Tikrit Journal for Agricultural Sciences (2022) 22 (3): 158-165
https://doi.org/10.25130/tjas.22.3.18

IRAQI Academic Scientific Journals

ISSN:1813-1646 (Print); 2664-0597 (Online)
Tikrit Journal for Agricultural Sciences
Journal Homepage: http://www.tjas.org
E-mail: tjas@tu.edu.iq

TJAS Tikrit Journal for Agricultural Sciences

Organic Matter and Heavy Metals Sorption

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KEY WORDS:

organic substances, metal complexes, Stability constant, FA-metal complex

Hu-metal complex.

ARTICLE HISTORY:

Received: 16/08/2022

Accepted: 07/09/2022

Available online: 30/9/2022

Tikrit Journal for Agricultural Sciences (TJAS) Tikrit Journal for Agricultural Sciences (TJAS)

ABSTRACT

Organic matter content in soils is highly variable and includes dead and living organisms and their decomposition products. plant residue and humic substances. Thermodynamically, organic matter is unstable in soils and later will oxidize to Co_2, and H_2O. The effective substances of organic matter decomposition are fulvic and humic acids (FA+Hu) which contain Several functional groups that release electrons or protons during their decomposition leaving behind several radical groups that act as electron donner to ward heavy metal ions forming FA and Hu-metal soluble and insoluble complexes. Those metallic-organic Complexes are variable by their Stability constant (SC) which is absolutely pH-dependent. The less stable the metal complex, the higher mobility in soil, In contrast, a highly stable metal complex is less soluble and mobility. So, organic matter plays an important role in the accumulation, leaching, and transportation of heavy metal Cations present in water and soils as chelates of different Stability and supplying plant roots by these ions and behavior as a buffering substance to heavy metal mobility.

INTRODUCTION

Organic matter (OM) is a wide term include residual of plants, animals and microorganisms with different degree of decomposition (Walker et al. 2003; Liu et al. 2022). Soil organic matter (SOM) is a complex substances which simplified easily by soil microorganism to alow molecular weight materials (Bolan and Duraisamy, 2003). In the most soils, the final decomposition product and/or by product of (OM) results are, humic acid organic acids of high and low molecular weights, amino acids, waxes, protein, lipids, peptides, lignin, aromatic and aliphatic hydrocarbons (AL- Hamandi, 2018). The final decomposition of (SOM) can be divided into -fulvic acid (FA), humic acid (HA) and humine which widely exist in soil and presents an important fraction of soil component (Weber, 1988). Earth crust containing about (50* 10"tan) of organic matter as humus(Killops and Killops,2013). The general characteristic's of humic substances are:- increasing dissolved organic substances. Laboratory practical experiments concluded that humic acid reduces many heavy metal ions such as (Fe^{+3} to Fe+, Cu^{+2} to Cu^0, and Hg^{+2} to Hg^0 (Matthews,1983). While Minkina. et, al (2006) reported that (SOM) interactive, With Zn, Pb, and Cu resulted changes in (SOM) product, reduce (HA) and increased (FA) content.

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Definitions of the components of organic matter

- Fulvic acids(folvate):- have a high acidity with less degree of polymerization, high mobility, and exist in acid soils with low biological activity
- Humic acids (humates):- Spherocolloide shape, medium mobility, acidity, and occur in neutral soils with high biological activity.
- Humins: have low acidity, and a high degree of polymerization and occur in every soil) (Kabata-pendias, 2000) cation exchange capacity (CEC) for humic Substances are vary between 200- 450 C.mole Kg-1, being lower for (FAS) and higher for (HAS).

Soil properties are controlled by soil organic matter (SOM) because these substances increase soil CEC from 20% to 70% (Evans et, al, 2003). This great Sorption Capacity for heavy metals is very important in reducing the activity of excess heavy metals. (Laxen, 1985). Cu, Ni Cr, and Cd are enhanced Significantly by heavy metals interaction with humic Substances which have been described as chelation. Coagulation, Surface Sorption, and ion exchange (Tan, 2010). The reactions between cations and organic substances lead to the form of water-soluble and insoluble compounds and some of the organic matter product acts as reducing materials to enhance the mobile Zing of trace elements (McBride et, al, 1997) (Table1). Dissolved organic Substances could effectively form complexes with heavy metal ions in Soil (Bolton and Evans, 1991) Which Can be moved through the Soil matrix downward and may contaminate groundwater (Li and Shuman, 1996). Also Boyle and Fuller (1987), Lamy et al. (1993) reported that Zn and cd mobility was enhanced by heavy metal ions tend to accumulate in the products of organic matter decompositions, products with fewer metal ion content, and the higher binding energy between metal cans and organic groups (Zunino et, al.1979). In order to be interested and some information about insoluble complete behavior, we should seek by a complex Stability constant (CSC) concept which can be identified as an equilibrium constant that forms a chelate or soluble complex the stability index value has been used by Halder et, al (2020). Which describes the ratio of metal-OM to the amount of metal in inorganic fractions. Pure fulvic acid (FA) and humic acid (HA) stability index show that heavy metal ions of Mn^{+2}, Zn^{+2}, Pb^{+2}, and Cu^{+2} are more ready to form complex with (HA) than with (FA) and over pH (4 to5) large quantities of Cu^{+2} are complexed with (HA), but at pH range between (6-7) Cu^{+2} ions complexed with FA. Both heavy metal ions Pb^{+2} and Cu^{+2}showed high affinity to complicated organic acids compared to Mn^{+2} and Fe^{+2} ions (Kabata-pendias, 2000). The findings reported by Förstner and Müller (2013) Pauli (1975) ; Van Dijk (1971). Stevenson (1972), Vlasov and Michylova (1975) indicate that the stability constant of metallio-organic complexes, although variable, pH depending, and other medium properties can be ordered as the following sequence:

Hg>Pb> Cu>Ni> Fe > Zn>Mn.

Decomposition of O.M results in many organic substances, such as phenols, hydroxy acids, amino acids, and phosphoric acids which naturally exist in soils. These compounds behave as a chelating agent for heavy metals. Metal complex's solubility depends on binding Strength and formed complexes which are determined by the organic group's size and mobility of formed complexes (Kabata-penelias, 2000).

Metallio-organic and pH dependent

Chelation and complexation of heavy metal ions with organic substances in water have been studied by Sholkovitz and Copland (1981). They reported that the solubilities of (HA) complexes with (Cd, Ni, Cu, Mn, and Fe) differ from that concluded from inorganic Solubility consideration. These ions complexing with humic substances are solubilized at (Moderate-high) PH ranging between (3-9) and precipitate at low pH values ranging between (1.5-3.5). Thus heavy metal ions in natural waters have a high mobilization because of their reduction by humic Substances, adsorption, and complexation (Weber, 1988). Organic matter (OM). plays an important role in the accumulation, leaching, and transportation of cations present in water and soil as chelates of extra stability and supplying plant roots with these ions. The equilibrium exchangeable constant has been studied extensively to determine the Stability constant for organic matter-metallic complexes in soils (Kitagishi and Yaman, 1981; Chen et al 2022). Stability constant (SC) values determined by some

Table (1): Solubility constant of metal-HA and FA expressed as logK at different pH value

No.	Cation	pH_7	pH_5				$pH_{3.5}$	pH_3	
		HA	HA	HA	FA	FA	FA	HA	FA
		(Kitagishiond and Yaman,1981)	(Kitagishiond and Yaman,1981)	(Takamatsu and Yoshida,1978)	(Norvell,1972)	(Schnitzer and Khan,1981)	(Norvell,1972)	(Kitagishiond and Yaman,1981)	(Schnitzer and Khan,1981)
1	Cu	12.3	12.6	8.7	8.7	4.0	5.8	6.8	3.3
2	Ni	9.6	7.6	-	4.1	4.2	3.5	5.4	3.2
3	Co	-	-	-	3.7	4.1	2.2	-	2.8
4	Pb	-	-	8.3	6.2	4.0	3.1	-	2.7
5	Zn	10.3	7.2	-	2.3	3.6	1.7	5.1	2.3
6	Mn	5.6	0	-	3.8	3.7	1.5	0	2.1
7	Cd	8.9	5.5	6.3	-	-	-	5.3	-
8	Fe	4.8	6.4	-	5.8	-	5.1	5.4	-
9	Ca	6.5	0	-	2.9	3.4	2.0	0	2.7
10	Mg	5.5	0	-	2.1	2.2	1.2	0	1.9
11	Fe	6.6	8.5	-	-	-	-	11.4	6.1
12	Al	-	-	-	-	-	-	-	3.7

authors illustrate the ability of HA and FA to form stable complexes with heavy metal ions (Schnitzer and Kerndorff,1981). The FA-metal complexes which have lower (SC) are more Soluble and available to plant nutrients, many authors from (3to7) (Table1). Gamble (1986) findings a clearer effect of hydrogen potential (PH) on heavy metal ions sorption on (HA) (Table2). Iron binding (Fe^{+2} and Fe^{+3} ions) in a low pH Solution is very strong and somewhat non-exchangeable with other metal ions. Calcium high stability constant proved that can have a high competition with (Mn) and (Zn) in exchangeable processes (Escrig and Morell,1998; Yang et al.,2022). Studies on soil organic acid fractionations by Steponova (1974) concluded that there is high affinity between heavy metal ions and (FA). Also Taylor (2003) mentioned that (FA) heavy metal ions content is much higher than found in (HA).

Table (2): Metal Sorption on HA at various pH value percentage of initial metal concentration

No.	Metal	$pH_{5.8}$	$pH_{3.7}$	$pH_{2.4}$
1	Mn	13	3	0
2	Co	45	2	0
3	Zn	64	8	0
4	Cd	77	7	0
5	Cr	100	70	0
6	Ni	61	6	5
7	Al	100	86	7
8	Cu	97	59	12
9	Pb	96	80	19
10	Fe	100	96	81
11	Hg	98	98	99

*** Note: After (Gamble,1986)   Initial mettle concentration (0.005 $mol.L^{-1}$)**

reported that (SOM) has a low influence on heavy metals uptake by plants (Kördel, 1997). The highest values for (SC) were recorded by Takamatsu and Yoshida. (1978) for Cd^{+2}, Pb^{+2} and Cu^{+2} complexed with humic acid (HA) at pH 5 and that recorded by Kitagishi and Yamane (1981) for Ni^{+2}, Cd^{+2}, Cu^{+2}, and Zn^{+2} at pH_7. Andrzejewski and Rosikiewicz (1975) reported that Ni^{+2}, Co^{+2}, and Mn^{+2} complexes with (HA) were soluble, while complexes of Cr^{+3}, $Cu^{+2}$and Fe^{+2} with humic acid (HA) were soluble. Augustyn and Urbaniak (1979) observed that Zn^{+2}, Cu^{+2}, and Fe^{+2} are more retained by HA compared to Other heavy metal ions (HM1) such as Al^{+3} and Fe^{+3} which form highly stable complexes with Fulvic acid that interfere easily with Al-hydro oxide crystallization (Kodama and Schnitzer, 1980; Yang et al., 2020). Metal complexes Stability with (HA) and (FA) increases as pH increase. Gamble (1986) reported that there are great variable's in the natural system of organic substances in soil and equilibrium function should be determined instead of equilibrium constant. His calculation is based on the average weight of equilibrium function theory, so metal affinity sorption on AH at pH 3.7 take the following order :

Fe>Pb> Cr>Cu> Cd > Zn>Co

Also, Schnitzer and Kerndorff (1981) emphasized the affinity of metal ions to form water-insoluble complexes with FA, this order depends on pH media as follows:

Fe= Cr =A1>Pb = Cu>Hg> Zn=Ni=Cd-Mn

Metal FA complexes are more available to plants compared to those binding with HA which resulted both soluble and insoluble complexes and hydrous oxide. So, HA is relatively in soluble complexes with heavy metals in acid media and considered an organic storage for heavy metals in soils and can regulate heavy metals mobility in soils,(Kabata-penelias, 2000; Abdelrady et al.,2020). FA metal complexes solubility is controlled strongly by FA: metal ratio, so when this ratio is less than (2) water-insoluble complexes formation is favored. According to Bloom and McBride (1979), HA and peat in acid media are likely to bind most divalent cations Zn, Co, Ni, Mn, and Fe as hydrated ions and they conclude that Cu^{+2} ions which in accordance with the functional oxygen group and result from a strong Cu bandit.

Tyler and Olsson (2002) stated that Hg and cd in soft acid media prefer (thiol) legand soft base while acid metals (Mn, Fe) prefer (OH^-, COO^-) hard base legand group and moderate acid metals such as (Pb, Zn, Cu) tend to form complexes with stronger weak base. In different coal samples Gluskoter, (1977) obtained an index of metal-OM affinities and they distinguished three affinities groups:

Metals of high organic affinities such as B, Br Sb, and Be-

Metals of medium affinity, Ni, Ce, Cr, Cu, and Co -

Metals of law organic affinity but interact with all organic substances, Mn, Mo, Fe, As, and Zn.

Ability of organic matter retention for heavy metals

organic matter (O.M) has a high ability to fix 50% of total heavy metals content in soil and behavior as buffering substances to heavy metal mobility (Trofimova et al. 2017).

Stated that the ability of HA to fix heavy metal cation differs widely between soil horizons and both organic matter acids (HA and FA) to solubilize heavy metals play important role in their cling (Herencia et al, 2008). HA of a soil containing (4%) organic matter may bind about: Fe:17.834, Pb: 4.450 , Zn:1.016 , Mn:0.933 and Cu:1.618($Kg.ha^{-1}$) (Halder et al. 2020).

HA ability to complex with heavy metal ions has been Calculated by Vlasov and Michylova (1975) as follows :

Zn: 3:3-Co:3.2 -Cu:3.3 - Mn: 2.6 and Fe: 3.0 $gm.Kg^{-1}$HA.

According to Rashid (1974), each gm of amino acids in soil may mobilize about 4.5 - 450 mg of different heavy metals with high affinity to Co and Ni and low affinity to Mn. HA sorption Capacity increases as acidity increases, Violante et al (2010) measured the amounts of metals sorbed by HA at pH 5-6 and obtained the following values :

Au: 16- Ce:31-Cd:9-Sr:18 - Cu: 18 and Pb: 120 gm.Kg-1HA.

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المواد العضوية وامتصاص المعادن الثقيلة

مجبل محمد الجميلي **حذيفة معن الحمندي**

قسم علوم التربة والموارد المائية / كلية الزراعة / جامعة تكريت/ العراق

الخلاصة

تختلف الترب في محتواها من المادة العضوية والتي تشمل احياء التربة الميتة ونواتج تحللها وبقايا النباتات والمادة الدبالية ثرموديناميكيا , تعتبر المادة العضوية غير ثابتة في التربة ولاحقا سوف تتأكسد الى ثاني اوكسد الكاربون وماء.

من المواد الفعالة الناتجة من تحلل المادة العضوية هما حامض الهيومك وحامض الفولفك واللذان يحتويان على مجاميع فعالة قادرة على اطلاق البروتينات والالكترونيات من خلال تحللهما تاركة خلفها جذور كيميائية تتفاعل بصيغة واهبة للإلكترونات اتجاه ايونات العناصر الثقيلة مكونة معقدات ذائبة وغير ذائبة لكل من حامض الفولفيك وحامض الهيوميك وهذه المعقدات العضوية المعدنية مختلفة فيما بينها بصفة الثباتية والتي تعتمد بصورة رئيسة على قيمة الاس الهيدروجيني للوسط .

اذان المعقد الاقل ثباتية هو الاعلى في الذوبانية والحركة في التربة وبالعكس المعقد الاكثر ثباتية هو الاقل ذوبانية وحركة في التربة . لذا تلعب المادة العضوية دورا مهما في التربة من خلال تجمع وغسل ونقل ايونات العناصر الثقيلة الموجودة في المياه والتربة بصورة مخلبية مختلفة الثباتية لتحفيز جذور النباتات بهذه العناصر وتتصرف كأنها مخزن منظم لتجهيز هذه العناصر.

الكلمات المفتاحية:
المخلفات العضوية , المعقدات المعدنية , عامل الثباتية ,المعقد المعدني للفولفك اسد , المعقد المعدني للهيومك اسد.