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Effect of humic substances on the electrochemical reduction of *p*-nitrophenol

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p-Nitrophenol (PNP) is the main hydrolysis product of methylparathion (MP), one of the most commonly used organophosphate insecticides in the world. Such a product is very toxic for human and animals. Humic substances (HS) are natural recalcitrant organic matter found in soil and waters that have an ability to interact, immobilize, and degrade pesticides. This article presents electroanalytical and UV-Visible studies, conducted to understand the effect of the HS on the PNP reduction process and therefore to understand how the HS can influence PNP degradation in the environment. Electroanalytical results showed that the HS benefit the reduction of the nitro-group of PNP by electrocatalysis. UV-Visible spectra showed that the catalytic effect of HS occurs due to the interaction between the PNP and the HS followed by a proton donor mechanism.

Keywords: Humic substances; *p*-Nitrophenol; Electroanalysis; UV-Visible spectroscopy

1. Introduction

The main hydrolysis product of MP (figure 1) is *p*-nitrophenol (PNP) [1]. According to Manzanilla-Cano *et al.*, the degradation process can be catalysed by transition metals ions like Cu(II) [2]. According to the Environmental Protection Agency, the effects on human health by exposure to PNP for long periods are not completely understood [3].

Humic substances (HS) are natural recalcitrant organic materials resulting from the micro-organism activities on the natural organic material present in soils and waters. Such substances have hydrophilic and hydrophobic sites, due to chemical functions as carboxyl acids, conjugated phenols, and aromatic rings. The HS can interact with

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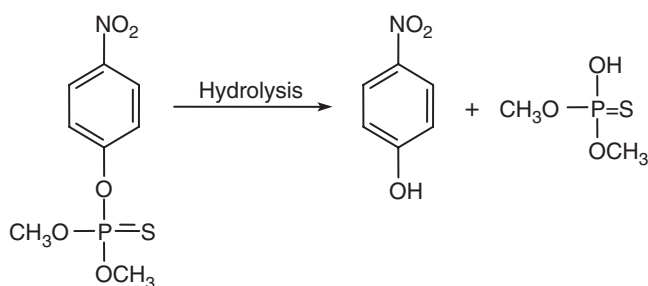


Figure 1. Hydrolysis reaction of methylparathion [1].

organic molecules modifying their chemical activity, efficiency, and mobility. In soils, the HS are important sources for water and nutrients sorption, improving the soil quality for plant production. The HS are known also by their ability to bind organic and inorganic contaminants [4, 5].

Electrochemical methods have been used to study interactions of organic species (pesticides) and inorganic (heavy metals) with HS [6–8]. These works describe several chemical and physical mechanisms. The herbicide metribuzin was determined by a carbon paste electrode modified with HS from vermicompost. It was observed that the current of the reduction peak increases on the modified electrode regarding to the unmodified electrode showing that the herbicide interacts with the HS by a sorption mechanism, increasing the measured current [8]. In a study of the interaction between atrazine and hidroxyatrazine with HS extracted from Brazilian soil, the authors had described that hidroxyatrazine was sorbed by HS due to an electron-transfer complex. In addition, the hydrophobic interactions are pH-dependent sorption [9]. In an earlier study with Imazaquin and HS extracted from a Brazilian oxisoil, the authors had observed that the chemical interactions had involved hydrogen bonding, proton transfer, and cation exchange (at low pH); however, interactions can occur mainly by hydrophobic interactions (weak forces) [10].

Compounds which are derived from the nitro-aromatic group, as the MP and PNP can be analysed by electrochemical techniques like palarography and voltammetry, due to the easy reduction of the nitrobenzene group in mercury electrode [11–17]. The PNP has also been studied by voltammetry with a C18 modified carbon-paste electrode [1] and by a boron-doped diamond electrode [18].

The by-products of MP and PNP obtained by electrolysis [15] are not stable under atmospheric conditions and are easily transformed into other related compounds. In weak acidic conditions ($\text{pH} \leq 6.0$), nitro-groups are reduced to hydroxylamine, which is oxidized, generating other products like quinones and azo-derivatives.

The objective of this work is to evaluate the effect of HS in the electrochemical reduction of PNP in order to understand its electrocatalytic influence. For that, samples containing *p*-nitrophenol with HS were analysed by differential pulse voltammetry in mercury electrodes, and the modification of the reduction peaks was analysed in terms of possible reactions or associations between the HS and the PNP.

2. Experimental

2.1 Characterization of the humic substances

The HS used in this study were a standard humic acid (HA) and fulvic acid (FA) (Suwanee River, GA), cat. # 1S101H and 1S101F, respectively, obtained from the International Humic Substances Society (IHSS). They were characterized by electron spin resonance (ESR) spectroscopy to determine the amount of organic free radicals (OFR) of the samples, which is an indication of the degree of humification [19]. Solid samples of humic or fulvic acids (~25 mg) were put into quartz tubes (0.5 mm i.d.) for ESR analysis with a Bruker EMX ESR spectrometer, operating at the X-band frequency at room temperature. Organic semiquinone-type free radicals (spins concentration) of HS were quantified using an approximation where the spin density was obtained, multiplying the signal intensity by the square width ($I \times \Delta H^2$), based on a secondary standard (a ruby crystal calibrated with strong pitch). Experimental conditions were: microwave power around 0.2 mW and modulation amplitude 0.1 mT.

The acidity of the FA and HA samples was determined by potentiometric techniques [20]. The values were obtained by the International Humic Substances Society [21].

2.2 Influence of the HS on the electrochemical reduction of PNP

Solutions of PNP (5 mg L^{-1}) were prepared after dilution of a stock ethanolic solution (2000 mg L^{-1}) in an electrolyte containing 50 mg L^{-1} of HS and sodium acetate 0.01 mg L^{-1} . Differential pulse voltammograms (DPV) were obtained immediately after the addition of the pesticides to the solutions containing the HS and 24 h after the addition (keeping the samples under stirring and protected from light). The solution pH was measured after each determination. Voltammograms of HA and FA solutions (50 mg L^{-1}) with no PNP addition were also obtained.

Differential pulse voltammograms were obtained with an electrochemical trace analyser, model 293 from EG&G PARC, with a hanging mercury electrode (model 303, EG&G PARC). Platinum wire was used as auxiliary electrode and Ag/AgCl as reference. The experimental parameters were: scan rate of 20 mV s^{-1} , pulse height of 50 mV, and scan increment of 5 mV. Before each determination, the samples were purged with N_2 for 10 min. All determinations were made in triplicate.

2.3 UV-Visible analysis

Interactions of the PNP (5 mg L^{-1}) with the HS (50 mg L^{-1}) were evaluated with UV-Visible spectroscopy in sodium acetate solutions (0.01 mol L^{-1}), varying the pH solution from neutral to acid (6.5–2.5). The UV-Visible measurements were obtained immediately and 24 h after the addition of the PNP in the solution, with a Shimadzu UV-Visible spectrometer (model UV-1601PC).

3. Results and discussion

According to the literature [4–8], the FA samples present a higher solubility, in either acid or alkali media, and a higher acidity compared with the HA, which present a low solubility in acid medium.

Table 1. Acidity and OFR values for the Suwanee River standard HA and FA samples.^a

	HA	FA
COOH (mol kg ⁻¹) ^b	8.43	10.44
AR-OH (mol kg ⁻¹) ^b	3.79	2.69
Total acidity (COOH + AR-OH)	12.22	13.13
OFR (spin g ⁻¹ × 10 ¹⁷)	4.66	2.69

^aOFR measured by electronic spin resonance. Microwave power: 0.2 mW; modulation amplitude: 0.1 mT. COOH and Ar-OH: carboxylic and aromatic acidity, respectively.

^bValues obtained from IHSS [21].

The total acidities (COOH + Ar-OH) of FA and HA were similar, but the carboxylic acidity was higher in the FA sample, as can be seen in table 1.

The OFR values obtained by ESR (table 1) are indicative of the HS humification degree and their hydrophobicity necessary to understand the interactions between HS and hydrophobic organic substances like pesticides. According to the literature [5, 19], the ESR signal is mainly due to a semi-quinone type free radical. As can be seen, the FA sample shows a lower OFR and probably lower hydrophobicity [5].

Differential pulse voltammograms of PNP and HS are presented in figure 2. The PNP presented two reduction peaks: the first at -310 mV and a second with a higher current at -670 mV. These results are in agreement with the literature [1].

For the HA and FA fraction, no significant reduction peak was observed at the negative potential range for the concentration used (50 mg L⁻¹), which was 10 times higher than the PNP concentration used (5 mg L⁻¹).

According to Hernández and co-authors [1], PNP presents a reduction mechanism similar to the MP, but with different values of potential due to the presence of the dimethyl-phosphate group in the MP modifying the redox property of the nitro-aromatic groups [15].

Changes were observed due to the addition of the HS in the solutions with PNP. Immediately after the addition of FA (figure 2a) or HA (figure 2b), an increase in the reduction peak at -310 mV and a drastic decrease in the reduction peak at -660 mV were observed for both FA and HA. After 24 h of interaction, the less cathodic peak decreased, and another peak appeared close to the more cathodic peak, at approximately -550 mV. This behaviour can be attributed to conformational changes of HS due to interactions with the PNP, which changes the electronic distribution of the electroactive molecule and the charge distribution in the system [22].

Changes in the reduction peak potentials to less negative potentials indicate an electrocatalysis phenomenon that can indicate a catalytic degradation of the PNP due to interactions with the HS. A decrease in peak current intensities after 24 h of contact between the HS and the PNP can also be indicative of some degradation of the PNP or strong adsorption/immobilization of the PNP on the HS.

The first stage of the electrochemical reduction of the PNP (-310 mV) becomes favoured after the HS addition compared with the second peak (-660 mV), showing an alteration of the electronic environment in the electroactive substance or showing that HS can act like a proton donor, favouring the reduction by equilibrium displacement [23]. Determinations of the pH in the bulk solution, made immediately before each voltammetric determination, showed no significant pH variation for $t = 0$ and $t = 24$ h.

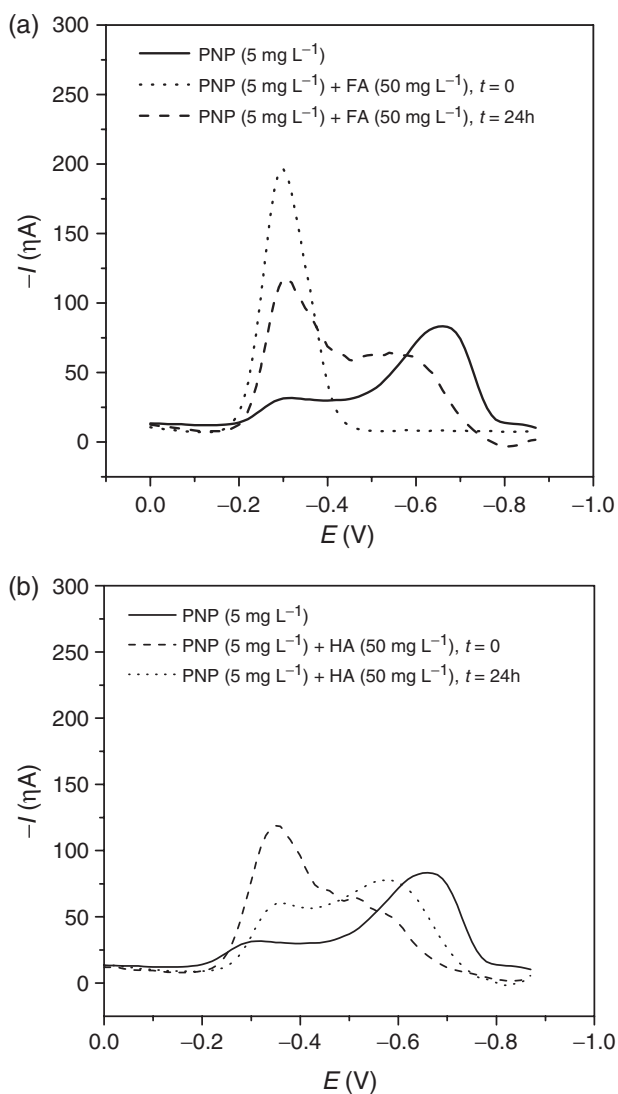


Figure 2. Differential pulse voltammograms of PNP and with the presence of (a) FA and (b) HA immediately after the mixture ($t=0$) and 24h after the mixture ($t=24$ h). Conditions: sodium acetate 0.05 mol L^{-1} as electrolyte, scan rate 20 mV s^{-1} and pulse height 50 mV .

Voltammograms of PNP in acid and neutral conditions are presented in figure 3. The potential displacement to a less negative potential as the pH decreases indicates a dependence of the reduction process on the H^+ concentration in the solution, in agreement with previous results described in the literature [11]. The reduction mechanism of the nitro-group involves the addition of H^\bullet ($\text{H}^+ + \text{e}$) to the system generating $-\text{NO}$, $-\text{NHOH}$ or $-\text{NH}_2$, and H_2O [16].

The results presented in figure 2 also show that the effect of the FA on the reduction peaks variation is more intense than on the HA. This is probably due to differences in their acidity and molar weight that makes the HA less proton donors than the FA.

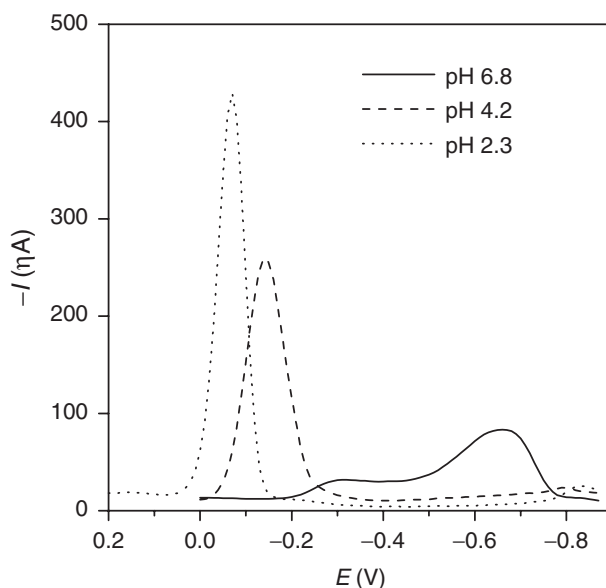


Figure 3. Differential pulse voltammograms of PNP at different pHs (6.8, 4.2, and 2.3) obtained with 0.01 mol L^{-1} NaCl as electrolyte and HCl for acidulation of the samples (pH = 4.2 and pH = 2.3), scan rate 20 mV s^{-1} and pulse height 50 mV .

Interactions of PNP with FA and HA were also analysed by UV-Visible spectrometry. Figure 4 shows the FA, PNP + FA, and PNP UV-Visible spectra in pH 6.8 and also PNP in pH 2.3. Figure 5 shows similar spectra, but with HA in place of FA.

The PNP presents two absorbance bands at approximately 320 nm and 400 nm, and the HS an intense band at about 210 nm with a slow decrease in absorbance, characteristic of the complex constitution of the HS. When the PNP are added to the HS solution, there is an increase in the peak at 320 nm, compared with that at 400 nm, characteristic of acidic medium as verified with the spectrum of the PNP at pH 2.3. According to Fourage *et al.* [24], the absorbance bands at 320 and 400 nm correspond to nitrophenol and nitrophenolate forms, respectively. Humic substances present a naturally similar acid–basic behaviour. According to the literature [5], both humic and fulvic acids are efficient proton donors. Humic substances have hydrophilic and hydrophobic sites, because of several chemical functions as carboxyl acids, conjugated phenols, and aromatic rings, and can interact with organic molecules modifying their chemical activity, efficiency, and mobility. Interactions by hydrogen bonding, between HS phenolic and PNP nitro groups, favour the reduction of the former one, with the phenolic groups acting as proton donors.

These results show that the PNP present similar voltammetric and UV-vis behaviours when in contact with HS at neutral pH or without HS in acidic medium. UV-Visible spectra were also obtained after 24 h of contact, but no changes were observed (data not shown).

These results show that HS can favour the electrochemical reduction of nitro groups in the environment if the medium has reductive conditions, as in the sediments of lakes as described by Keum [25], thus demonstrating the ability of iron to act as an electron source for the reduction of nitro-aromatic substances in an aqueous medium.

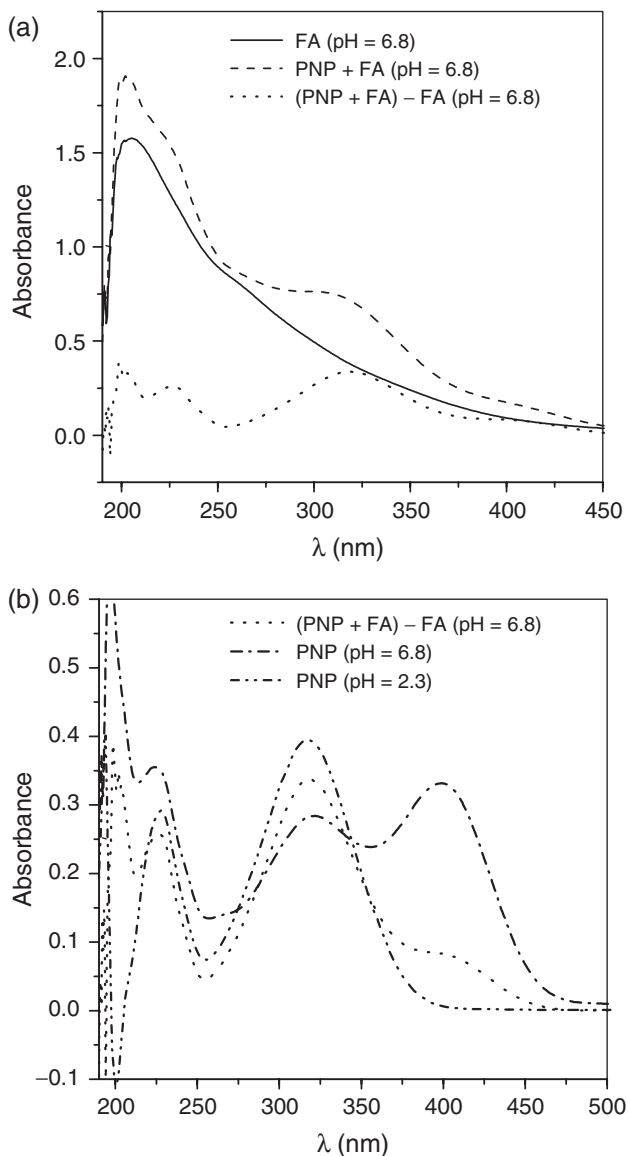


Figure 4. (a) UV-Visible spectra of PNP (5 mg L^{-1}) + FA (50 mg L^{-1}), pH = 6.8; FA (50 mg L^{-1}) and (PNP + FA) - FA; (b) (PNP + FA) - FA, PNP (5 mg L^{-1}), pH = 6.8 and PNP (5 mg L^{-1}), pH = 2.3.

4. Conclusions

Electroanalytical and optical methods have been shown to be useful in evaluating the interaction between HS and PNP. The reduction potentials of PNP are dependent on H^+ concentration, and either humic or fulvic acids are able to be proton donors, catalysing the degradation of nitro aromatic compounds by the reduction route. For this, the differences in interactions of PNP with either FA or HA, verified by the

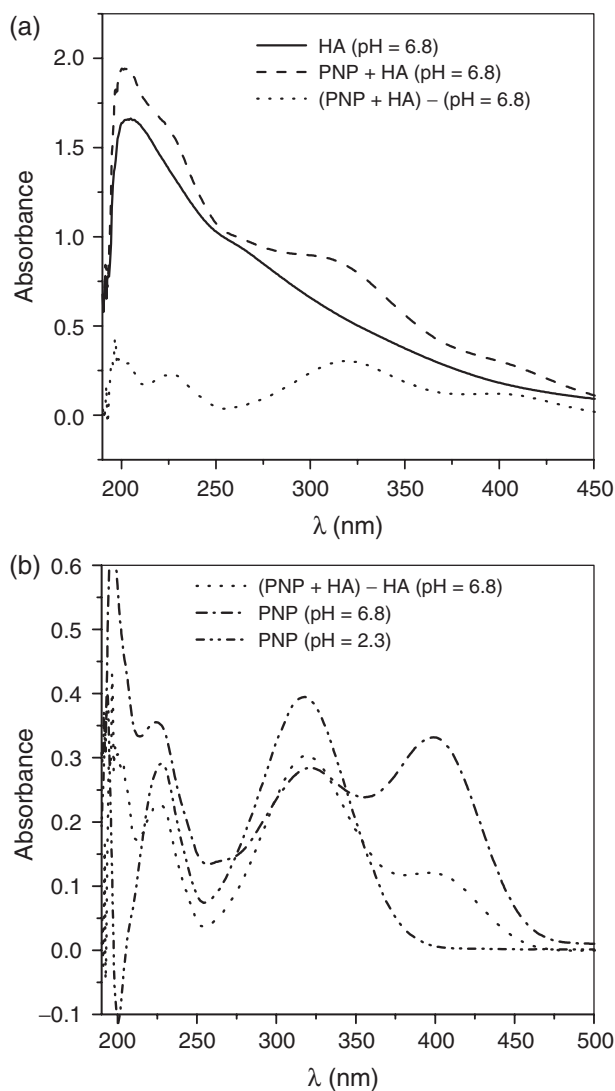


Figure 5. (a) UV-Visible spectra of PNP (5 mg L^{-1}) + HA (50 mg L^{-1}), pH = 6.8; HA (50 mg L^{-1}) and (PNP + HA) - HA; (b) (PNP + HA) - HA, PNP (5 mg L^{-1}), pH = 6.8 and PNP (5 mg L^{-1}), pH = 2.3.

electrochemical technique, demonstrated that the intensity of interaction can depend on the humic substance characteristics. In the environment, the presence of HS and the reduction conditions are naturally found in aquatic media and can effectively act to degrade such compounds.

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