identify and quantify the phenol as degradation product, the indophenol reaction was applied. In this reaction the product between monochloramine and phenol is a blue dye, which can be spectrophotometrically determinate (HWANG *et al*., 2015). **Figure 3** presents the UV-VIS spectra of samples produced from 4CP degradation at pH range 2 to 10 after incubation times for 6 and 24 h and after treatment with the indophenol reaction. The absorption maximum at 700 nm was in accordance to Hwang et al (HWANG *et al*., 2015), confirming the phenol production. As observed in **Figure 3**, the phenol concentration did not increased significantly with time, and remained at about 1 μmol L^{-1}. This observation suggests that could have other degradation by products. Raja et al (RAJA *et al*., 2005) observed a similar behavior in a Fenton-mediated degradation study of 4-CP.

Figure 3. UV-VIS spectra of samples supernatant produced at different pH values after the indophenol assay for phenol identification. 6 h (a) and 24 h (b).



4 CONCLUSIONS

The 4-CP degradation was confirmed by monitoring the absorption band at 298 nm. Additionally, the phenol production was followed by reaction with monochloramine which produces a blue colored solution with maximum absorption at 680 nm. The absorbance decreasing at 298 nm suggest the 4-CP degradation. The small increase of phenol concentration with time suggested that production of other byproducts may occur and be useful for remediation of contaminated water. However this issue requires more investigation.

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ANEXO

HIGHLIGHTS

§ Fe-NPs were used for degradation of 4-chorophenol;

§ Fe-NPs are composed by α-Fe phase and presented particles size of 113 ± 66 nm;

§ Synthesized Fe-NPs showed good catalytic activity.

GRAPHICAL ABSTRACT