

Metal ions removal from water by Humic Acid particles

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Abstract

The current increase of anthropogenic activities causes elevation of metal concentrations in aquatic systems and soils. Natural product such as Humic Acid (HA) may be used as adsorbent or as chelating agent for the remediation of the metallic pollution. In the present work, HA macromolecules was found to form complexes in water with various divalent cations such as Ca(II), Cu(II), Ba(II) Mg (II) and Zn (II). However, the interaction of HA functional groups and the divalent cation was found to be affected by, the nature and the concentration of the divalent cation, the contact time and the aqueous phase pH. In the presence of salt, the HA particle size increased, whereas the absorbance and the surface charge density of HA aqueous dispersions decreased. The cupric ions Cu (II), as compared to the others ions, were found to be the most efficient in increasing the HA particle size and reducing both the absorbance and the surface charge density of the HA aqueous dispersions.

The overall data indicate that the interaction of HA with various ionic species (protons, hydroxyls, divalent cations) may involve ion exchange, complexation, chelating and adsorption processes.

Keywords: Humic Acid, metallic pollution, particle size, absorbance, fluorescence, contact time, surface charge density

1. Introduction

Humus are organic compounds left and accumulated in soils after partial oxidative degradation of the dead biomass residues. Humic acid (HA) is that fraction of humus that is soluble in strong base but precipitates at pH values less than 2. HA is a macromolecule which is rich in aromatic units, aliphatic chains, functional groups, and reveals flexibility and high sensitivity to chemical agents [1]. Humic Acid (HA) is some of the most valuable components of the soil environment, mainly due to its large sorption capacity and also because it is one of the most charged substances among the naturally occurring polyelectrolytes. Because of this feature, HA demonstrates a great impact on soil-buffering capacity [2], and especially the form, bioavailability and retention abilities of metals in soils [3].

Interaction of HA with divalent cations in soil

In soil, as well as, in aquatic medium, Humic Acid (HA) interacts with various species such as metal ions, hydroxides and oxides via various processes such as ion-exchange, surface-adsorption, chelation, coagulation, and peptisation. Further, HA binds also to clay minerals to form complexes having properties and soil stability. Such behaviours of HA particles in soil affect the plant growth, since the primary nutrients (Nitrogen, Phosphorus and Potassium), the secondary nutrients (Calcium, Magnesium, and Sulphur) and the micronutrients (Boron, Zinc, Iron, Copper, Manganese, Molybdenum and Chlorine) may form complexes with HA particles. Regarding the divalent metallic cations investigated in the present work, Me (II), where Me is Ca, Cu, Ba, Mg and Zn, the soluble forms of Me-HA complexes probably enable a slow and gradual release of metal for plant consumption. However, at high metal concentration, the Me-HA complexes become insoluble and their accumulation in the soil leads to toxic effects [4, 5].

The complex formation between the HA and the divalent metallic cation results from the HA chemical structure. This latter is a natural organic polyelectrolyte having anionic functional groups, bearing carboxylic and phenolic groups. These functional groups may have strong interactions and/or form complexes with trace metal ions as observed by several authors [6-9]. On the other hand, the presence of divalent cations in aquatic environment have a relatively strong effect on the adsorption of HA from water onto mineral particles such as quartz and clay particles [10-12, 1]. Others authors have shown that the interaction occurring between HA particles and ionic species is controlled by the pH, and/or the ionic strength of the aqueous phase [8, 13-17]. Such HA interaction with ionic species is due to both specific and columbic interactions [15, 18]. According to Gu et al. [18], the adsorption mechanism of HA onto iron oxide, is based on the ligand-exchange between HA carboxylic/phenolic groups and the mineral surface. Other investigations dealing with the sorptive behaviour of HA on solid surface, have demonstrated that the HA adsorption increases with increasing salt concentration at fixed pH, and that the adsorbed trace metals (Cu^{2+} , Pb^{2+}) on humic-coated mineral oxide reduced the mobility of colloids [6, 19].

In a recent work, we reported on HA surface charge, and batch adsorption experiments (closed flow-through reactor), on quartz sand particles [1]. In the present work, our investigations deal with the interaction of a commercial HA with various divalent cations Ca(II), Cu(II), Ba(II) Mg(II) and Zn(II), in aqueous medium. The aim of the study is to throw light on the interaction mechanisms occurring between the divalent cation and the HA functional groups. Such interaction was tuned by varying various parameters such as, the cation-HA contact time, the aqueous phase pH, the HA and the divalent cation concentration.

2. Material and methods

2.1. Materials

A commercial Humic Acid (HA) purchased from Aldrich was used in the present work. The HA-aqueous dispersions having concentrations in the range 10-50 ppm were prepared by diluting a 100 ppm stock aqueous solution of HA. The HA aqueous dispersion pH was varied in the range pH=3-11, by adding aliquots of either HCl or NaOH standardized

aqueous solutions to the HA dispersions. Appropriated amounts of various salts MgCl₂ (Aldrich), BaCl₂ (Rectapur), CuCl₂ (Aldrich), CaCl₂ (Prolabo), ZnCl₂ (Aldrich), were weighted in volumetric flasks which were then filled with water to yield divalent cation with the desired final concentration.

2.2. Methods

2.2.1. Absorbance and fluorescence

The absorbance of the sample was measured at wavelength, $\lambda=380$ nm, by using a Shimadzu UV-VIS spectrophotometer. The fluorescence emission spectra in the wavelength range 400-600 nm, and excitation wavelength $\lambda=378$ nm, were measured with a fluorometer Shimadzu RF-5001 PC type.

2.2.2. Streaming Induced Potential

The interaction of HA acid particles with various divalent cations, was evaluated by titration of the HA aqueous dispersion with the respective salt, CuCl₂, ZnCl₂, MgCl₂, CaCl₂ and BaCl₂, and measuring the resulting Streaming Induced Potential (SIP). A potential measuring device (particle charge detection, PCD, Müteck instrument) was used for the measurements of the SIP values, as described elsewhere [20]. It should be mentioned that the PCD Müteck instrument allows the measurement of only relative potential values, [21].

2.2.3. Dynamic Light Scattering

The sizes of HA particles dispersed in aqueous solution in the absence and in the presence of various salts, were measured by dynamic light scattering (DLS), using Coulter Model N4S (Coultronics) apparatus [22]. This technique analyses particles in suspensions within the diameter range 3–3000 nm and operates with a laser 4 mW helium-neon (wavelength = 632.8 nm), and an optical system to detect at 90° angle the light scattered by the sample. The DLS measures, as described elsewhere [23], were based on a conventional Rayleigh z-average data analysis, and it calculates the average particle size from the measurement of the sample diffusion coefficient by photon correlation spectroscopy. Briefly, an autocorrelation function, $G(\tau)$, of the scattered-light intensity $I(t)$ is collected over 64 values of the delay time (τ). For monodisperse dispersions, the autocorrelation function $G(\tau)$ is a single decaying exponential, where the decay constant is inversely related to the HA particle diameter, according to the Stokes-Einstein equation and assuming spherical geometry for the particle shape. However, for polydisperse HA aqueous dispersions, the autocorrelation function, $G(\tau)$ is the sum of the exponentials for each component size. In this case, the HA particle average size value is calculated by the methods of cumulants [22, 23].

For the measurement of the HA particle size as function of time, a stopwatch was used. Thus, a known volume (3 ml) of the HA aqueous dispersion was placed in the sample cell to which ≈ 980 μ l of salt was added, and at the same time, the stopwatch was triggered to measure the elapsed time. The particle size was measured at regular intervals of one minute and for a total duration of 30 min.

2.2.4. Scanning Electronic Microscopy

- For the Scanning Electron Microscopy (SEM) analysis, the HA aqueous dispersions and their mixtures with various salts were first prepared and after a while, they were filtered through a Millipore filter (GSWP 0.22 μ m, diameter of 47 mm). Thereafter, the filters containing the filtrates were placed in the oven heated at temperature $T=60$ ° C for two days. The dried HA samples were then observed by SEM. The SEM images were performed by using an FEI Quanta 400 ESEM. The instrument is equipped with the Everhart Thornley Detector (ETD) as a Secondary Electron (SE) detector, and Energy Dispersive X-ray detector, Oxford, INCA Instruments. The electronic microscope was operating at electrical potentials of between 12.5 and 30 kV, and working distance (WD) ranging between 9.1 and 11 mm.

3. Results and discussion

3.1. Absorbance and fluorescence

Fig 1 shows the variation of the absorbance as measured at $\lambda=380$ nm, for HA aqueous dispersions at various pH.

Fig. 1

As can be observed in Fig 1, as the HA concentration increases, the absorbance increases in accordance with the BEER-LAMBERT law. In addition, Fig 1 shows that the absorbance reaches its highest values at pH=3 and pH=11, as resulting from the increase of the HA surface charge at these extreme pH values. The lowest absorbance of HA aqueous dispersion is reached at pH=7.26. Figs 2 and 3 indicate decrease of, respectively, the absorbance and the fluorescence emission intensity of HA aqueous dispersion, when the salt and the CuCl₂ concentrations increase.

Fig. 2

Fig. 3

Such behaviours of HA aqueous dispersions in the presence of divalent cations result from the surface charge screening of HA particles and reduction of the electrical double layer thickness at the solid-water interface, leading hence to HA particle aggregation and fluorescence quenching.

3.2. Particle size

Fig. 4, shows the HA particles size variations with the cation-HA contact time, for various salts (CaCl₂, BaCl₂, ZnCl₂, MgCl₂, CuCl₂).

Fig. 4

In all instances, the data indicate that the presence of salt increases the HA particle size, but at different degrees. Thus, the cupric ions, as compared to the others ions, give the highest HA particle size.

The comparison of the HA particle size data allows us to make the following classification (1):



Thus, the cupric ions, compared to the others cations, are the most efficient in forming complexes with HA particles.

3.3. Streaming Induced Potential (SIP)

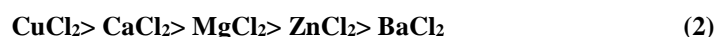
Fig. 5 shows the variation of the Streaming Induced Potential (SIP) of HA particles versus the mole number of the various salts added to HA aqueous dispersion.

Fig. 5

In the absence of divalent cations, the HA particles are negatively charged as resulting from the ionisation of its functional groups (mainly carboxylic groups) at natural pH=8. It was then expected that the initial SIP value of HA aqueous dispersion was negative and the addition of the positively charged divalent cation will decrease the initial SIP magnitude. As shown in Fig. 5. It should be noted that instrument allows the measurement of only relative potential values; that is why the SIP initial value was not constant as can be seen in Fig. 5.

Further, Fig. 5 shows also that the divalent cations screen the HA negative surface charges at different degrees. Thus, important decrease in HA particles SIP initial value is observed in the presence of cupric ions as compared to the others divalent cations. Such decrease in the SIP value results from the strong complexation occurring between the negatively charged HA functional groups and the positively charged cupric ions.

From the data depicted in Fig. 5, it possible to classify the chelation efficiency according the following order (2):



Hence, lowest amount of CuCl₂ salt whereas higher amount of BaCl₂ salt, are needed for the neutralization of the HA aqueous dispersion.

And as we mentioned above, cupric ions are also the most effective for neutralizing the HA surface charge,

Therefore, there is a correlation between the particle size and streaming induced potential measurements of HA particles aqueous dispersions in the presence of various salts.

3.4. Scanning Electronic Microscopy (SEM)

Fig. 6 below shows SEM image of the HA aqueous dispersion retentate recovered on Millipore filter (0.22 μm). This HA dispersion was prepared in the absence of salt and at initial HA concentration of 103 ppm.

Fig. 6

The image shows both some residual retained HA particles, and the filter surface which is made of cellulose ester fibers. As can be seen in Fig. 6, few HA particles are retained on the filter, in agreement with the UV analysis of the filtrate (83.5 ppm). Thus a large fraction of HA particles (sizes smaller than 0.22 microns) are in the permeate. These data agree with the particle size measured in the absence of any salt which gives a diameter of HA particle around 149 nm.

Fig. 7 shows SEM image of HA particles, as prepared in the presence of ZnCl_2 salt, and filtered through a Millipore filter (0.22 μm).

Fig. 7

The image in Fig. 7 shows agglomerated HA particles resembling to sheets. Further, Fig. 7 indicates the absence of large cracks in the dried retentate which results from the less efficient complexation occurring between HA and the divalent cation, the almost salt added to HA particles is in the permeate.

Fig. 8 shows SEM image of HA particles, as prepared in the presence of CuCl_2 salt and filtered through a Millipore filter (0.22 μm).

Fig. 8

As can be observed in Fig. 8, the image indicates the presence of large cracks in the dried retentate as resulting from the efficient complexation occurring between HA and the cupric ions, i.e. a large fraction of CuCl_2 salt remains in the retentate. Cracks can result from the salt drainage (due to the low solubility of HA in the water) to the edges of the drops during the drying process at 60 ° C. The presence of salt at the edges of the drops is responsible for the retention of water, and the latter during its evaporation leaves cracks.

Conclusions

The present study has shown that natural substances such as Humic Acid (HA) macromolecule play a role in metallic depollution of both polluted water and soil. The HA-divalent cation interaction was found to be function of various parameters such as the pH of the aqueous phase, the HA and the metal ion concentrations.

Among the metal ions investigated here, Cu (II) ions were found to interact efficiently with HA functional groups, leading in water to HA particles having larger sizes, and giving in the dried state, HA sample retaining the maximum amount of salt. The HA aggregates observed in the presence of the divalent cations result from the association of HA nanoparticles.

Acknowledgment

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Figures and Tables captions

Fig. 1: Absorbance of HA aqueous dispersions at various pH and HA concentrations.

Fig. 2: Absorbance of HA aqueous dispersions in the presence of different kind of salts at various concentrations.

Fig. 3: Emissions spectra of HA aqueous dispersions in the presence of CuCl₂ at various salt concentrations.

Fig. 4: Variation with time of the HA particle size, as prepared in the presence of various salts.

Fig. 5: Variation of the Streaming Induced Potential (SIP) of HA particles in the presence of various divalent cations with increasing amounts.

Fig. 6: SEM image of the HA aqueous dispersion retentate, prepared in the absence of salt, and recovered on Millipore filter (0.22 μm).

Fig. 7: SEM image of HA particles, as prepared in the presence of ZnCl₂ salt, and filtered through a Millipore filter (0.22 μm).

Fig. 8: SEM image of HA particles, as prepared in the presence of CuCl₂ salt and filtered through a Millipore filter (0.22 μm).

Fig. 1

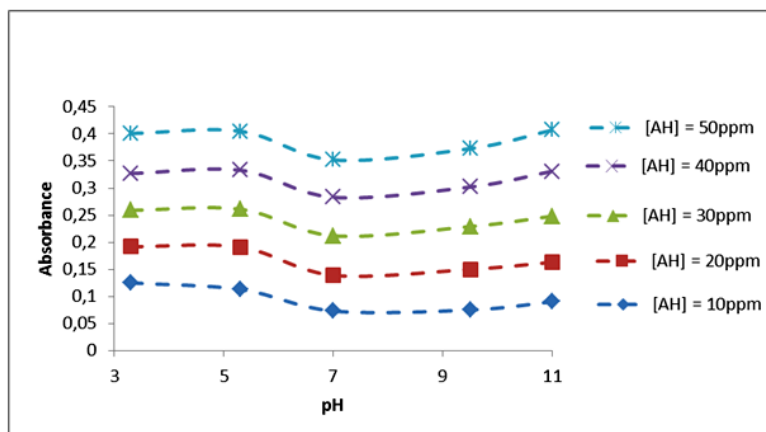


Fig. 2

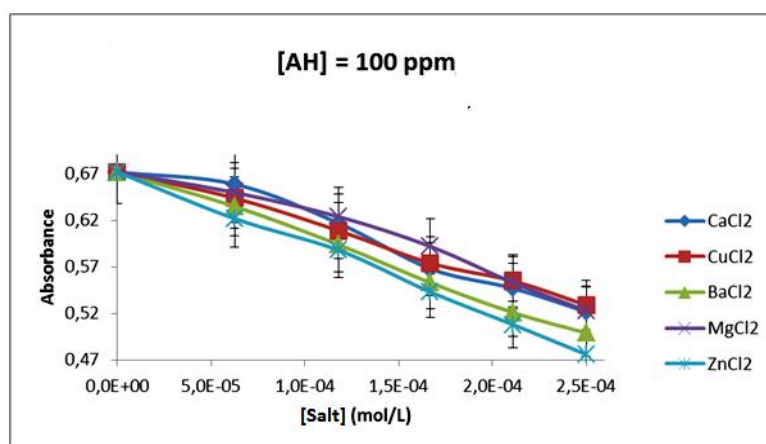


Fig. 3

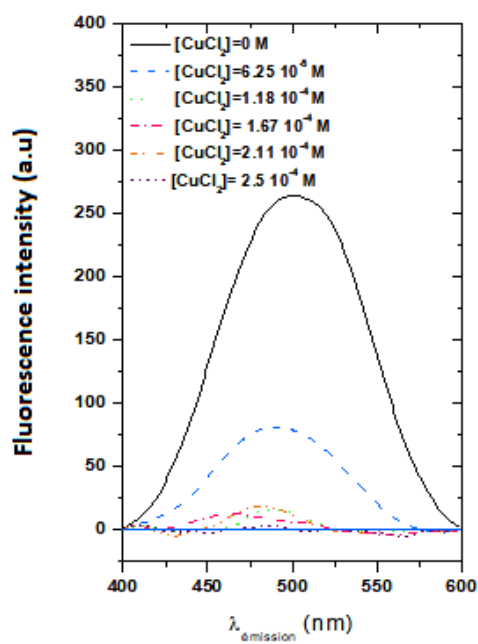


Fig. 4

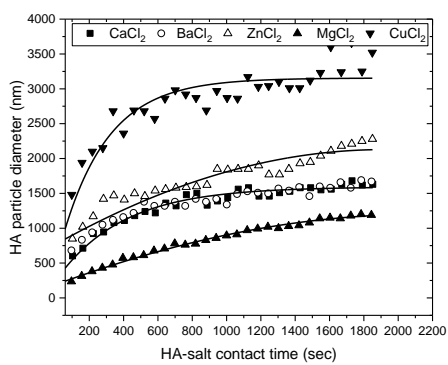


Fig. 5

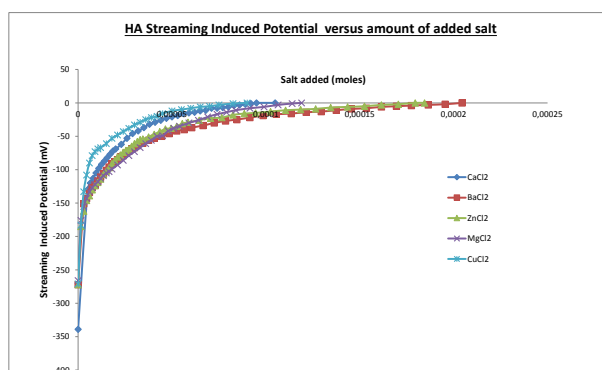


Fig. 6

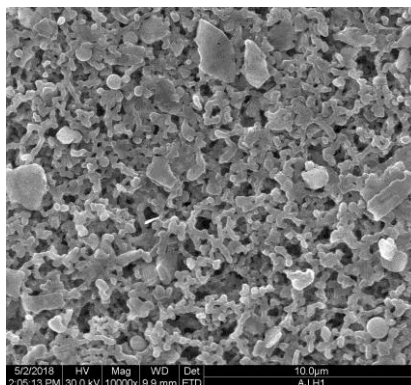


Fig. 7

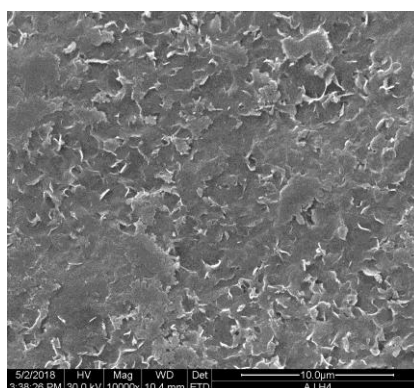


Fig. 8

