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The Study of Distribution Equilibrium of Zn^{+2} on Humic Acid Extracted by Amol Forest Soils in Various PHs and Determining Equilibrium Constant Kex by Flame Atomic Absorption Technique

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ABSTRACT

Humic acid is soil fertilizing factor. It is solid macromolecule dissolved in water and alcohol. Based on the researches on its structure, it has active acid factors of carboxyl benzoic and phenol. As a cation exchange between soil and plant to achieve the required cation of plants. Ion exchange depends upon the Ph of environment and it is slow. This acid by fertilizing elements as azoth is effective in plants growth. Thus, the soils with more humic acid are more fertile.

Zinc as a heavy metal is selected as it is a necessary food element for natural growth of plants. In this investigation, ion exchange technique Discontinue or in pot is used and surface adsorption zinc is 2.497mol/kgr at Ph=7 is measured by flame atomic absorption technique and equilibrium constant K_{ex} for an initial concentration of eq/lit 8×10^{-3} is calculated as 0.72 and for oneH^+, a Zn^{+2} is changed. Thus, soils in the north of Iran have good capability in agriculture and this acid can be used for extraction of metals. In this project, relative error is 0.714 and cv=1.25.

KEYWORDS: Humic acid; Zinc; Cation zinc; Flame atomic absorption; Forest soil

INTRODUCTION

Humic acid is one of the main components of Humus.

It is a solid macromolecule dissolved in water, alcohol and acids and is dissolved only in strong alkaline as NaOH.

After an initial microscopic activity, long chain of organic maters in soil is turned into small molecules (sugar, phenol, amino acids). Then, the small molecules produce big molecules with molecular mass ranging gr/mol $10^4 - 10^5$ by microscopic synthesis or polymerization. Thus, humic acid is formed.

PH meter titration curve and its direction by caustic soda show that it is a weak acid with carboxyl benzoic and phenol factors.

According to Konova (1961) the more the aromatic cyclic structure in humic acid molecule, its resistance to dissolved electrolytes of soil is reduced.

Two types of grey and brown Humic acids are determined.

By increasing Homification degree, great amounts of fixed azoths enter by microorganisms in Humus compound and Humus azoth value is increased. By increasing azoth, the share of grey humic acid is increased. The azoth of grey Humic acid is different based on soil type and it reaches maximum 7.5%. Humic acid is mostly consisting of S,P,N,O,H,C and a few of other elements.

Various recommendations are presented regarding the structure of this acid and its core by IR range is consisting of an aromatic cyclic structure and some carboxyl and phenol group.

The density of reactive groups and Humic acid molecules are different form one soil to another but it is said its main structure is not changed.

One of the important features of Humus is its cation exchange capacity and it is high. Cation exchange is related to active chemical groups in organic matters.

During Humus process, organic matters of Ligin are changed and Carboxyl groups (-COOH) and phenolic OH are increased

As the hydrogen of this group can be change with cation, thus, cation exchange capacity in Humus is increased and its value is more than exchange capacity of new organic residual added to soil.

Free mineral elements of soil namely metal cation are absorbed by soil colloid and they are soil exchange elements.

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Multi-valency ions are absorbed into colloid sooner than one-valency ions. Some ions as Zn^{++} and Mn^{++} are absorbed by colloids and only Al^{+++} can be replaced by them and release them. Zinc concentration in plant tissues is naturally ranging 25 to 150 microgram/gr. If this value is lower than 20microgram, zinc shortage is appeared in plant. Concentrations more than 400 microgram/gr show zinc toxicity.
One of the signs of zinc deficiency is tissues death, short between nodes stubborn, growth stopping, fruit change and etc.

MATERIALS AND METHODS

Humic acid is extracted by forest soil after being purified of all impurities by caustic soda 0.5M and Hydrochloridric 5M. The mixture is including Humic acid and we heat it for 0.5 hr by mixing on hot bath to 80℃ the it stay for 1 day to have the sediment. After filtering, the sediment as Humic acid for purification is dried by acid Hydrochloridric 0.5M and water and it is distilled twice [3,4]. For the experiments, it is required to powder the sediment and pass it from a sieve and it is turned into some particles diameter 75-150μm.

Experiment method

To do the reaction between Humic acid and aquatic dissolutionZn^{+2}, we use ionic exchange *discontinue or in pot*. Cation exchange reaction kinetic is slow [3].

1 gr humic acid is purified and is mixed with various volumes of buffer solution Zn^{+2} ، (500ppm) in flask 200mL of poly ethylene and reaches volume by distilled water. Then, the mixture is mixed for one week by magnetic mixer with low speed to complete cation ion between Zn^{+2} and humic acid sites. After the end of the time, we separate solid and liquid phases by filter paper and funnel. Solid phase is saturated by 5ml *persulfate* ammonium and 5ml sulfuric acid 18M is mixed in a Chinese capsule and is heated for 4 hours at the temperature 300℃ to vaporize all its organic matters and what remains in capsule is ZnO ash. Then, the contents of Chinese capsule are washed by dark chloridric acid and are reaching volume in a volume flask 100mL and distilled water. Then, by atomic absorption method C_l (Zn^{+2} concentration in solid phase) and then Cs (Zn^{+2} concentration in solid phase) are measured.

Materials and measures

a. Materials: Acid Hydrochloridric, Acid sulfuric, Hydroxide sodium, Zinc metal powder, Ammoniac, acetic acid glacial, ammonium persulfate, acetate sodium (all materials are provided from Merck Company of Germany).
b. Measures: *pH meter,CD620* Digital with glass/Calomel electrode pair made in Chemistry Zag- Atomic absorption GBC model 911 made in Spain- Mechanical mixer E.L.M-IR device.

Fixation mechanism

Distribution curves of aquatic solution Zn^{+2} and Humic acid in PHs 3, 5, 6, 7 are provided. These results are consistent completely with ion exchange theory. The important analysis factor here is distribution coefficient $P\left(\frac{L}{kg}\right) = C_s/C_L$ [4, 5, 6].
Reaction between Zn^{+2} and Humic acid sites (H^+ of weak acid factors) is as followings:

$$nRH + Zn^{+2} \rightarrow RnZn^{2-n} + nH^+ \qquad (1)$$

According to the above reaction$H^+/_{Zn^{+2}}$, curve slope $logP = f(pH)$ is stoichiometry ratio of cation exchange reaction. The reaction equilibrium constant is including:

$$K_{ex} = \frac{|RnZn^{2-n}||H^+|^n}{|RH|^n|Zn^{+2}|} \qquad (2)$$

When inequality *1>y>0 is satisfied, distribution curve is under H+ form. It means that* $|Zn^{+2}| < |H^+|$
If y>1, we can have $|Zn^{+2}| \geq |H^+|$ and distribution curve is under Zn^{+2} form.
By putting distribution coefficient instead of

$$|RH| = (1 - \mathrm{y})\mathrm{ce}, \frac{|RnZn^{2-n}|}{|Zn^{+2}|}$$

In relation (2), we have:

$$K_{ex} = p\frac{|H^+|^n}{(1-y)^n ce^n} \qquad (3)$$

After taking logarithm of two sides of equation (3), we have:

$$\log p = npH + \log K_{ex} + nlog\ ce + nlog\ (1-y) \qquad (4)$$

If x=0, y=1, we have

$$p \rightarrow p_{max} = \frac{C_{s\,max}}{Co}$$

$$\log p_{max} = \log p_o + n\log(1-y) \qquad (5)$$

$$\log p_o = npH + \log K_{ex} + n\log C_e \qquad (6)$$

Thus, $\log P_0 = f(pH)$ is a line, its slope is n stoichiometry ratio and intercept is $\log k_{ex} + n\log C_e$. If CL approaches zero, p approaches p0, then X=Y=0 and we have $Co = |H^+|_L$, $p = K_{ex}$ and this is determination limit.

RESULTS AND DISCUSSION

By potansiometry investigation, Humic acid extracted from forest soil has active acid factors as carboxyl Benzoic with pK_a =4.7 and phenol $pK_a = 8.7$ [1]. Carboxyl Benzoic group at Ph=7 is ionized as 9.5% and phenol group (phenol group at Ph.=10 only 95.24% is ionized) at PH higher than 10 is completely ionized [7, 14,17] and at PH=7 only lower than 1% is ionized. Based on the limitation of zinc hydroxide sediment on PH higher than 7 and phenol group can not react with Zn^{+2} and if it enters reaction, the curve slope is equal to 2 and our complex form in various stages is as followings:

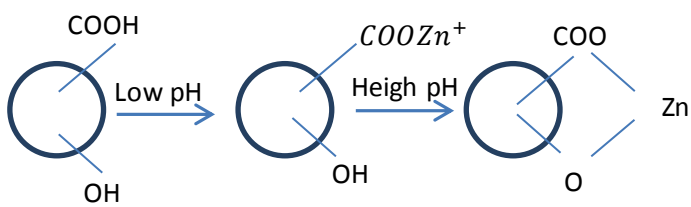
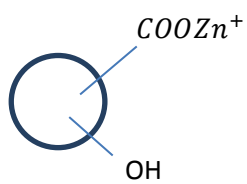


Figure 1- The mechanism of Zn^{+2} fixation on Humic acid

The results showed slop equal to 1, it means that for each $[Zn^{+2}]$, a $[H^+]$ is exchanged (Figure 2).

Distribution coefficient at Ph.=7, 10^3 and distribution coefficient of limit when CL approaches zero is $10^4 - 10^5$ and fixed zinc in this Ph is 2.497 to dry matters [3,5, 8]. For an initial concentration of $8 \times 10^{-3} eq/lit$ ، $K_{ex} = 0.72$ and intercept 0.32 and line slope 0.167 are calculated.



The results of K_{ex} interpretation show the isotherms of cation exchange (Figure 3) and values K_{ex} in various concentrations are smaller than 1 and the exchange is done with carboxyl Benzoic group and has lower ionic affinity to the state in which exchange is with phenol group as the complexes forming phenol group are more stable than the complexes forming carboxyl Benzoic group with zinc [3, 8, 9].

Distribution curve of buffer solution $Zn^{+2}({}^{NH_4{}^+}/_{NH_3})$ with concentration 500ppm at Ph=9.25 was investigated and it showed *mol/kg 1.81=*$C_{s\,max}$ to dry matters and phenol group participates in complex formation.

The fixation results Zn^{+2} on Humic acid extracted by forest soil of Naharkhoran of Gorgan and Amol showed that the density of reactive groups is different from one soil to another because cation exchange valiancy of Humic acid of these soils is different with different carbon percentage [10, 15, 16].

Conclusion

In this study, Zn^{+2} fixation on Humic acid extracted by forest soil of Amol at various PHs was investigated. Humic acid with active acidic factors carboxyl Benzoic and Phenol and average cation exchange capacity (CEC) is about 5 *eq/kgr* to dry matters. The reaction between , Zn^{+2} and active factors of Humic acid have slow Kinetic. The bond between them is ionic [7, 8]. At PH=13, phenol groups are completely ion. Thus, they can not have bond with Resin by hydrogen bond [14]. By increasing heavy metal cation load, cation exchange is increased. By increasing cation concentration by increasing CEC, the complex structure will be more stable [9].

Based on the importance of humic acid as a cation exchange in soil, its plays an important role in plants feeding and growth. Also, zinc is used as a necessary food element for natural growth of agricultural products (corn, bean, cotton, grape, onion, soybean, citrus trees, peach, pine, lettuce and spinach) and the stud of the above research is revealed [11, 13, 10].

The measurements were done by flame atomic absorption method and the relationship between absorption and concentration at (0.5-3ppm) is linear and based on complex making of humic acid extracted by forest soil, we can use it in eliminating the contamination of water and soil. And also it is used in heavey metals separation [10, 11, 12].

$\log P_0$ and $\log P_{max}$ changes to PH factor in various initial concentrations for $C_e = 2.3$eq/kgper M. s on humic acid extracted from forest soil of Amol

$C_0(eq/lit)$	0.5×10^3		1×10^3		2×10^3		3×10^3		4×10^3	
pH	$\log P_{max}$	$\log P_0$	$\log P_{max}$	$\log P_0$	$\log P_{max}$	$\log P_0$	$\log P_{max}$	$\log P_0$	$\log P_{max}$	$\log P_0$
3	*3.024*	*3.137*	*2.723*	*2.836*	*2.422*	*2.535*	*2.246*	*2.359*	*2.121*	*2.234*
5	*3.297*	*3.542*	*2.996*	*3.241*	*2.695*	*2.94*	*2.519*	*2.764*	*2.394*	*2.639*
7	*3.662*	*6.722*	*3.361*	*6.421*	*3.06*	*6.12*	*2.884*	*5.944*	*2.759*	*5.819*

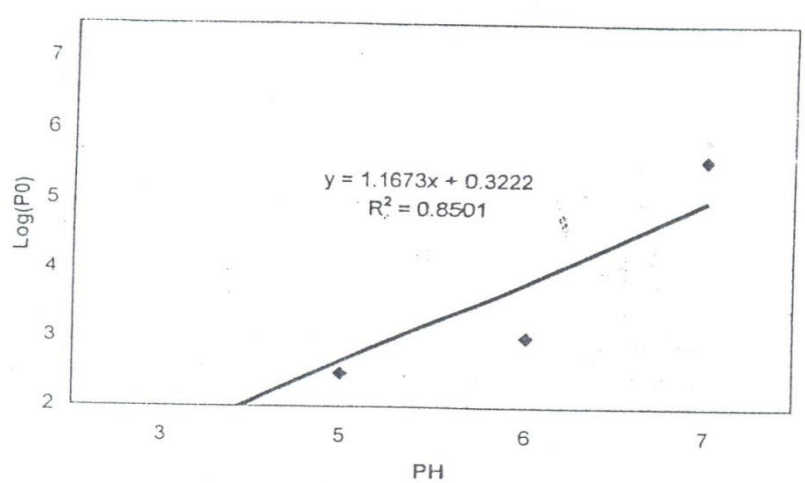


Figure 2- The logarithm changes of distribution coefficient of limit to PH factor for aquatic solution fixation Zn^{+2} 15.38×10^{-3}eq/lit on one gram dry humic acid extracted by forest soil of Amol

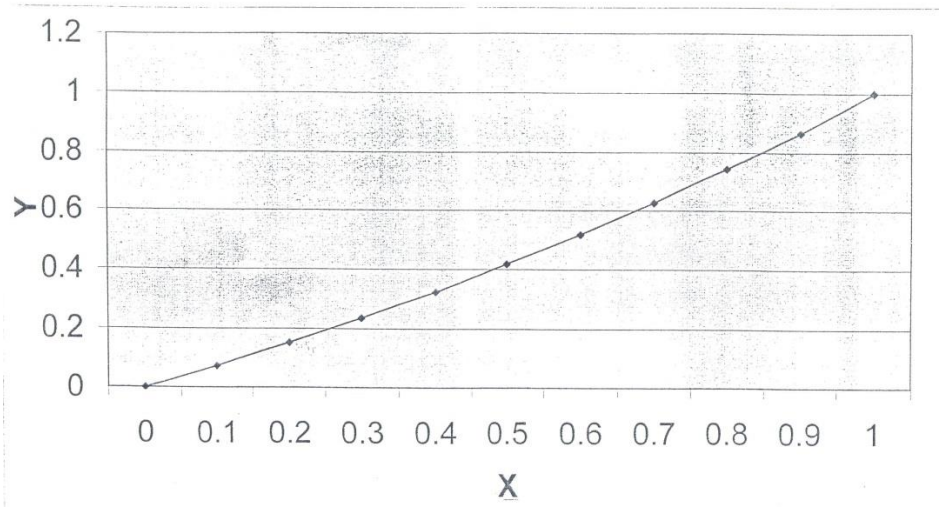


Figure 3- The changes of ion coefficient Zn^{+2} in solid phase (Humic acid) to the ion coefficient changes Zn^{+2} in aquatic phase

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