

The influence of humic acids extracted from Chaouia soil on the behavior of transition metal ions and pesticides

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Abstract

Humic acids (HAs) exist ubiquitously in environments and have a variety of functional groups, which allow them to complex with metal ions and pesticides. Furthermore, these interactions can not only alter the environmental behavior, but also influence the removal and transportation of those pollutants. The study of the interaction between Cu (II), VO (II) and Mn (II) with HAs provides environmental information on the oxidation states of paramagnetic metals and their mechanisms of binding to humic acids. Electron spin resonance (ESR) study demonstrates that VO (II) and Cu (II) ions are bound with oxygen ligands to HAs, while the Mn (II) complex occurs as $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$. Additionally, Cu (II) ions are more strongly bound to soil HAs than Mn (II) ions. The effect of the presence of HA on photolysis of Tribenuron-methyl (TRB) and Imazapyr (IMAZ) herbicides in water was studied by irradiation of different mixtures of HA/herbicide (0.5:1 and 1:1 by volume). The kinetic rate constant k of TRB and IMAZ decreases from 0.0029 h^{-1} to 0.0012 h^{-1} and from 0.242 h^{-1} to 0.014 h^{-1} in 0.5/1 HA/herb and 1/1 HA/herb respectively. The obtained results clearly demonstrate that HA substances exhibit a screening effect on the photochemical degradation of the two herbicides. The protective effect of HAs on the TRB and IMAZ degradation could be explained with an inclusion and/or adsorption of the herbicide molecules in the humic matrix.

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1. Introduction

Water pollution has become a critical issue worldwide. The presence of various contaminants such as trace metals ions and organic compounds into the environment and their fate are matters of increasing concern in recent years [1, 2].

The fate of these contaminants in soil and surface water depends upon the physico-chemical behavior of these pollutants. Humic acid (HA) and fulvic acid (FA) exist ubiquitously in the environment and have a variety of functional groups, which allow them to complex with metal ions and pesticides [3], which would provide much needed information on the mobility, transport and immobilization of these elements in terrestrial and aquatic environments. Moreover, these interactions can not only alter the environmental behavior, but also influence the removal and transportation of heavy metals. Thus, this complexation by humic substances can enhance or retard uptake and toxicity of these compounds by organisms [4]. Additionally, transition metals such as VO, Cu, and Mn are biologically essential at trace levels, but can be toxic when present in excess amounts. These elements are found in soil to be incorporated into the structure of humic acids [4, 5]. The humic substances are subject of increasing attention because of their reactivity as sunlight absorbers. They have a significant ability to absorb light and transfer this energy to other substrates and in some cases strongly affect photolysis of xenobiotics [1,5]. Ge and Chen, [6] have reported that humic substances may have some impact as a photosensitizer when irradiated at wavelength longer than 290 nm. They have also been reported to produce oxygen species upon irradiation [7], and be able to photo induce the transformation of pesticides [5, 8]. They could behave as quenchers or as light scatters on the photodegradation kinetics of veterinary drugs and herbicide as well because of their known reactivity under sunlight on the surface of water [9]. Previous research has demonstrated that the presence of herbicide in environmental matrices is affected by different parameters. Additionally, it has been demonstrated that those herbicides are sensitive to UV visible light [10]. However, several factors and experimental conditions such as pH, temperature, oxidative species, irradiation wavelength and water matrix components can affect the photo chemical pathways of certain pollutants in aquatic system. Tribenuron-methyl benzoate (TRB) and Imazapyr (IMAZ) are two widely used herbicides to control a wide range of weeds in cereal crops and sugar beet [11, 12]. However, in long or short term use, these pollutants have a direct relationship with adverse effects in ecosystems and human health [13, 14]. The Food & Agriculture Organization (FAO) carried out in 2015 a survey about the effect of pesticides on human health and environment in Morocco [15]. The results of survey determined that Chaouia plain is an important agricultural area with a big cereals, fodder crops and industrial crops plantations. This plain is characterized by the excessive use of pesticides and groundwater for the agriculture leading to the contamination of the unconfined aquifer by drift, vertical drainage and leaching, the soil of Chaouia plain is also characterized by the high concentration of dissolved organic matter (DOM), which is mostly composed of humic substances (HSs) and can be viewed as a natural constituent in aquatic systems [16]. This work highlights the influence of humic acids extracted from Chaouia soil on the behavior of VO, Cu, and Mn transition metals. The phenomena, factors and potential mechanisms involved in the process are also discussed thoroughly. we tried to assess contributions of photolysis to the degradation of Tribenuron-methyl (TRB) and Imazapyr (IMAZ) herbicide in aqueous solutions by partial simulation of natural conditions with addition of HA and exposure to light.

2. Materials and methods

2.1. Humic acids (HAs) extraction

The HA used in this investigation are from surface horizon (0–20 cm) of soil originated from Chaouia, which is agricultural and semiarid area in Morocco. Main physicochemical properties of the soil from which HA were extracted are ($C_{\text{total}} = 1.56$; $N_{\text{total}} = 0.16$; $\text{pH}(\text{H}_2\text{O}) = 7.7$). HA were extracted by 0.1 M NaOH and 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ (v/v) mixture

under nitrogen [17]. The sample was suspended in 2N HCl to remove carbonates and the above mixture was added with stirring for 16 h. The solution was centrifuged to eliminate suspended clay and acidified at pH lower than 2 with 6N HCl. The HA precipitate was separated by centrifugation and purified by HCl/HF 0.5% (v/v) treatment. Dissolution into alkaline solution and precipitation by acid was repeated three times. The final alkaline solution was passed through an Amberlite IRN 77 cation exchange resin column to obtain an acid form of HA, which dialyzed against distilled water and freeze dried. Characterization of HA was achieved by elemental analysis and determination of acidities [18] with ESR spectroscopy technique. ESR spectroscopy is an adequate technique for the study and for obtaining structural information about transition metal ions in soil organic matter. It can also provide unique information on the oxidation states of paramagnetic metals and their mechanisms of binding to HAs [19]. Therefore, an ESR study of the interaction between VO (II), Cu (II) and Mn (II) with HAs can provide environmental information. 50 mL of HA at concentration (30 mg/L, were exposed for photodegradation at various illumination time. Experiments were carried out at pH = 7.0 (pH of environmental interest), buffered with a mixture of K_2HPO_4 3.9×10^{-4} mol/L and KH_2PO_4 6.1×10^{-4} mol/L (1/1; v/v).

2.2. Metal ions/ HA complexes

Solutions of VO (II), Cu (II) and Mn (II) were prepared by dissolving sulphates in distilled water to produce concentrations of 1, 3, and 5 % (wt-metal ion/wt-HA). Samples containing 100 mg of HA were dissolved in 0.1 M NaOH and precipitated by 6 N HCl at pH values below 2. After centrifugation the fresh coagulates were separately mixed with solutions of VO (II), Cu (II) and Mn (II) ions. The pH value was adjusted in the range of 4-5 by addition of HCl or NaOH. This range of pH corresponds to the dissociation of carboxylic acid groups of HAs [11]. In aqueous systems, HAs are normally insoluble at pH values lower than 6.5. These insoluble HAs are able to react with trace metal ions more efficiently than solubilized ones [11]. Exceptionally for Mn (II)-HA, in order to study the simultaneous competition of Mn (II) and Cu (II) and to identify which is more strongly bound to HA, amounts (<1 mg) of Cu (II) ions were added to Mn(II)-HA solutions. The mixtures were shaken for 24 h at room temperature and each mixture was centrifuged. The precipitates were separated from the supernatant solutions and washed alternatively with distilled water and 1 N HCl in order to remove the non-complexed ions.

2.3. Analytical procedure

2.3.1. Electron Spin Resonance (ESR) Analysis

ESR spectra were recorded at -170 °C, on powder, by a VARIAN spectrometer operating at X band frequency. The spin Hamiltonian parameters of ESR spectra (e.g. g-values and hyperfine coupling constants A) were calculated. For g determination, DPPH (2,2-Di-(4-tert-octaphenyl)-1-picrylhydrazyl) was used as reference substance.

2.3.2. UV-Vis absorption

UV-Vis absorption spectra were recorded using Uvikon 930 spectrophotometer. Total Organic Carbon (TOC) contents were determined with a calibrated Carmograph8 apparatus [19].

2.3.3. Photo-reactor

Photo-degradation processes were carried out using a cylindrical photo-reactor placed in suntest Heraeus apparatus. The irradiation source was xenon lamp (T = 20 °C), which provides a good simulation of solar light. The lamp was placed above the surface of the solution. The solution was homogenized by continuous stirring with a magnetic stirrer.

3. Results and discussions

3.1. Humic acids properties

The main characteristics of HA are shown in table 1. The characteristics of HA are close to those reported in the literature data [20] with some differences in the determined chemical properties such as total acidity and acid group. The spin Hamiltonian parameters (A and g) were calculated from spectra according to the literature data [21]. From all formed complexes, the A and g parameters are listed in table 2. The values of these parameters provide no significant difference from each complex at different percentages. This result indicates that incorporated metal ions occupied the same site in the HAs. The results from the ESR data (A and g parameters) for the investigated complexes are summarized in table 2. For the VO (II)-HA complex, vanadyl ions are strongly immobilized in inner-sphere complexes by HA, with four oxygen donor atoms in equatorial plane of the VO (II) group [18, 20]. For Cu (II)-HA complexes, Cu (II) ions are also associated with four oxygen donor atoms. In the case of Mn (II) complexes, A_{iso} and g_{iso} , suggested that Mn (II) ions are incorporated as $[Mn(H_2O)_6]^{2+}$ by electrostatic bounding only [18, 20]. Oxygen functional groups involved in the complexation of VO (II) and Cu (II) ions can originate from two carboxylates or two hydroxy-phenol for neutralizing the charge of the ions, two other oxygen groups can provide carbonyls or methoxyls [18]. Consequently, VO (II) and Cu (II) ions are bound with oxygen ligands to HAs, while the Mn (II) complex occurs as $[Mn(H_2O)_6]^{2+}$. Also, Cu (II) ions are more strongly bound to soil HAs than Mn(II) ions. These results are in correlation with literature data [18 and 20].

Table 1. Analytical characteristics of extracted HA.

Parameters	Unit	Values
C	%	41.70
H	%	2.51
N	%	2.47
O	% (by difference)	53.32
Total acidity	meq / g	6.04
Phenolic acidity	meq / g	0.77
Carboxylic acidity	meq / g	3.93
Mineral acidity	meq / g	1.34

Table 2. ESR data for VO(II)-HA Cu(II)-HA Mn (II)-HA complexes.

ESR data M(II)-HA	A/(G)	A (G)	A _{iso} (G)	g//	g _⊥	g _{iso}
VO (II)-HA						
1%	197.8	75.8	116.5	1.9354	1.9878	1.9703
3%	193.5	75.7	115.0	1.9193	1.9863	1.9640
5%	194.8	73.2	113.8	1.9340	1.9855	1.9684
Cu (II)-HA						
1%	135.8	Not detected	Not detected	2.3292	2.0759	2.1603
3%	135.2			2.3324	2.0759	2.1614
5%	136.7			2.3364	2.0759	2.1627

Mn (II)-HA						
1%	Not detected	Not detected	96.0	Not detected	Not detected	2.0036
3%			96.4			2.0036
5%			96.4			2.0036

3.2. Photolysis of HA

HA extracted from Chaouia soil, were evaluated for their individuality and properties through elemental analysis E4/E6 ratio and total acidity. HA fraction was composed of EI-C and EI-N (41.7 % and 2.47 % respectively). However, the E4/E6 value, which is the ratio of absorption intensities at 465 and 665 nm, is widely used to characterize HA. The E4/E6 ratio is supposed to decrease with increasing condensation of aromatic humic constituent's [12]. The E4/E6 ratio is governed by the molecular size [22]. Figure 1 represents the values of (TOC) and E4/E6 ratio as a function of time. The results show that the E4/E6 ratio as well as the TOC value are both constant with increasing time of irradiation, reflecting photo-stability of HA molecules after 24 h of continuous irradiation. Higher degree of aromaticity of HA's was evidenced by lower E4/E6 ratio value of 1.91.

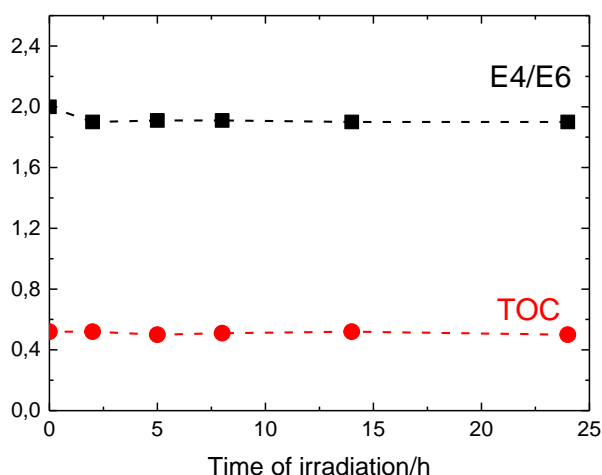


Figure 1. E4/E6 and TOC at different irradiation times.

3.3. Photolysis of HA in the presence of herbicide (TRB and IMAZ) molecules

In order to assess the contributions of photolysis to the degradation of herbicides in aqueous solutions by partial simulation of natural conditions with addition of HA and exposure to sunlight, different mixtures of HA/herbicide (0.5/1 and 1/1 by volume) were prepared and irradiated by solar light. According to the results dissipated in figure 2 & 3, the addition of the HA to the solution of TRB or IMAZ herbicides results in a decrease in kinetic rate constant (k) and a significant increase in the half-life ($t_{1/2}$). The kinetic rate constant k of TRB decreases from 0.0029 h^{-1} to 0.0012 h^{-1} , however the half-life time ($t_{1/2}$) increases from 267.8 h to 552.2 h in 0/1 HA/herb and 1/1 HA/herb respectively. The kinetic rate constant k of IMAZ decreases from 0.242 h^{-1} to 0.014 h^{-1} , however the half-life time ($t_{1/2}$) increases from 2.9 h to 49 h in 0/1 HA/herb and 1/1 HA/herb respectively. The overall kinetic rate constant was decreasing with increasing HA concentration. This screening effect can be explained by prevailing HA-photosensitized reactions over the shielding effect. The second possibility is less probable, as an inclusion and/or adsorption of the herbicide molecules in the humic matrix.

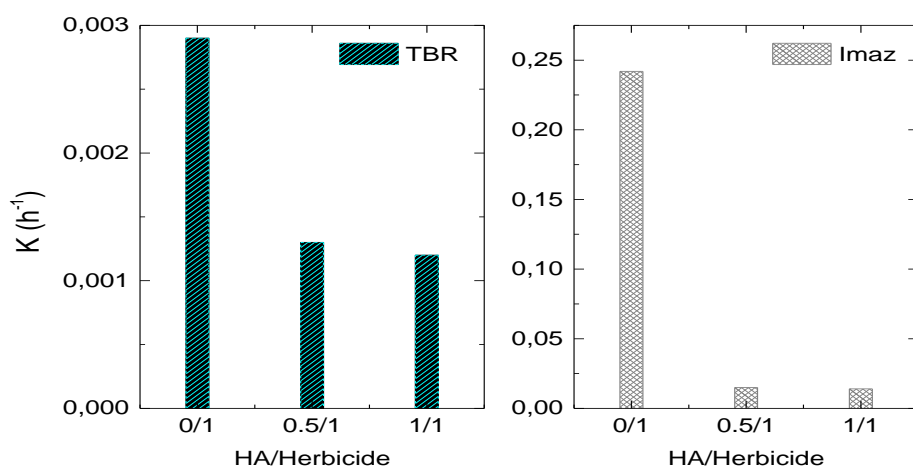


Figure 2. Kinetic rate constant (k) of photolysis of TRB and IMAZ in the presence of HA.

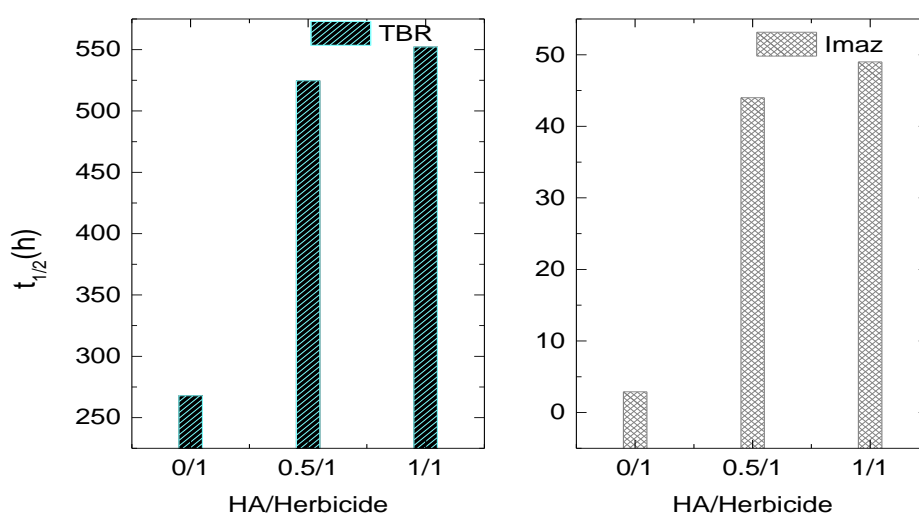


Figure 3. The half-life time ($t_{1/2}$) of photolysis of TRB and IMAZ in the presence of HA.

4. Conclusion

The present study indicated that HAs have complex effects on the removal and environmental behavior of transition metal ions and pesticides. Furthermore, this work demonstrated that the presence of HAs could significantly modify the mechanisms controlling metal ions removal and transportation in aquatic environments. These mechanisms involved complexation, the functional groups involved in complexation can originate from carboxylates and carbonyl groups also the competition between Cu (II) and Mn (II) shows that Cu (II) is more strongly bound to HA, adsorption, electrostatic force, catalysis and so on. The photochemical behaviour of HAs isolated from agricultural soil has been found photostable in buffered solution upon 24 h of irradiation. HAs substances exhibit a screening effect on the photochemical degradation of herbicides. This protective effect induced a decrease of photolysis rate and favors herbicides activity of TRB and IMAZ.

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