

Adsorption of Fe and Zn by Clay-humic Complexes

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THIS EXPERIMENT studied the adsorption of humic acid (HA) by coarse (2-1 mm) and fine (<1 mm) clay fractions separated from alluvial soil (Shibin El-Kom) and the adsorption of Fe and Zn on the formed clay-humic acid complexes at different pH-values. The adsorbed amounts of HA ($\mu\text{g HA/g clay}$) on the fine clay-fraction were larger than those adsorbed by the coarse fraction and these amounts were increased by adding HA. In other words, the HA concentration in clay-humic acid complexes was increased by adding HA. The adsorbed amounts of Fe and Zn ($\mu\text{g metal/g complex}$) increased higher HA-concentrations in the complex. Moreover, these amounts increased with increasing pH-values from 4.0 to 7.0. The highest values of adsorbed Fe or Zn were found with the complexes formed with the fine clay. The amounts of Fe or Zn adsorbed by clay- HA complexes, related to ionic strength of the solution, were the amounts in presence of 0.004N NaCl and they were higher than those in presence of 0.004N CaCl_2 . Moreover, the amounts of adsorbed Fe were higher than those of adsorbed Zn in all experimental treatments.

Keywords: Clay, humic acid, complex adsorption, pH, ionic strength.

Several mechanisms are involved on the adsorption of humic substances by clay minerals, the main ones being: 1- Physical adsorption, 2- Van der Waals, 3- Electrostatic attraction of chemical elements, 4- H-bonding and 5- Coordination complexes. The latter two mechanisms are considered as separate although strictly speaking they fall within the other three categories. Two or more mechanisms operate simultaneously, depending on the properties of the organisms species, nature of the exchangeable cation on the clay, surface area, acidity and moisture content of the system (Stevenson, 1994).

Khalil *et al.* (1987) studied the effect of brown humic acid concentration on its adsorption by Na-montmorillonite. They found that this adsorption increased with increasing amounts of brown humic acid. Abo El-Fadl *et al.* (1994) found that the amount of humic acid adsorbed by montmorillonite increased with increasing concentrations.

Humic acid is a polyanion, the negative charge of which arises from the ionization of carboxyl groups with varying (acid) strength. Therefore, the extent of ionization is dependent on the ambient pH (Stevenson, 1982). In this instance, ionization reaches a maximum at pH 7.65, corresponding to a concentration of titratable carboxyls of 2.60 meq/g. When the pH of the medium falls away from 7.65, ionization progressively diminishes. Since intermolecular charge-charge repulsion is concomitantly reduced, the conformation of HA changes from a stretched-out chain to an increasingly coiled (spheroidal) shape (Ghosh and Schnitzer, 1980).

Taylor and Theng (1995) found that the complexes of kaolinite with humic acid have a greater propensity for sorbing Cd than the clay itself and the sorption increased with the amount of humic acid increase in the complex. The increased propensity of complexes of kaolinite with humic acid to sorb Cd, compared to the clay itself, may be indicative of soil organic matter complexes being able to reduce availability of Cd to plants. The sorption increase with increasing amounts humic acid is not apparent except for the complex containing 390 µg HA/g (maximum concentration) while the complex with 390 µg HA/g has a lower binding capacity for Cd. However, steric hindrance due to interpenetration of adsorbed chains could make some carboxyl groups in the molecule to become inaccessible or only slowly accessible to Cd.

The present investigation aims at studying the humic acid adsorption by fine and coarse clay fractions and the interaction between Fe or Zn with the formed clay-humic acid complexes at different pH values.

Material and Methods

Surface soil samples (0-30 cm) were collected from the Experimental Farm, Faculty of Agriculture, Minufiya University, Shibin El-Kom, Egypt. The samples were air-dried, ground to base through a 2 mm sieve. The particle size

distribution and chemical properties were determined and the obtained data were recorded in Table 1.

TABLE 1. Particle size distribution and some chemical properties of the used soil.

a- Particle size distribution (%)

C-sand	F-sand	Silt	Clay	Soil texture
7.9	13.1	33.2	45.8	Clay

b- Chemical properties

pH (1.25 soil water susp)	EC dSm ⁻¹	OM %	CaCo ₃ %	CEC meq/100 g soil	DTPA extractable micronutrients (ppm)			
					Fe	Mn	Zn	Cu
7.59	0.64	2.30	2.35	31.85	6.45	10.32	3.01	4.10

The separation of the soil grains

The carbonate salts of the alluvial soil were removed as follows: 50 g soil sample + 30 ml sodium acetate (1.0N) were transferred to 100 ml beaker and the mixture was heated on a waterbath until 80°. This process was repeated three times until the system is free carbonate. This is the end of the reaction and supernatant was decanted (Jackson, 1973).

The organic materials were removed by adding 30 ml of H₂O₂(15%) three times to 5 g soil. Soil was transferred into a 250 ml beaker, strong stirred and left to stand for one hour. The beaker was heated on a waterbath for 30 min and left overnight. The soil sample then was transferred into a centrifuge tube and washed with distilled water to remove the soluble salts resulted from organic matter degradation. The sample was airdried and ground (Jackson, 1973).

It was suspended in distilled water and the clay fractions (2-1 mm and <1 mm) were separated by decantation method, according to Stock's law. The clay particles were transferred to a large bottle. After wards, the two clay fractions were centrifuged, airdried and ground (Jackson, 1973).

Extraction and fractionation of humic substances

Humic acid was isolated from the alluvial soil, using the method described by Posner (1966) 100g of soil sample were added to 500 ml (0.5 N NaOH) and 1 ml

saturated SnCl_2 solution was added to prevent oxidation of organic matter. The mixture was shaken for 3 hr then left to stand overnight and the supernatants (humic substances) were separated by centrifugation for 20 min at 6000 rpm. The humic substances were fractionated by acidification of the supernatants to pH 1.5 with 1.0N HCl. The acidic solution was left overnight. The acid-soluble fraction was fluvic acid, whereas the acid-insoluble fraction was humic acid (Kononova, 1966). Fulvic acid was separated from humic acid by centrifugation of acid solution at 6000 rpm for 20 min.

Purification of humic acid

The separated humic acid in the centrifuge tubes was washed several times with 0.05 N HCl until the supernatant became colourless. The humic acid was transferred to dialysis cellophane bags and dialysed against distilled water until the test for Cl in the distilled water outside the bags was negative. Then humic acid was airdried (Chen *et al.*, 1978).

In order to reduce the ash content of the purified humic acid and to increase the purity, 10 g of the airdried humic acid were shaken with 100 ml of Khan's mixture (0.5 ml conc HCl + 0.5 ml of HF 48% and 99 ml of H_2O) at room temperature for 42 hr (Schnitzer and Khan, 1978). After shaking, the acid mixture was centrifuged and supernatant was removed, and the humic acid gel was dialysed against distilled water until Cl became free. Then humic acid was airdried and analyzed for elementary composition (C, H, N and O%), ash content (%), total acidity and functional groups (COOH, total -OH, phenolic -OH and alcoholic -OH) as meq/100 g humic acid, using the methods described by Kononova (1966) and Stevenson (1982 and 1994). The obtained data were recorded in Table 2.

TABLE 2. Chemical composition of the used humic acid.

<i>a- Elemental composition (%)</i>							
C	H	N	O	Ash	Atomic ratios		
					C/N	C/H	C/O
53.22	5.71	2.90	38.17	2.48	18.35	9.32	1.39
<i>b- Total acidity and functional groups (meq/100mg)</i>							
Total acidity	COOH	Total -OH	Rhenolic-OH	Alcoholic-OH			
797.5	479.1	349.2	318.4	30.8			

Sorption of iron and zinc on clay-humic complexes

Clay-humic complexes were prepared by adding a humic acid solution containing 150, 250, 350 and 450 µg humic acid (A, B, C and D) to one gram of two separated airdried clay fractions and pH value was adjusted at 7.0. The mixtures were shaken overnight at room temperature and centrifuged at 6000 rpm for 20 min. The clear supernatants were collected in a brown bottle to determine their content of humic acid and the adsorbed humic acid obtained by calculating the difference between total humic acid added and the non-adsorbed one.

In order to determine the ionic strength and pH of the soil solution, (Edmeades *et al.*, 1985) 10 ml of 0.004 N CaCl₂ at pH 4 were added to 50 mg of coarse clay, fine clay or the complex (A, B, C and D), followed by a solution of ZnCl₂ containing 40 µg Zn (Christensen, 1984). The mixtures of clay-humic and Zn-solution contained in beakers were stirred for 1 hr using a magnetic stirrer, keeping the pH at 4. After standing for another hour to allow the clay to settle out, the supernatant was decanted into a sample cup and its content in Zn was determined using a atomic absorption spectrometer. In the second group of experiments, the pH was adjusted to 5.5 and 7 by addition of 0.01 M HCl or NaOH with a micropipette. The effect of cation valence (ionic strength) was assessed by using 0.004 N NaCl (instead of 0.004 N CaCl₂) as the suspending electrolyte. All measurements were done twice and blank runs were carried out in all cases. This experiment has been repeated with iron. The amounts of adsorbed Fe or Zn were calculated as a difference between the total amounts of the used metal and the amounts found in the supernatants.

Results and Discussion

Data in Table 3 show the amounts of different additions of humic acid adsorbed by coarse (2-1 mm) and fine (< 1mm) clay fractions at pH 7.0. The data indicate that the adsorbed amount markedly increased with increasing concentrations of humic acid added. They also show that, at the same concentration of added humic acid, the amount adsorbed by fine clay was higher than that by coarse clay. This can be attributed to the high surface area of the fine fraction (Stevenson, 1994). He added that the binding of organic anions by clay minerals is possible. The results are in agreement with those obtained by Abou Hussien (1991), El-Fadl *et al.* (1994) and Taylor and Theng (1995).

TABLE 3. Adsorption of humic acid on coarse (2-1 mm) and fine (<1 mm) clay separated from an alluvial soil at pH 7.0.

Humic acid added (μg)	Coarse clay (2-1 mm)		Fine clay (1 mm)	
	Humic acid adsorbed on clay ($\mu\text{g/g}$ clay)	Adsorbed (HA) added (HA) $\times 100$	Humic acid adsorbed on clay ($\mu\text{g/g}$ clay)	adsorbed (HA) added (HA) $\times 100$
150 (A)	117	78.0	138	92.0
250 (B)	171	68.4	200	80.0
350 (C)	223	63.7	274	70.5
450 (D)	265	58.8	295	65.5

Schulthess and Sparks (1989) suggested that the adsorption selectivity of a solid phase is controlled by both the affinity of the aqueous ion for the surfaces and the ion concentrations present in the solution. The affinity (or bonding strength) of the aqueous ion for the surface is related to the degree of hydration of the adsorbed ion.

Data in Tables 4- 5 show variation of adsorbed amounts of either Fe or Zn on the clay-humic acid complexes (μg metal/g complexes), as affected by different fractions of clay that formed the clay-humic acid complexes, pH medium and ionic strength. The data show that the amounts of adsorbed Fe and Zn on fine fractions (<1 mm) were higher than those adsorbed on coarse fractions (2-1 mm) in all treatments of clay-humic acid complexes. This may be due to the high specific surface area and cation exchange capacity of the fine fraction, compared to those for the coarse fraction (Jackson,1973).

Data in Tables 4-5 also show that the adsorption of Fe and Zn on clay-humic complexes was higher than that on pure clay. The amounts of adsorbed Fe or Zn on clay-humic complexes increased by increasing the amounts of humic acid added to form the clay-humic complexes except for the high rate (450 μg HA). These increases may be attributed to the increase of both the surface area and the cation exchange capacity of adsorbent surfaces, as well as the increase of the humic acid content. The obtained data are in agreement with findings reported of Radwan (1993), Abou Hussien (1995) and Hamad (1997) who found linear relationships between the adsorbed Fe or Zn and the organic matter content of

the adsorbent. The calculated correlation-coefficients between the amounts of adsorbed Fe or Zn and the content of organic matter were positive and significant. The decrease of amounts of adsorbed Fe or Zn as $\mu\text{g}/50 \text{ mg}$ clay humic acid complex with the complexes have a high amount of humic acid may be resulted from the aggregation effect of humic acid on clay, which became larger and stable. The results are in harmony with those obtained by Hatton and Pickering (1980).

TABLE 4. Adsorption of Fe on clay-humic acid complexes.

pH	Clay-humic complexes	Fe adsorbed $\mu\text{g}/\text{g}$ coarse (2-1 mm) clay-humic complexes		Fe adsorbed $\mu\text{g}/\text{g}$ fine (<1mm) clay-humic complexes	
		0.004N CaCl_2	0.004 N NaCl	0.04 N CaCl_2	0.004 N NaCl
4.0	Clay	56.40	93.00	89.00	158.00
	Clay-humic complex (A)	137.00	274.4	153.00	303.60
	Clay-humic complex (B)	178.00	407.00	224.40	445.00
	Clay-humic complex (C)	266.60	483.60	321.00	548.40
	Clay-humic complex (D)	182.60	233.00	228.00	350.00
Mean		164.12	298.00	203.00	361.00
5.5	Clay	72.40	107.60	103.60	183.00
	Clay-humic complex (A)	162.40	305.60	193.00	376.40
	Clay-humic complex (B)	198.00	742.00	239.20	514.00
	Clay-humic complex (C)	299.00	605.00	336.00	680.00
	Clay-humic complex (D)	201.00	266.00	241.00	377.00
Mean		186.56	351.12	222.56	426.00
7.0	Clay	85.00	122.20	117.00	245.00
	Clay-humic complex (A)	207.00	413.00	270.40	463.40
	Clay-humic complex (B)	265.00	489.00	312.40	575.00
	Clay-humic complex (C)	322.00	628.00	421.00	720.00
	Clay-humic complex (D)	245.00	353.00	294.00	428.00
Mean		224.80	401.00	282.88	486.28

TABLE 5. Adsorption of Zn on clay-humic acid complexes .

pH	Clay-humic complexes	Zn adsorbed $\mu\text{g/g}$ coarse (2-1 mm) clay-humic complexes		Zn adsorbed $\mu\text{g/g}$ fine (<1mm) clay-humic complexes	
		0.004N CaCl_2	0.004 N NaCl	0.04 N CaCl_2	0.004 N NaCl
4.0	Clay	49.00	64.20	65.00	106.00
	Clay-humic complex (A)	122.40	201.00	138.00	238.40
	Clay-humic complex (B)	161.00	300.60	187.00	309.00
	Clay-humic complex (C)	237.00	375.00	265.00	402.40
	Clay-humic complex (D)	145.00	175.00	171.00	213.00
Mean		142.88	223.16	165.20	253.68
5.5	Clay	59.00	82.60	87.00	137.00
	Clay-humic complex (A)	133.00	247.40	169.00	268.00
	Clay-humic complex (B)	177.00	334.00	220.00	360.40
	Clay-humic complex (C)	265.00	427.00	305.00	469.00
	Clay-humic complex (D)	190.00	217.00	198.40	275.40
Mean		164.80	261.52	195.80	301.88
7.0	Clay	67.00	110.00	107.00	175.60
	Clay-humic complex (A)	153.00	291.40	203.00	332.00
	Clay-humic complex (B)	208.40	391.60	269.00	22.80
	Clay-humic complex (C)	293.40	490.00	348.40	553.20
	Clay-humic complex (D)	199.00	256.40	231.60	325.60
Mean		148.16	307.88	231.80	361.72

The effect of pH on the amount of adsorbed Fe or Zn on clayhumic complexes is presented in Tables 4 &5. Data indicate that the amount of Fe or Zn adsorbed by the two fractions of clay-humic acid complexes are increased by increasing the pH values from 4.0 to 7.0. This increase may be due to the suggested model. The enhanced Fe-or Zn- adsorption at high pH values may

stem from reduced competition with Fe^{2+} + or Zn^{2+} on common clay adsorption sites and higher bonding energy of $\text{Fe}(\text{OH})_2$ or $\text{Zn}(\text{OH})_2$ to the surface as compared to Fe^{2+} or Zn^{2+} (Stevenson, 1982). This author added that the main pH-effect was due to the strong bonding of $\text{Fe}(\text{OH})^+_2$ or $\text{Zn}(\text{OH})^+_2$ to the surface. The Fe-HA or Zn-HA complex has an affinity to clay that is significantly lower than $\text{Fe}(\text{OH})_3$ or $\text{Zn}(\text{OH})_2$ respectively. The obtained data are in agreement with the findings of Hatton and Pickering (1980) and of Slarek and Pickering (1980) who reported that the adsorbed amount of some metals (Fe, Zn, Cu etc.) increased by increasing of the pH from 3.0 to 6.0 and they added that in alkaline media there was competition between the ability of the organic material to form soluble metal humates and the tendency of the clays to strongly retain the sparingly soluble metal hydroxy species formed at $\text{pH} > 6$.

Data in Tables 4 & 5 indicate that the amounts of Fe or Zn absorbed by clay-humic acid complexes at different pH-values with 0.004N NaCl were higher than those with 0.004N CaCl_2 . This may be attributed to the competition effect of Ca^{2+} with the studied metals (Fe & Zn) for adsorption or retention on the exchangeable sites of the adsorbent surface. Taylor and Theng (1995) pointed out that the amount of adsorbed metal could be accounted by the HA content of the respective clay-HA complexes. However, sorption from 0.004 N CaCl_2 is much smaller than from a solution of NaCl of the same normality in agreement with Boekold *et al.* (1993). Thus, Fe or Zn is capable of displacing all Na, but only the part of the Ca initially associated with clay-humic acid complex.

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إدمصاص الحديد والزنك على معقدات الطين وحمض الهيوميك

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تناولت هذه الدراسة التعرف على إدمصاص حمض الهيوميك على الطين الخشن (٢-١) والناعم (أقل من ١ مم) المفصول من أرض رسوبية (شبين الكوم) وكذلك إدمصاص الحديد والزنك على معقد الطين وحمض الهيوميك المتكون عند قيم pH مختلفة ولقد كانت الكميات المدمصة من حمض الهيوميك (ميكروجرام حمض/ جرام طين) على الطين الناعم أعلى من تلك المدمصة على الطين الخشن وكذلك فقد ازدادت الكمية المدمصة من حمض الهيوميك بزيادة التركيز المضاف من حمض الهيوميك وبعبارة أخرى فقد ازداد محتوى المعقد من حمض الهيوميك بزيادة المضاف من حمض الهيوميك. ولقد ازدادت الكميات المدمصة (ميكروجرام فلز / جرام معقد) من الحديد والزنك بزيادة محتوى المعقد من حمض الهيوميك وكذلك ازدادت هذه الكميات بزيادة الـ pH من ٤ إلى ٧ وكانت أعلى قيم للحديد والزنك المدمص على المعقد المتكون فى وجود الطين الخشن. ولقد ارتبطت تلك الكميات المدمصة من الحديد والزنك بالقوة الأيونية للمحلول حيث كانت هذه الكمية فى وجود كلوريد الصوديوم ٤... مكافىء أكثر من تلك المدمصة فى وجود كلوريد الكالسيوم ٤... مكافىء . وفى جميع معاملات التجربة كانت الكميات المدمصة من الحديد أكثر من تلك المدمصة من الزنك .