

THE INFLUENCE OF DIFFERENT ELECTROLYTES ON SULFENTRAZONE DECHLORINATION BY IRON-NICKEL BIMETALLIC NANOPARTICLES

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Abstract - Kinetic studies of sulfentrazone herbicide dechlorination by Fe/Ni nanoparticles were performed in the presence of different electrolytes such as: Cl⁻, SO₄²⁻, NO₃⁻, Cu²⁺, Na⁺ and Zn²⁺. In the presence of Cl⁻ and SO₄²⁻ the reaction occurred efficiently, reaching approximately 100% of dechlorination after 30 minutes of reaction. In the presence of NO₃⁻ and Cu²⁺ ions the sulfentrazone dechlorination was significantly inhibited, because these ions tend to compete with the substrate for the electrons donated by Fe⁰. In the presence of Na⁺ ions, the dechlorination efficiency remained approximately 100%, however, this electrolyte provided an increase on the reaction rate, due to the increase of the ionic strength in the system. The Zn²⁺ ions has no influence on the dechlorination efficiency, but the reaction rate was reduced due to the formation of a protective layer formed by the sorption of Zn²⁺ ions on the surface of the nanoparticles.

Keywords: Bimetallic nanoparticles; Electrolytes; Fe/Ni; Dechlorination; Sulfentrazone.

INTRODUCTION

Water is a natural resource essential for maintaining life on our planet. However, the drinking water supply has been affected by climate factors and anthropogenic actions, such as the disposal of domestic and industrial waste into water bodies, indiscriminate use of agrochemicals, and deforestation (Pereira and Freire, 2005). Agriculture is a practice that contributes to water pollution, since it makes use of fertilizers, insecticides and herbicides. These agrochemicals can be considered persistent organic pollutants (Gondal et al., 2016), which are substances that can remain for a long time in the environment due to the fact of being resistant to natural removal processes (Sacco et al., 2015).

After application, the movement of pesticides in the soil can occur through leaching, runoff and

volatilization processes (Vieira et al., 1999), that can promote contamination of soil and surface water and groundwater. In addition, the contamination of water located near agricultural areas by pesticide residues can occur during the application of these substances, being of great concern (Mekonen et al., 2016).

Sulfentrazone (Figure 1) is an herbicide used to combat weeds and it can be applied in pre-emergence to control infestations in coffee, sugarcane, citrus, eucalyptus, and soybean crops (Rodrigues and Almeida, 2005). This agrochemical is classified by the Brazilian *National Health Surveillance Agency* (Anvisa) as an extremely toxic herbicide (class I) and its half-life in soil varies according to local edaphoclimatic conditions, being estimated between 110 and 280 days (Vivian et al., 2006). Once present in the soil, this compound can have high persistence and mobility, and because it has a strong potential

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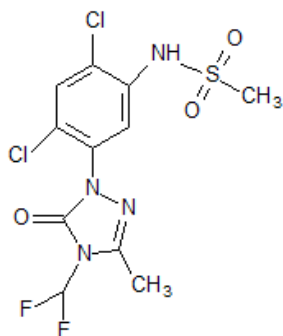
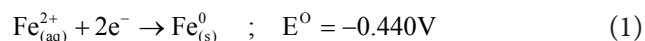


Figure 1. Structural formula of sulfentrazone.

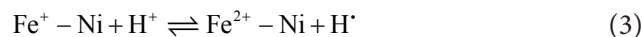
for leaching, it can reach groundwater (Epa, 1997). Therefore, it is highly necessary to develop processes able to promote the removal of this pollutant from contaminated water.

Among the processes used for the treatment of halogenated organic compounds, the reductive dehalogenation using Fe^0 has emerged as a promising alternative (Lim and Zhu, 2008). The redox pair $\text{Fe}^0/\text{Fe}^{2+}$ (Eq. 1) has a low standard reduction potential ($E^\circ = -0.440\text{V}$); consequently, iron is a strong reducing agent compared to several substances such as organochlorines, carbonates, hydrogen, sulfate, oxygen, and nitro aromatic compounds (Pereira and Freire, 2005). Therefore, it can be used to remove many types of contaminants such as heavy metals, organohalogenated compounds, nitro and azo compounds and oxyanions (Liu et al., 2014).



The oxidation of zero valent iron in aqueous solutions, under aerobic and anaerobic conditions, promotes an increase of pH (Pereira and Freire, 2005). Consequently, precipitates such as $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, Fe_3O_4 , Fe_2O_3 , FeOOH , $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ and green rusts can be formed (Crane and Scott, 2012) and deposited on the surface of the nanoparticles, leading to the formation of a protective layer and thus preventing the transfer of electrons from Fe^0 to the halogenated compound (Liu et al., 2014).

In order to prevent the formation of protective layers on the metal surfaces, it is common to combine the metallic iron with another catalyst metal, such as Ag, Pd, Ni, Cu or Pt (Liu et al., 2014), forming bimetallic nanoparticles. In addition, the introduction of a second metal may enhance the nanoparticle reactivity due to the increase in the number of active sites and the formation of atomic hydrogen (Eq. 2–5) (Bokare et al., 2008). The atomic hydrogen adsorbed onto the metal surface is used in the hydrogenation of the pollutant compound (Schrick et al., 2002).



Bimetallic nanoparticles have been used efficiently to degrade several pollutants (Bokare et al., 2008; Li et al., 2017). However, in the environment, these compounds coexist with several electrolytes, which can interfere in the reaction, favoring or inhibiting the degradation process. Some authors have already investigated the effect caused by the presence of electrolytes in the medium: Shih et al. (2011) investigated the effects of Cu^{2+} , Ni^{2+} and Fe^{3+} on the degradation of pentachlorophenol by Fe/Pd nanoparticles. Tso and Shih (2017) evaluated the influence of the anions chloride (Cl^-), nitrate (NO_3^-) and bicarbonate (HCO_3^-) on the removal of decabrominated diphenyl ether using Fe/Ni nanoparticles stabilized by carboxymethylcellulose. Lim and Zhu (2008) evaluated the effects of several anions such as nitrate, nitrite, perchlorate, phosphate, carbonate, silica, sulfate, sulfite, and sulfide on the dechlorination of 1,2,4-trichlorobenzene by Pd/Fe nanoparticles.

In a previous work carried out in our laboratories, the conditions for sulfentrazone dechlorination by Fe/Ni nanoparticles were studied (Nascimento et al., 2016). However, what effects could be caused by the presence of different electrolytes during the dechlorination process were not evaluated. Thus, in this work the effects caused by the presence of different electrolytes such as $\text{HSO}_4^-/\text{SO}_4^{2-}$, Cl^- , NO_3^- , Na^+ , Cu^{2+} and Zn^{2+} on sulfentrazone dechlorination by Fe/Ni nanoparticles were evaluated.

EXPERIMENTAL METHODOLOGY

Reagents

All the reagents used were of analytical grade and the aqueous solutions were prepared with purified water from a Milli-Q system and stored at 4°C . Acetonitrile was obtained from Sigma-Aldrich. Nitric acid was obtained from Neon. Hydrochloric acid was obtained from Alphatec, while copper sulfate pentahydrate, ethanol, sulfuric acid, iron sulfate heptahydrate, nickel chloride hexahydrate, sodium sulfate, zinc sulfate heptahydrate and sodium borohydride were obtained from VETEC. Sulfentrazone (minimum 91%) was purchased from FMC.

Preparation and characterization of the Fe/Ni bimetallic nanoparticles

Bimetallic nanoparticle preparation was conducted according to the methods reported by Nascimento et

al. (2016). The nanoparticles were stored in a freezer. The characterization of the bimetallic nanoparticles was made using Transmission Electron Microscopy – TEM (FEI Tecnai G2-20), Energy Dispersive X-ray Spectroscopy (EDS) and Flame Atomic Absorption Spectrophotometry – FAAS (Shimadzu AA-6701F). The surface analysis of nanoparticles was performed by adsorption chromatography of nitrogen and calculated by the BET (Brunauer-Emmett-Teller) method in a Quantachrome instrument (NOVA 1200e). The measurements were performed with 20 cycles of adsorption and 20 cycles of desorption of nitrogen and degassing at the temperature of 80 °C for a period of 5 hours.

The nanoparticle characterization was described in a previous study (Nascimento et al., 2016). The characterization of the nanoparticles by TEM revealed that the nanomaterials were smaller than 20 nm and that they formed agglomerates. The presence of iron, nickel, sodium and oxygen was evidenced by EDS analysis, while the analysis using Flame Atomic Absorption Spectroscopy showed that the contents of Fe and Ni in the nanoparticles corresponded to $70.9 \pm 2.7\%$ and $9.7 \pm 0.6\%$, respectively (Nascimento et al., 2016).

Sulfentrazone dechlorination

The dechlorination assays were performed by adding 0.200 g of Fe/Ni nanoparticles to 200 mL of sulfentrazone solution (2.58×10^{-5} mol L⁻¹) in a cylindrical reactor with temperature controller. The reactor was connected to a thermostatic bath, model MQBTC 99-20 (Microquímica), to keep the temperature constant at 25.0 ± 0.1 °C. The system was stirred during all the reaction time.

For the evaluation of the effect of HSO₄⁻/SO₄²⁻, Cl⁻ and NO₃⁻ anions, solutions of H₂SO₄ (0.3 mol L⁻¹), HCl (0.1 mol L⁻¹), and HNO₃ (0.5 mol L⁻¹) were added to the system, respectively. The volume and concentration of acid added to the system was sufficient to keep the pH constant at 4.0, since this is the optimum pH value for the reaction, as reported in a previous study (Nascimento et al., 2016).

In the analysis of the effect of the cations, the pH control was performed with H₂SO₄ (0.3 mol L⁻¹) and Na⁺, Cu²⁺ and Zn²⁺ cations were inserted in the system at concentrations of 5, 10, and 20 mmol L⁻¹ through the addition of Na₂SO₄, CuSO₄·5H₂O and ZnSO₄·7H₂O salts. During the reaction, aliquots were withdrawn at different time intervals up to 30 minutes, filtered on a 0.45 μm cellulose membrane and analyzed by High Performance Liquid Chromatography (HPLC-UV). All experiments were performed in duplicate and the relative dispersion of the replicates were expressed based on the coefficient of variation.

Analytical procedures

The concentration of sulfentrazone remaining in the solution was quantified by HPLC (Shimadzu LC 20AT) with UV-Vis detector (Shimadzu SPD 20A), using a C18 stainless steel column (Shimadzu VP-ODS Shim-pack 150 mm × 4.6 mm internal diameter). The following chromatography conditions were applied: isocratic elution, mobile phase consisting of acetonitrile: water: phosphoric acid (50:49.9:0.1 v/v/v), injection volume of 20 μL, flow rate of 1.0 mL·min⁻¹, wavelength of 207 nm, and total running time of 8 minutes.

The sulfentrazone herbicide was identified by comparing the retention time of the analytical standard (5.18 min) with the samples and the quantification of the remaining herbicide was performed through the analytical curve.

RESULTS AND DISCUSSION

Characterization of the Fe/Ni bimetallic nanoparticles

The isothermal adsorption and desorption of nitrogen by the Fe / Ni bimetallic nanoparticles can be seen in Figure 2A.

The surface area of the PN-LIB, calculated by the BET method, was equal to 23.00 m² g⁻¹. The volume and the average size of pores were calculated by the

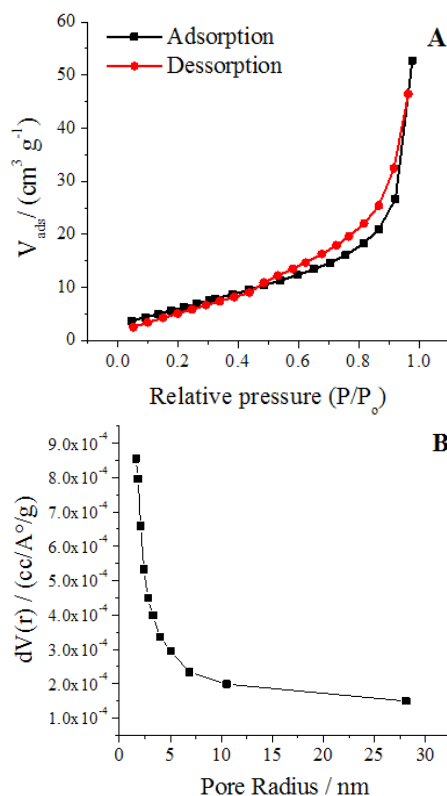


Figure 2. (A) Adsorption/desorption isotherms of nitrogen by the Fe/Ni bimetallic nanoparticles; (B) pore-size distribution curve.

BJH (Barrett-Joyner-Halenda) method, being $0.0833 \text{ cm}^3 \text{ g}^{-1}$ and 1.847 nm , respectively. These results were similar to those found by Bokare et al. (2008) whose area was $26 \text{ m}^2 \text{ g}^{-1}$ for iron-nickel bimetallic nanoparticles. Others researchers found a bigger area for bimetallic Fe/Ni nanoparticles supported on biochar equal to $59.83 \text{ m}^2 \text{ g}^{-1}$ (Li et al., 2017). The pore size distribution of Fe/Ni nanoparticles (Figure 2B) demonstrates an organized and ordered porosity and a narrow distribution of uniform pores.

Effect of $\text{HSO}_4^-/\text{SO}_4^{2-}$, Cl^- and NO_3^- anions on sulfentrazone dechlorination by Fe/Ni nanoparticles

In order to evaluate the influence of $\text{HSO}_4^-/\text{SO}_4^{2-}$, Cl^- and NO_3^- anions on sulfentrazone herbicide dechlorination by Fe/Ni nanoparticles, H_2SO_4 , HCl , and HNO_3 were added to the system constantly, in order to maintaining the pH at 4.0. Previous studies have verified that sulfentrazone dechlorination by Fe/Ni nanoparticles has maximum efficiency at pH 4.0, because under this condition the passivation of the nanoparticles is prevented (Nascimento et al., 2016).

As can be seen in Figure 3, the herbicide dechlorination occurred efficiently in the presence of sulfuric and hydrochloric acids, providing approximately 100% dechlorination after 30 minutes of reaction, which demonstrates that $\text{HSO}_4^-/\text{SO}_4^{2-}$ and Cl^- ions do not inhibit sulfentrazone dechlorination.

The high dechlorination rate of sulfentrazone in the presence of Cl^- can be explained because Cl^- ions can act by accelerating the corrosion of the iron and thus generating more electrons in the medium (Chen et al., 2016), while the sulfate anion acts in the removal of ferrous hydroxides, which inactivate the nanoparticles (Le et al., 2011). Similar results were obtained in other studies. Tso and Shih (2017) observed that the removal rate of decabrominated diphenyl ether by

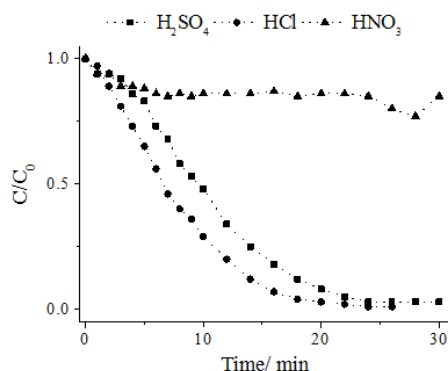
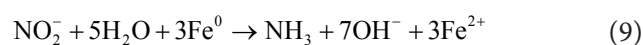
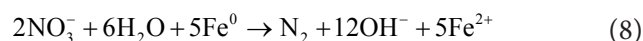
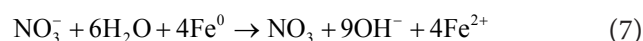
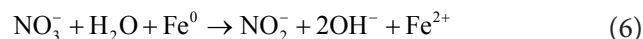


Figure 3. Normalized concentration of sulfentrazone as a function of time in the presence of H_2SO_4 , HCl , and HNO_3 . Experimental conditions: $C_0 = 2.58 \times 10^{-5} \text{ mol L}^{-1}$; Volume of solution = 200 mL; pH = 4.0; Reaction time = 30 min; Mass of nanoparticles = 0.200 g; $T = 25.0 \text{ }^\circ\text{C}$. The coefficient of variation between the replicates was lower than 5%.

carboxymethylcellulose-stabilized Fe/Ni nanoparticles was enhanced in the presence of Cl^- ions. Lim and Zhu (2008) verified that the SO_4^{2-} anion has no influence on the dechlorination process of 1,2,4-trichlorobenzene by Pd/Fe nanoparticles. Chen et al. (2016) observed that the removal efficiency of hexachlorobenzene by Fe^0 nanoparticles increased in the presence of Cl^- and SO_4^{2-} ions. Le et al. (2011) observed that the *para*-chloronitrobenzene reduction rate by Fe^0 nanoparticles increased in the presence of Cl^- and SO_4^{2-} ions.

In Figure 4 it can also be seen that, in the presence of nitric acid, the dechlorination efficiency is greatly reduced. To maintain the pH at 4 (optimized reaction condition), 2 mL of HNO_3 (0.5 mol L^{-1}) was added to the system, i.e., the concentration of HNO_3 in the system was equal to 157.5 mg L^{-1} . HNO_3 dissociates almost completely in aqueous medium, releasing nitrate ions into the solution. Once present in the medium, nitrate ions in the presence of Fe^0 may be reduced as can be seen from equations 6-9 (Lim and Zhu, 2008).



According to Huang et al. (1998), at pH values ≤ 4 the reduction of nitrate ions to ammonia by zero valent iron is favorable. Yang and Lee (2005) also promoted the reduction of nitrate in acid medium, obtaining ammonia as the main product of the reaction. Thus, it is possible to verify that the low efficiency of sulfentrazone dechlorination by the Fe/

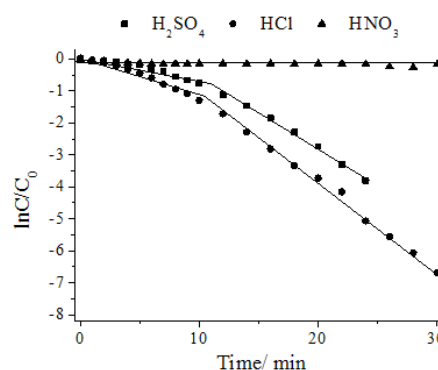


Figure 4. $\ln C/C_0$ of sulfentrazone versus time in the presence of H_2SO_4 , HCl , and HNO_3 . Experimental conditions: $C_0 = 2.58 \times 10^{-5} \text{ mol L}^{-1}$; Reaction time = 30 min; Volume of solution = 200 mL; pH = 4.0; Mass of nanoparticles = 0.200 g; $T = 25.0 \text{ }^\circ\text{C}$. The coefficient of variation between the replicates was lower than 5%.

Ni nanoparticles is due to a competition between the nitrate and sulfentrazone ions for the reactive sites of the nanoparticles, since the reaction occurred at pH 4, which facilitates the reduction of nitrate to ammonia.

Similar results were also found by Lim and Zhu (2008) who observed that in the presence of nitrate and nitrite ions, the dechlorination of 1,2,4-trichlorobenzene using Pd/Fe nanoparticles was less effective. This is due to the fact that these ions can compete with the compound for active sites on nanoparticles, and can also passivate the iron surface, hindering the dechlorination of 1,2,4-trichlorobenzene. Li et al. (2017) verified the nitrate removal by bimetallic Fe/Ni, and verified that about 94% of the nitrate was converted to ammonia by the Fe/Ni nanoparticles.

Kinetic studies of the dechlorination of sulfentrazone were performed and it was verified that the reaction followed the pseudo-first order model, with a mechanism change after approximately 10 minutes of reaction, as can be seen in the graph shown in Figure 4. However, this change in slope was not observed for the system in which HNO_3 was added, since the dechlorination rate was very low, thus making it difficult to observe the mechanism change.

This mechanism change of the reaction was observed in a previous study carried out in our laboratories. The first mechanism of dechlorination was attributed the direct transfer of electrons from iron to sulfentrazone and second mechanism was attributed to the formation of atomic hydrogen (H^*), which is catalyzed by nickel and is responsible for the substrate reduction (Nascimento et al., 2016).

The observed rate constants (k_{obs}) for the dechlorination of sulfentrazone in the presence of $\text{HSO}_4^-/\text{SO}_4^{2-}$, Cl^- and NO_3^- are listed in Table 1. It can be observed that the first mechanism of dechlorination (k_{obs} equals to 0.0766, 0.1331 and 0.0251 min^{-1} for H_2SO_4 , HCl and HNO_3 , respectively) is slower than the second one (k_{obs} equals to 0.2250 and 0.2743 min^{-1} for H_2SO_4 and HCl , respectively), showing that the reaction involving atomic hydrogen is faster when compared to the reaction involving electron transfer.

As can be seen in Table 1, the dechlorination rate of sulfentrazone was slightly faster when HCl was used, i.e., ≈ 1.7 and 1.2 times faster than H_2SO_4 in

Table 1. Rate constants of sulfentrazone dechlorination by Fe/Ni nanoparticles in the presence of H_2SO_4 , HCl and HNO_3 .

Acid	k_{obs} (min^{-1})	
	1 st phase	2 nd phase
H_2SO_4	0.0766 ($\pm 1.29 \times 10^{-3}$)	0.2250 ($\pm 4.56 \times 10^{-3}$)
HCl	0.1331 ($\pm 2.84 \times 10^{-3}$)	0.2743 ($\pm 2.57 \times 10^{-3}$)
HNO_3	0.0251 ($\pm 8.00 \times 10^{-8}$)	-

Experimental conditions: $C_0 = 2.58 \times 10^{-5}$ mol L^{-1} ; Volume of solution = 200 mL; pH = 4.0; Reaction time = 30 min; Mass of nanoparticles = 0.200 g; T = 25.0 °C.

the first and second phases, respectively. Yin et al. (2012) also verified an improvement in the removal of nitrobenzene by Fe^0 nanoparticles in the presence of Cl^- and SO_4^{2-} . According to these authors, in the presence of Cl^- ion, the removal rate was higher when compared to the SO_4^{2-} ion.

Effect of Na^+ , Cu^{2+} and Zn^{2+} cations on sulfentrazone dechlorination by Fe/Ni nanoparticles

The dechlorination of sulfentrazone occurred efficiently (approximately 100%) with both the addition of H_2SO_4 and HCl . Since $\text{HSO}_4^-/\text{SO}_4^{2-}$ anions did not negatively influence the herbicide dechlorination, sulfate salts were used to introduce Na^+ , Cu^{2+} and Zn^{2+} ions into the system.

Effect of Na^+ ions

In Figure 5 it is possible to observe the dechlorination of sulfentrazone as a function of time in the presence of different concentrations of Na^+ . As can be observed, the presence of Na^+ ions in the system did not alter the final rate of sulfentrazone dechlorination, reaching approximately 100% within 30 minutes. Similar results were observed by Shih et al. (2011), who reported that Na^+ ions showed no influence on the dechlorination of pentachlorophenol by Pd/Fe nanoparticles.

The dechlorination in the presence of Na^+ followed the pseudo-first order model, with a change of reaction mechanism, similar to the experiments involving anions. The k_{obs} values for both mechanisms of dechlorination are listed in Table 2. Although the dechlorination efficiency did not change in the presence or absence of Na^+ , the dechlorination rate was slightly increased with the presence of sodium ions. In the first phase of reaction, the k_{obs} increased from 0.0766 min^{-1} in the absence of Na^+ to 0.1338 min^{-1} in the presence of 20 mmol L^{-1} of Na^+ , while in the second phase, the reaction rate increased from 0.2250 to 0.2947 min^{-1} .

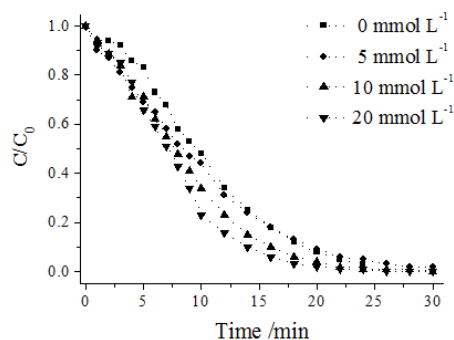


Figure 5. Normalized concentration of sulfentrazone as a function of time in the presence of different concentrations of Na^+ . Experimental conditions: pH = 4.0; $C_0 = 2.58 \times 10^{-5}$ mol L^{-1} ; Volume of solution = 200 mL; Reaction time = 30 min; Mass of nanoparticles = 0.200 g; T = 25.0 °C. The coefficient of variation between the replicates was lower than 5%

Table 2. Dechlorination efficiency and k_{obs} of sulfentrazone dechlorination by Fe/Ni nanoparticles in the presence of different concentrations of Na_2SO_4 , CuSO_4 , and ZnSO_4 .

Cation	Concentration/ (mmol L ⁻¹)	Dechlorination efficiency/%	$k_{\text{obs}}/\text{min}^{-1}$	
			1 st phase	2 nd phase
Without Cation	0	100.0	0.077($\pm 1.29 \times 10^{-3}$)	0.225($\pm 4.56 \times 10^{-3}$)
Na ⁺	5	98.9	0.107($\pm 1.03 \times 10^{-3}$)	0.233($\pm 2.20 \times 10^{-3}$)
	10	99.9	0.134($\pm 3.20 \times 10^{-7}$)	0.295($\pm 1.22 \times 10^{-3}$)
	20	99.5	0.125($\pm 9.52 \times 10^{-5}$)	0.208($\pm 5.18 \times 10^{-4}$)
Cu ²⁺	5	98.4	0.083($\pm 1.86 \times 10^{-5}$)	0.167($\pm 5.20 \times 10^{-5}$)
	10	38.0	0.025($\pm 1.86 \times 10^{-5}$)	0.009($\pm 1.81 \times 10^{-6}$)
	20	13.1	0.073($\pm 1.05 \times 10^{-4}$)	
Zn ²⁺	5	97.7	0.034($\pm 2.38 \times 10^{-5}$)	0.179($\pm 1.60 \times 10^{-4}$)
	10	90.4	0.023($\pm 2.74 \times 10^{-5}$)	0.109($\pm 5.00 \times 10^{-5}$)
	20	91.8	0.031($\pm 2.38 \times 10^{-5}$)	0.113($\pm 1.96 \times 10^{-4}$)

Experimental conditions: $C_0 = 2.58 \times 10^{-5}$ mol L⁻¹; Mass of nanoparticles = 0.200 g; Volume of solution = 200 mL; pH = 4.0; Reaction time = 30 min; T = 25.0 °C.

Sodium ($E^\circ = -2.71$ V) has a much lower reduction potential than iron ($E^\circ = -0.44$ V), so it does not interfere in the reductive dechlorination of sulfentrazone and can be considered an inert electrolyte in the system. Thus, the increase in the dechlorination rate must be associated with the increase in the ionic strength of the system, since the presence of sodium ions enhances the electrostatic interaction between the ions in solution, favoring the transfer of electrons and, consequently, speeding the reaction process.

Effect of Cu²⁺ ions

The effect of different concentrations of Cu²⁺ ions on the dechlorination of sulfentrazone by Fe/Ni nanoparticles can be observed in Figure 6, where it is noticed that the increasing concentration of Cu²⁺ caused a negative effect on the dechlorination process. Sulfentrazone dechlorination by Fe/Ni nanoparticles in the presence of 20 mmol L⁻¹ of Cu²⁺ was strongly inhibited. As the concentration of Cu²⁺ ions increased from 5 to 20 mmol L⁻¹, the dechlorination efficiency

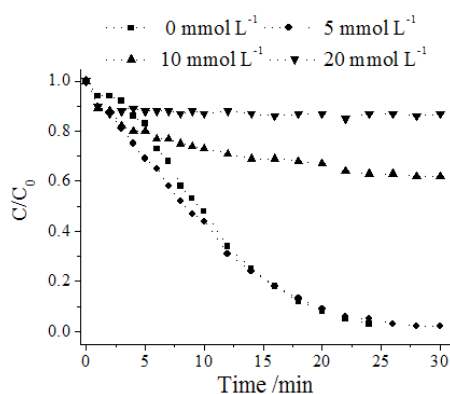
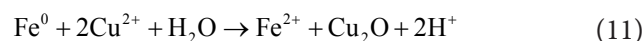


Figure 6. Normalized concentration of sulfentrazone as a function of time in the presence of different concentrations of Cu²⁺. Experimental conditions: pH = 4.0; $C_0 = 2.58 \times 10^{-5}$ mol L⁻¹; Volume of solution = 200 mL; Reaction time = 30 min; Mass of nanoparticles = 0.200 g; T = 25.0 °C. The coefficient of variation between the replicates was lower than 5%

decreased from approximately 100% to only 13% after 30 minutes of reaction.

The dechlorination in the presence of Cu²⁺ followed the pseudo-first order model, with a change of reaction mechanism, similar to the experiments with Na⁺ cation. The k_{obs} values for both mechanisms of dechlorination are listed in Table 2. In general, the kinetics of the second phase decreased considerably with Cu²⁺ concentration increase. For 5 mmol L⁻¹ of Cu²⁺, the k_{obs} were equal to 0.083 and 0.167 min⁻¹ for the first and second phases, while for 10 mmol L⁻¹ Cu²⁺, the k_{obs} values decrease to 0.025 and 0.009 min⁻¹ for the first and second phase, respectively. However, for 20 mmol L⁻¹ of Cu²⁺, it was not possible to observe a change in the reaction mechanism, suggesting that this step is strongly influenced by the presence of this electrolyte.

A possible explanation for this inhibitory effect of Cu²⁺ ions may be associated with their reduction potential ($E^0 = +0.34$ V), which is higher than Fe²⁺ ($E^0 = -0.44$ V); therefore, Cu²⁺ tends to be reduced to Cu⁰. According to Karabelli et al. (2008) Fe⁰ nanoparticles are able to promote the reduction of Cu²⁺ ions to Cu⁰ and Cu₂O according to equations 10 and 11.



Other works have also reported on effects of the presence of copper. Shih and Chen (2010) observed that the presence of Cu²⁺ ions made pentachlorophenol (PCP) molecules less accessible for the reductive dechlorination by Pd/Fe nanoparticles, indicating that Cu²⁺ and PCP ions may undergo complexation, thus decreasing the reactivity of PCP. Kim and Carraway (2000) reported that iron nanoparticles coated with copper were less efficient in the dechlorination of PCP when compared to nanoparticles composed only of iron. It is noteworthy that in that case, Fe/Cu nanoparticles were used.

Therefore, it is believed that Cu^{2+} ions compete with sulfentrazone for the electrons coming from Fe^0 oxidation, generating the Cu^0 and Cu_2O species. These species can be deposited on the surface of the nanomaterials, occupying the reactive sites, thus hindering the sulfentrazone dechlorination. Because of these phenomena, the k_{obs} were ≈ 3 and 19 times lower in the first and second mechanism, respectively, when the concentration of Cu^{2+} increased from 5 to 10 $\text{mmol}\cdot\text{L}^{-1}$.

Effect of Zn^{2+} ions

The effect of different concentrations of Zn^{2+} can be seen in Figure 7. The sulfentrazone dechlorination rate showed a slight reduction with Zn^{2+} concentration increase, being ≈ 100 , 97.7, 90.4 and 91.8% in the presence of 0, 5, 10 and 20 $\text{mmol}\cdot\text{L}^{-1}$ of Zn^{2+} . From the k_{obs} values described in Table 2, it is possible to observe that the reaction rate decreased in both phases of degradation when Zn^{2+} ions were added to the system. In the absence of Zn ions the k_{obs} were equal to 0.077 and 0.225 min^{-1} for the first and second phases, respectively, and already in the presence of 20 $\text{mmol}\cdot\text{L}^{-1}$ of Zn^{2+} the k_{obs} was equal to 0.031 min^{-1} for the first phase and 0.113 min^{-1} for the second phase.

It is known that zero valent iron can be used to remove/degrade several pollutants, including various metals. According to Li and Zhang (2007) because the reduction potential of zinc ($E^0 = -0.76\text{V}$) is close to that of iron ($E^0 = -0.44\text{V}$), the mechanism of removal of Zn^{2+} ions by Fe^0 nanoparticles is mainly due to sorption and/or complexation. Efecan et al. (2009) also observed that the nanoparticles of Fe^0 are capable of uptake of Zn^{2+} ions.

Thus, it is believed that the reduction in the dechlorination rate of sulfentrazone in the presence of Zn^{2+} ions may be associated with the sorption of these ions on the nanomaterial surface, forming a protective

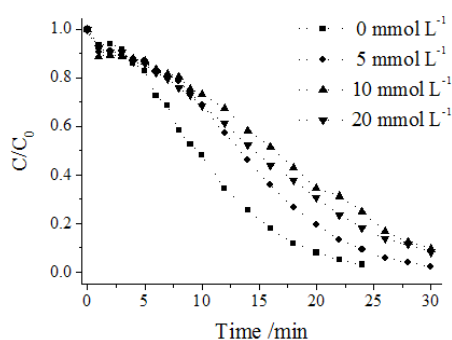


Figure 7. Normalized concentration of sulfentrazone as a function of time in the presence of different concentrations of Zn^{2+} . Experimental conditions: $\text{pH} = 4.0$; $C_0 = 2.58 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; Volume of solution = 200 mL; Reaction time = 30 min; Mass of nanoparticles = 0.200 g; $T = 25.0 \text{ }^\circ\text{C}$. The coefficient of variation between the replicates was lower than 5%.

layer and thereby reducing the availability of the nanoparticles for the herbicide dechlorination.

CONCLUSIONS

The electrolytes evaluated in this work influenced the dechlorination of sulfentrazone by Fe/Ni nanoparticles. With respect to the anions, it can be concluded that sulfate and chloride do not interfere in the herbicide dechlorination. However, nitrate strongly inhibits the reaction, since these ions tend to be reduced by zero valent iron, decreasing the availability of the active sites responsible for sulfentrazone dechlorination. Among the cations, the results show that Na^+ ions have no influence on the dechlorination efficiency of sulfentrazone. However, Na^+ increased the dechlorination rate, because it favors the transfer of electrons and increases the ionic strength of the system. Cu^{2+} ions showed a high inhibitory effect due to Cu^0 and Cu_2O precipitation, resulting from oxidation of Fe^0 . The precipitated copper deposits on the surface of the nanoparticles, occupying its adsorptive and reactive sites, and hindering the reduction of sulfentrazone. Although Zn^{2+} ions influence little the rate of sulfentrazone removal, the dechlorination rate was decreased due to a protective layer formed by the sorption of these ions on the surface of the bimetallic nanoparticles. Thus, it is possible to conclude that the presence of different electrolytes in the system can influence positively or negatively the dechlorination rate of the sulfentrazone herbicide, which will depend on the type of electrolyte and its concentration.

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