

Colloidal and Dissolved Organic Carbon- The Comparative Effects on Bioactive Metals

S.O.AYINLA

Science Education Department,
(Igbaja Campus)
Al-Hikmah University, Ilorin, Nigeria.
Adewole Housing Estate, Adeta Road,
P.M.B.1601, Ilorin, Kwara State.

sherro4real@yahoo.com; soayinla@alhikmah.edu.ng

Abstract

Bioactive metal ions are essentially required for various metabolic processes in human body. Insufficient supply of these metal ions can adversely affect the chemistry of the body system. One of the basic sources of the bioactive metal ions is the soil through consumption of crops. The role of organic carbon in binding to bioactive metal ions was studied using AAS and IR spectroscopy. The comparative effect of the colloidal and dissolved organic carbon on the ability to bind bioactive metal ions was evaluated. This evaluation is important in order to ascertain the availability of these metal ions to the crops planted on soils. The IR analyses show various peaks at wave number 2900, 1500, 1200 and about 800cm^{-1} for all the samples studied, indicating the presence of carbon chemically combine with other elements. These carbons are classified as organic carbon since they were extracted into the organic phase or solvent. Peaks at wave numbers 3300cm^{-1} , round tip, and about 1750cm^{-1} were common to the colloidal phase portions, indicating the presence of functional groups $-\text{OH}$ and $\text{C}=\text{O}$ respectively. The mean concentrations of the bioactive metal ions, Fe, Zn and Cu in the colloidal organic carbon phases are significantly difference to the mean concentrations of the metal ions in the dissolved organic carbon phases, {at $P \leq 0.05$, $t_{\text{tabulated}} = 2.57$, $t_{\text{calculated}}(\text{Fe}) = 6.64$, $t_{\text{calculated}}(\text{Cu}) = 2.99$, $t_{\text{calculated}}(\text{Zn}) = 5.07$ }. The colloidal organic carbon bind bioactive metal ions more to a larger extent compare to the dissolved organic carbon due to the presence of the $-\text{OH}$ and $\text{C}=\text{O}$ groups acting as ligands. To make bioactive metal ions available to plants for absorption, there is a need to chemically convert most of the colloidal organic carbon in soils to dissolved organic carbon.

Keywords: Colloidal organic carbon, Dissolved organic carbon, Bio-active metals, Wave number, Absorption.

Introduction and Literature Review

With current increase in the population of the world, there is a need to have corresponding increase in crop production. Crops need essential elements for growth, human consuming the crops can also directly or indirectly access the essential elements in different forms to aid various metabolic processes. One possible role of the organic carbon is the formation of complex between the carbon serving as ligand and available metal ions in soil, another role is the tendency to act as a buffer, maintaining the amount of metal ions in solution at a constant value. This regulation is presumably mediated by biological processes because bioactive metal ions are

also utilized by micro-organisms [1]. Bioactive metals are those required by living organisms for various biological activities. The earth consists of approximately 116 elements and yet only 25 are essential for life [2]. The bioactive metals are classified as heavy metals and trace metals based on the amount required by organism. Those required in larger amount, like sodium, magnesium, potassium and calcium are classified as heavy metals. Manganese, iron, zinc, molybdenum e. t. c, needed in smaller amount are trace metals [3]. In terms of physiological importance, copper acts as co-enzyme in oxidase reactions and protein metabolism, iron is a constituent of cytochromes and zinc functions in relation to anxious metabolism while manganese is co-enzyme for part of kreb cycle [4]. Organic forms of carbon represent only a small proportion of the global carbon reservoir but they are instrumental in many reactions and influence environmental chemistry beyond their mass contribution [5]. Total organic carbon is the total amount of carbon bound in an organic compound. It can be measured using TOC analyzer or by Walkley-Back modified method [6]. The dissolved fraction of carbon of organic carbon is an operational classification, many researchers place the dissolve /colloidal cut at $0.45\mu\text{m}$ [7], but $0.22\mu\text{m}$ is also typical of particle size to be recognized as dissolve fraction. By this classification, the dissolve portions are not expected to be visible with naked eyes except through electron microscope. Organic colloids are poly-functional and are exclusively a humic substance of plant origin [8]. Factors that may affect the amount of metal ions bind to humic substances are the p H, the ionic strength of the solution and the organic functional group content. Humic substances therefore can form stable complexes with polyvalent metal ions. The presence of $-\text{COOH}$ group in fulvic and humic acid plays a predominant role in the complex formation process, and there are some evidences that suggest that $-\text{OH}$, $\text{C}=\text{O}$ and NH_2 groups may also play a role. Speciation of metals in soils can be described as extraction and quantification of soil phases which is functionally designated into elemental contents [9]. Ores minerals containing high concentration of one or more bioactive metals also occur and this constitutes the main commercial sources of the particular metal. In general, clay and shale tend to have high concentration of many elements that include the bioactive metals due to their ability to absorb metal ions [10]. Most direct methods for the determination of trace elements on soils and sediment fractions are used in-order to allow for a direct assessment of the different phases in soils. The direct instrumental speciation approach has been successfully developed recently. Laser ionization breakdown spectrometry still has certain potential to analyze soils directly [11]. Infrared spectra originate from the different modes of vibration and rotation of a molecule. At wavelength below $25\mu\text{m}$, the radiation has energy to cause changes in the vibration energy levels of the molecules, and these are accompanied by changes in the rotational energy level. These vibrations have frequencies which depend primarily on the masses of the two vibrating atoms and of the force constant of the bond between them. The frequencies are also slightly affected by other atoms attached to the two atoms concerned. These vibrational modes are characteristics of the organic functional groups in the molecule and are useful in identifying a compound, particularly in establishing the structure of an unknown substance [12]. If a solution containing a metallic salt is aspirated into a flame, a vapour which contains atoms of the metal may be formed. Some of these gaseous metal atoms may be raised to energy level which is sufficiently high to permit the emission of radiation. Larger number of the gaseous atoms will normally remain in an unexcited state. These ground state atoms are capable of absorbing radiant energy of their own specific resonance wavelength. It is at this wavelength that the atom emit if excited from the ground state. This is the underlining principle of atomic absorption

spectroscopy. The absorption wavelength allows for identification of the metals and quantification is based of Beer-Lambert law.

Experimental

Composite soil samples were collected from the Ikeja Industrial Estate along Sapara Street, off Oba Akran Road, Ikeja, Lagos-Nigeria. The first soil sample was taken from a site behind the premise of Berger paints Nigeria plc, (longitude,N06°61228' ,latitude,E003°33856').The second soil sample was taken from a site behind the premise of Nigeria-German chemicals (longitude,N06°60900',latitude E003°33903').The third sample site is in the premise of May and Baker Nigeria plc, (longitudeN06°60839',latitude003°33941').The soil samples were taken using soil auger .The samples were dried at ambient temperature for about two weeks, crushed and pass through a mesh, d<2mm.Representative samples were taken from the bulk of the top and bottom regions of each site. These were labeled 1T, 1B, 2T, 2B and 3T, 3B.To extract the organic carbon content of each sample, 3.0g of homogenized soil sample was taken in a beaker, to which was added 20ml chloroform. The mixture was heated below the boiling point of the solvent, before being filtered. The filtrate was concentrated for about 30 minutes .Ethyl acetate was added drop wise to the filtrate until colloidal phase is precipitated out and the mixture becomes turbid. This was allowed to separate out the clear phase and gently decanted to obtain the colloidal organic carbon phase and the dissolved organic carbon phase differently. The procedure was repeated for each of the sample. The colloidal and the dissolved fractions from each sample were labeled,1TC,1TD,1BC 1BD,2TC,2TD,2BC,2BD,3TC,3TD,3BC and 3BD.Each of these was analyzed for the organic functional group using Buck scientific M500 IR spectrophotometer and the metal content(Zn, Cu and Fe) was determined using ALPHA 4 atomic absorption spectrophotometer(Chem-tech analytical model) at the chemistry department University of Lagos, Nigeria.

RESULTS AND DISCUSSION

Table3.1: Concentrations of Zinc ion in mg/l in the Colloidal and the Dissolved Phases

Sample	Colloidal Phase	Dissolved Phase
1T	7.03	3.97
1B	5.28	2.53
2T	4.41	2.49
2B	8.32	2.73
3T	5.10	3.23
3B	5.92	3.28

Table3.2: Concentrations of Copper ion in mg/l in the Colloidal and the Dissolved Phases

Sample	Colloidal Phase	Dissolved Phase
1T	0.15	0.04
1B	0.08	0.04
2T	0.07	0.06
2B	0.10	0.03
3T	0.10	0.04

3B	0.25	0.05
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Table3.3: Concentrations of Iron ion in mg/l in the Colloidal and the Dissolved Phases

Sample	Colloidal Phase	Dissolved Phase
1T	0.88	0.49
1B	0.91	0.30
2T	0.75	0.17
2B	1.45	0.24
3T	0.82	0.20
3B	0.98	0.32

Table3.4: Analysis of the Metal ion Concentrations using t-test

Metal ion	Mean Concentration, colloidal (\bar{x})	Mean Concentration, Dissolved (μ)	Std. Deviation Colloidal (σ)	$t_{\text{calculated}}$	$t_{\text{tabulated}}$ (at $p \leq 0.05$)	Comment
Zinc	6.010	3.040	1.4360	5.07	2.57	Significant
Copper	0.125	0.043	0.0672	2.99	2.57	Significant
Iron	0.965	0.287	0.2502	6.64	2.57	Significant

Table3.5: Analysis of the IR Results Showing the Wave numbers and the Possible Functional groups

Sample	Wave number	Functional groups
1TC	3300,2900,2400,1500,1200	-OH, Alkanes, C≡N, -CH ₂ -, C-O
1TD	2900,2400,1500,800	Alkanes, C≡N, N=C, C-H
1BC	3300,2900,1750,1400,1500	-OH, Alkanes, C=O, C=C, -CH ₂ -
1BD	3300,2900,2400,1200,1500,800	-OH, Alkanes, C≡N, C-O, -CH ₂ -, C-H
2TC	3300,2900,2400,1500,1200,800	-OH, Alkanes, C≡N, -CH ₂ -, C-O, C-H
2TD	2900,2400,1500,1200,800	Alkanes, C≡N, -CH ₂ -, C-O, C-H
2BC	3300,2400,1750,1200,1500,800	-OH, C≡N, C=O, C-O, -CH ₂ -, C-H
2BD	2900,2400,1200,800	Alkanes, C≡N, C-O, C-H
3TC	3300,2900,1700,1500,1200,800	-OH, Alkanes, C=O, -CH ₂ -, C-O, C-H
3TD	2900,2400,1200,1500,800	Alkanes, C≡N, C-O, -CH ₂ -, C-H
3BC	3300,2900,1700,1500	-OH, Alkanes, C=O, -CH ₂ -
3BD	2900,2400,1500,1200,800	Alkanes, C≡N, -CH ₂ -, C-O, C-H

The IR spectra results show various peaks at wave numbers 2900, 1500, 1200 and at about 800cm^{-1} for all the samples, indicating the presence of carbons chemically bonded to other elements. These are classified as organic carbon since they were extracted into the organic phase (solvent). Peaks at wave numbers 3300 and about 1750cm^{-1} were common to the colloidal phase portions indicating the presence of the organic functional groups $-\text{OH}$ and $-\text{C}=\text{O}$ respectively. This might explain the reason why concentrations of metal ions in the colloidal phases are always greater than the corresponding concentrations in the dissolved organic phases. The mean concentrations of the bioactive metals ions in the COC phases are significantly difference to the mean concentrations in the DOC phases as indicated using t-test.

Conclusion and Recommendation

Although both COC and DOC are responsible for binding bioactive metal ions in soils among other factors, but COC bind more of the metal ions than DOC, possibly due to the presence of the $-\text{OH}$ and $-\text{C}=\text{O}$ groups acting as ligands in the COC phases. To make bioactive metal ions available for absorption by plants and indirectly make them available for various metabolic processes in human, the COC in soils should always be chemically converted to DOC.

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