

Mobilisation of Heavy Metals from Natural Pozzolan by Humic Acid: Implications for Water and Environment

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Abstract- Natural pozzolans and similar geomaterials derived from volcanic eruptions contain heavy metals in significant or trace amounts, viz Cr, Co, Pb, Cu, Ni, Zn. Rain water, being essentially soft water as is the case in tropical Africa, can dissolve these metals and thus facilitate their transport into surface waters or through soil into ground water. Soil humic substances produced principally by biogeochemical decomposition of plant residues are rich in humic and fulvic acids which are known to complex heavy metals. Mobilisation of heavy metals (Cr, Pb, Co, Cu, Ni, Zn) presented in a sample of black pozzolan from Djoungo, Cameroon, in the presence of humic acid extracted from river sediment was studied at $20.0 \pm 0.1^\circ\text{C}$, pH 6 and 8 in a Jar test (batch stirred reactor) for contact times of 5 min and 24 hr and variable humic acid concentration (0.5 to 75 mg/L). The heavy metals were analysed by plasma spectroscopy (ICP-AES). Results showed that generally, the presence of humic acid increases the release of these heavy metals by pozzolan and this depends on time and pH. At pH 6, humic acid mobilised more heavy metals than at pH 8. For some metals (Cr, Zn, Cu), the amount released in the presence of humic acid, increased and levelled off with increase in humic acid concentration. Whereas for others (Pb, Co), the amount increased continuously. This suggests that humic acid acts as a heavy metal sink in contact with pozzolan or volcanic scoria, immobilising them and preventing their transport to the water table.

Key words- Heavy Metals; Pozzolan; Humic Acid; Water

I. INTRODUCTION

Environmental contamination due to the products of volcanic activity is a major preoccupation today. During volcanic eruptions, various particles are projected on the ground, and according to their mineral composition and shape natural pozzolans and volcanic ash ..., may be found. Their chemical composition presents trace metallic elements such as chromium, copper, zinc, cobalt, nickel, vanadium, in their structure [1], [2]. These trace elements may diffuse through the soil and be found in ground waters in different areas. Considering the fact that the soils in volcanic areas are very fertile, many crops are cultivated in these areas, resulting in the increase of humic acid concentration in the soils.

Humic substances, mainly composed of humic and fulvic acids, are produced by the decomposition of organic materials of plant and animal origin. Due to their polyfunctional macromolecular structure that varies according to their biological origin and their formation process, humic substances can form complexes with heavy metals ([3]).

Physico-chemical properties of soil (porosity, texture, content of humic substance,) influence the mobility of

inorganic pollutants. The content of humic substance plays a major role on the ability of soil to raise the metal elements. Humic substances are commonly described as heterogeneous compounds containing both a large proportion of oxygen-containing functional groups, and segregated aromatic and aliphatic moieties ([4]). Many studies have been conducted to explain the interactions between heavy metals and humic substances in surface waters [13], [6] and in soils [7], [8]. Many functional groups are found in the structures of humic substances which includes COOH, phenolic, and alcoholic. The work of Reference [9] showed the participation of these functional groups in the complexation of cationic metals. The results of their work showed that in majority hydroxyl and carboxylic groups play a major role in the interaction with metallic compounds. The structural complexity of humic molecule less assume that during interaction there is contribution of other processes: interaction of other heteroatoms like nitrogen and sulfur [10], [11], simple physisorption phenomena, saturation of metal coordination in chelate type structure [12]. Reference [7] shows evidence of the formation of complex among Cu^{2+} , Pb^{2+} , Ca^{2+} and humic acid by infra red technique.

General retention of metallic compounds are due to coulombic interactions between positively charged cations and negatively charged anions of humic acid [13], and the cations compete for the anionic groups in the humic acid molecules [20]. The influence of pH on the surface activity of humic acid has been investigated by many authors [13], [14], and it was found that the surface tension for HA solution gradually decreased with increasing concentrations of HA. The structure and the conformation of humic acid were influenced by the pH and decreased with the concentration of humic acid.

The objective of this work is to gain a better understanding of the interaction between released pozzolan metals in aqueous solution and humic acid.

II. MATERIALS AND METHODS

A. Sampling, Extraction, and Characterization of Nyong Humic Acid (NHA)

The humic acid used in the present study was extracted from Nyong river sediment (Cameroon) ($3^\circ 51' \text{ N}$, $11^\circ 5' \text{ E}$). The sampling site, the separation and the purification method of humic acid fractions are described elsewhere [14]. Elemental analysis of NHA was carried out with Carlo Erba

1108 auto analyser. Infrared analysis (1 mg NHA mixed with 250 mg KBr) was carried out with a Bruker IFS 55 spectrometer in transmission mode (200 scans collected at 2 cm^{-1} resolution in the 4000-400 cm^{-1} range), and the FTIR bands are described elsewhere [14].

The $\{^1\text{H}-^{13}\text{C}\}$ CP/MAS spectrum was obtained with a Bruker ASX 500 instrument at 125.77 MHz, spinning at 10 kHz, with a $\pi/2$ pulse of 8 s, contact times of 1 ms, recycle delays of 5 s and around 14 000 transients; line broadening procedure (100 Hz) was applied before Fourier transform, and the chemical shifts were quoted relative to TMS. CPMAS ^{13}C NMR spectra of Nyong humic acid was described elsewhere [14].

B. Sampling, Preparation, and Characterization of Black Pozzolana of Djoungo (BPD)

The pozzolan used in this study comes from the Tombel graben located at Djoungo quarry (4.35°N, 9.37°E) in Cameroon. This quarry is exploited by a cement (Cimenterie du Cameroun) enterprise, for the manufacture of the cements in its cement factory.

Pozzolan samples were crushed with a hammer crusher (Retsch, Germany) and particles of sizes less than 600 μm were retained. The obtained sample was crush with a Retsch disk (Germany) and the resulting powder sieved under agitation (Retsch D 42781, Germany) with a Saulas sieve of 38 μm (France). The mean size of the particles measured with a granulometer Master Sizer (Malvern Instruments Ltd, England) was 10.4 μm .

Elemental analyses of pozzolan powder (particle of 10.4 μm medium size) were performed using ICP-AES (Quantometer JY 70 type II with ICP plasma, Jobin Yvon 70).

C. Experimentation

Experiments were conducted at room temperature ($20.0 \pm 0.1^\circ\text{C}$) in a batch reactor of 50 mL (polycarbonate centrifuge tubes) containing 0.25g of pozzolan and 40 mL of humic acid at various concentrations (0.5 to 75 mg/L), at pH 6 and 8 and contact time 5 min and 24 h. The polycarbonate centrifuge tubes were closed and placed on a shaker table model Gerhardt (Fischer Scientific, France) with a controlled horizontal oscillation of 350 rounds per minute (rpm). At the end of agitation, the tubes contents were centrifuged at 5000 rpm with an Eppendorf centrifuge 5804 (FRG) for 20 min. The contents were then filtered using 0.2 micron polycarbonate filters (CycloporeTM Track Etched Membrane, UK) and the filtrates were analyzed under the same conditions by ICP-MS to determine the trace elements leached into solution by the pozzolan and fixed by humic acid. Blanks with the same amounts of reagents were carried out under the same conditions to assess possible contamination.

III. RESULTS AND DISCUSSION

A. Chemical Composition of Pozzolan and Humic Acid

Chemical composition of Djoungo pozzolan is given in Table 1. Djoungo pozzolan contains mainly silica (46.08%), alumina (16.43%) and Fe_2O_3 (12.65%), and the percentage of CaO, MgO and alkalis is around 15%. From this analysis, the level of SiO_2 , Al_2O_3 and Fe_2O_3 is consistent with the general chemical composition of pozzolan [15], [16]. The amount of alkali and earth alkalino is above 15%. Our results are similar to that of Reference [1] who concluded that the scoria of

Djoungo was composed of plagioclase, pyroxene and olivine in a glass matrix. Trace elements (Table 1) were found in the pozzolan matrix.

TABLE I CHEMICAL COMPOSITION OF BLACKPOZZOLANA FROM DJOUNGO (OXIDES ARE EXPRESSED IN PERCENTAGE WEIGHT)

Major Elements						
SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Total
46.08	16.43	12.65	0.18	5.51	9.62	90.47
Na_2O	K_2O	TiO_2	P_2O_5	P.F.		Total
3.90	1.51	2.88	0.52	-0.28		8.53
Trace Elements (ppm)						
Sr=689.8	Ba=423.8	Zr=273.8	Pb=154.3	Cr=145.5		
Ni=49.1	La=45.2	Nd=42.2	Co=34.4	Rb=33.1		
Zn=116.1	Ce=89.4	Cu=49.61	Nb=57.1			
Ga=21.5	Y=26.1	Sm=8.3	Gd=7.1			

Elemental analysis of humic acid indicated 49.6% C, 4.3% H, 3.5% N, and 41.8% O contents. It appears, however, that the elemental composition of humic acid Nyong overall framework with the statistical average ([11], [17]).

B. pH and Time Effect

The effects of pH and time on the retention of trace elements are shown in Figures 1 to 5. Figure 1 presents the overall concentration of chromium with the Humic acid concentration. The amount of adsorbed chromium increased at low concentration of humic acid to reach a maximum and then it steeply remained constant at both pH and time. At both investigated pH, the amount of adsorbed chromium at 24h was higher than the adsorbed amount at 5 min, while the amount adsorbed at pH 6 was higher than the amount adsorbed at pH 8.

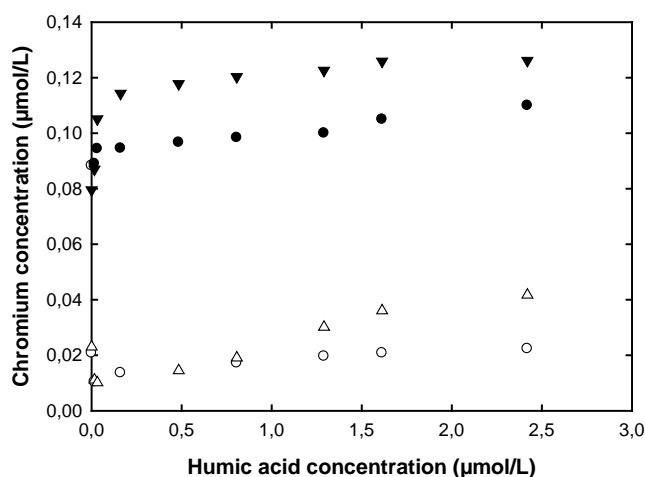


Fig. 1 Retention of chromium in solution by humic acid at pH 6 and 8 (● 5min at pH=6, ○ 5min at pH=8, ▼ 24h at pH=6, △ 24h at pH=8)

Figure 2 shows the retention of lead by humic acid. The amount retained increased continuously at both pH. At pH 6 there is a linear relationship between the amount of lead retained and humic acid concentration ($R^2 = 0.99$ at 24h and 0.96 at 5min). The curve at pH 8 shows two domains: at humic acid concentration between 0.016 and 1.61 $\mu\text{mol/L}$ there is stronger increase in the amount of lead adsorbed. For concentrations of humic acid higher than 1.61 $\mu\text{mol/L}$ the

amount adsorbed re-increased but with a lesser slope. The amount adsorbed at pH 8 is higher than the amount adsorbed at pH 6 at humic acid concentration higher than $0.5 \mu\text{mol/L}$. The strong increase can be attributed to the release of sodium ions from the functional group of humic acid and interaction with lead released in solution by pozzolan. The linearity observed at pH 6 shows a relationship between the rate of lead released in solution and the rate of lead adsorbed by humic acid.

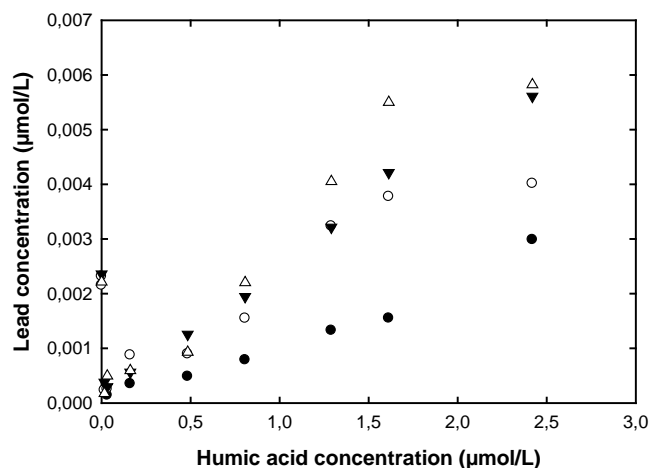


Fig. 2 Retention of lead in solution by humic acid at pH 6 and 8 (● 5min at pH=6, ○ 5min at pH=8, ▼ 24h at pH=6, △ 24h at pH=8)

Figure 3 illustrates the influence of pH and time on the retention of cobalt by humic acid. For both, there is a linear relationship between the amount of cobalt retained and humic acid concentration ($R^2 > 0.97$ at 24h and 0.96 at 5min). The amount of cobalt retained by humic acid at 24h was higher than the one at 5min and the amount adsorbed at pH 6 was higher than the amount adsorbed at pH 8. The explanations are the same as the case with lead.

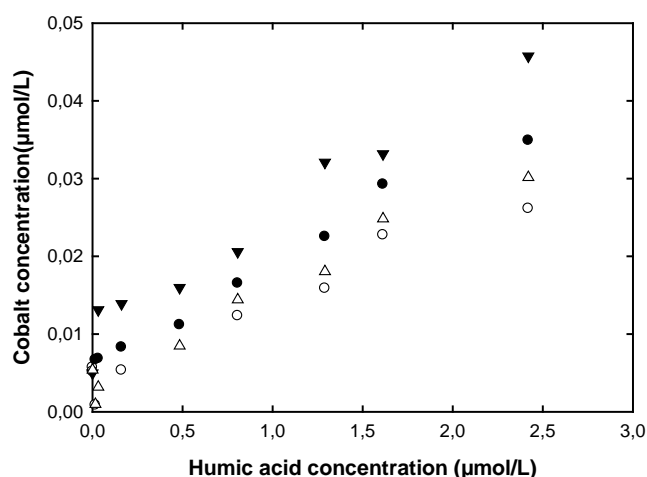


Fig. 3 Retention of cobalt in solution by humic acid at pH 6 and 8 (● 5min at pH=6, ○ 5min at pH=8, ▼ 24h at pH=6, △ 24h at pH=8)

Figure 4, the retention of nickel in solution by humic acid showed a linear increase as a function of humic acid concentration at pH 6 ($R^2=0.99$), while at pH 8 the amount adsorbed is low and did not vary with increasing humic acid (Fig. 4). The amount adsorbed at pH 6 was higher than the amount adsorbed at pH 8. The amount of nickel adsorbed at 24h was higher than the amount adsorbed at 5 min.

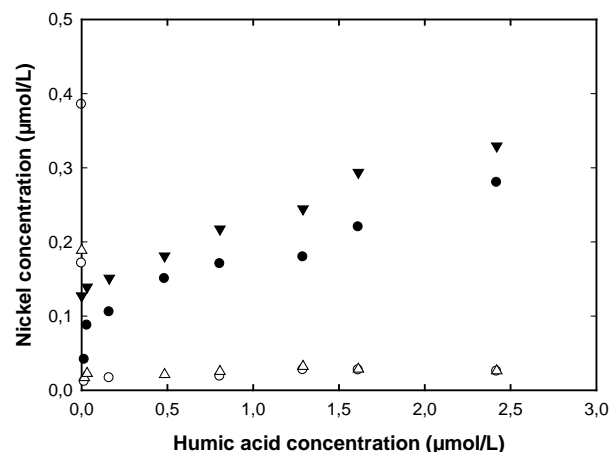


Fig. 4 Retention of nickel in solution by humic acid at pH 6 and 8 (● 5min at pH=6, ○ 5min at pH=8, ▼ 24h at pH=6, △ 24h at pH=8)

Figure 5 shows the amount of zinc retained as a function of humic acid concentration. At both pH values, the curve showed an initial steep slope until a humic acid concentration of $1.62 \mu\text{mol/L}$ and reached a plateau at an elevated equilibrium humic acid concentration indicating a high affinity for interaction of zinc with humic acid. The amount retained at pH 6 was higher than the quantity adsorbed at pH 8.

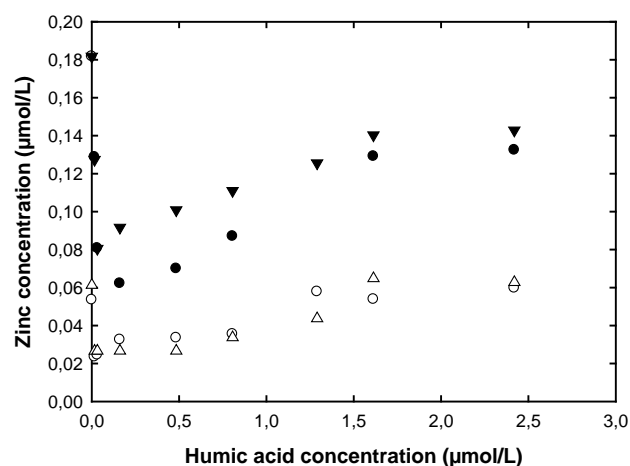


Fig. 5 Retention of zinc in solution by humic acid at pH 6 and 8 (● 5min at pH=6, ○ 5min at pH=8, ▼ 24h at pH=6, △ 24h at pH=8)

As shown in Figure 6, the amount of copper retained increased linearly at a humic acid concentration of $1.62 \mu\text{mol/L}$. After this concentration, there was re-increase with a lesser slope. The pattern of the curve at pH 6 was similar to that at pH 8 but the amount retained at 24h was higher than the one retained at pH 6.

In aqueous solution and in the absence of pozzolan there was release kinetics of minerals by the pozzolan. Adsorption tests showed us that the humic acid adsorbed weakly on pozzolan (0.032% to 0.008% at pH 6 and pH 8 respectively in 24h). Thus the dissolution of metals in solution is not related to the phenomenon of adsorption. There is an interaction which is a function of pH between the amount of metal dissolved and the amount of metal determined by humic acid. When the amount of dissolved metal reacts with humic acid, the dissolution continues and tends towards equilibrium.

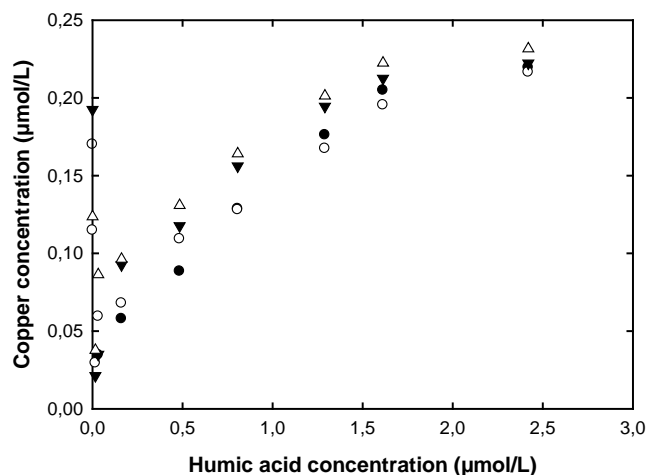


Fig. 6 Retention of copper in solution by humic acid at pH 6 and 8 (● 5min at pH=6, ○ 5min at pH=8, ▼ 24h at pH=6 ▲ 24h at pH=8)

C. Discussion

In general the amount of metals adsorbed at 24h is greater than the amount adsorbed at 5 min. the mobilization of trace metals is time independent except in the case of Cr at pH 6. When the concentration of humic acid increases, the levels of trace metals increase in the order: (i) pH 6; Cu > Zn > Cr, and (ii) pH 8; Ni > Cu > Zn > Cr. The linear increase in the case of Pb, Co, Ni at pH 6 and Pb, Co at pH 8 suggest stoichiometric complexation. A decrease in the adsorption of trace metals with an increase of pH was due to the competition between interaction with functional groups of humic acid and oxy hydroxide formation. The increase of metal adsorption with increase in the humic acid concentration was, however, consistent with the ligand exchange mechanism, as has been suggested for the interactions between humic substances and many metal cations [13].

Many functional groups were found in the structure of humic substances which included COOH, phenolic, and alcoholic [18]. Carboxyl and hydroxyl functional groups of humic and fulvic acids are known to form very stable complexes with many metal cations or hydroxy metal cations. The degree of dissociation of carboxyl and phenolic groups of the Humic molecule depends on the solution's pH. At pH 6 the carboxylic groups are completely ionized while the phenolic groups are ionized around pH 8. The interaction between functional groups of humic molecule and trace metallic elements depends on: (i) the conformation of humic molecule, in acidic medium the COOH groups are more ionized and can form complexes with metallic trace elements; (ii) the cationic exchange which is related to the amount of carboxylate and carboxylic groups present in the structure of humic molecule. In Figure 7 we can observe that the amount of sodium and potassium released by humic molecules in solution during exchange. These explain the fact that functional groups of humic acid exist in carboxylate and others in carboxylic. In view of the species present, the mechanisms of interaction are cationic-cationic and cationic-proton exchange through the carboxylate and carboxylic functions of humic molecule. These interactions lead to complex formation between the functional groups of humic acids and trace metallic elements. This is in agreement with References [19] and [20], who studied the complexing ability of natural and synthetic humic acids towards cadmium

and observed that hydrophobic moiety of the synthetic humic acid may provide a cage-type conformation around Cd^{2+} ion, imparting to the Cd^{2+} -humic complex the desired stability. Also in the works of Reference [21] on the formation of complexes between humic substances and metal cations showed that the higher the valence of the cation, the higher is the stable complex formed.

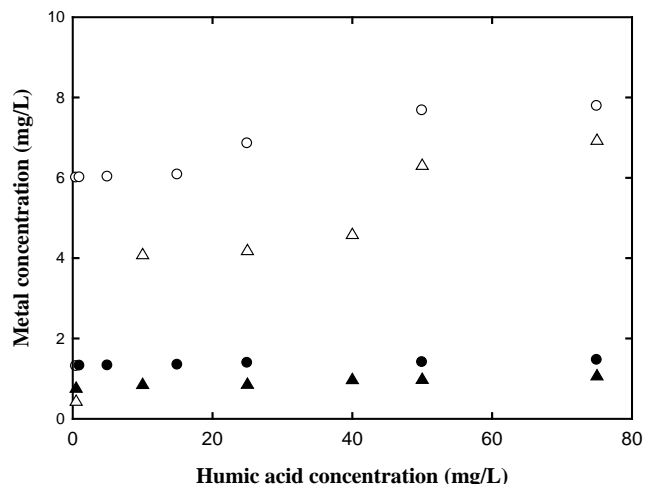


Fig. 7 Amount of sodium and potassium release in solution by humic acid at pH 6 and 8 (● Ca at pH=6, ○ Na at pH=6, ▲ Ca at pH=8 ▲ Na at pH=8)

IV. CONCLUSION

Pozzolan materials contain in their structure metals that can be released in aqueous solution. These metals react with humic molecule content of soil to form complexes. The capacity of adsorption of trace metallic elements by humic molecule is function of pH, time, amount of carboxylates and carboxylic sites that are related to the amount of humic molecule. In volcanic regions rain water can dissolve metals contained on pozzolan but the presence of humic molecule which mobilized metal reduces the migration of these metals to the ground water. This form of mobilization of metal by humic substances may avoid the contamination of ground water.

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