

Kinetics of zinc adsorption on soil minerals in the absence and presence of humic acid

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Abstract: Kinetics of Zn²⁺ adsorption on soil minerals (kaolinite and hematite) in the absence and presence of humic acid has been investigated under various conditions. The influence of pH, ionic strength and solution cations on the rate of the adsorption has been studied. The rate and the amount of adsorbed Zn²⁺ on soil minerals in the absence and presence of humic acid increased with decreasing ionic strength, increasing pH and in the presence of the background electrolyte K⁺ rather than Ca²⁺. Humic acid enhanced the rate and the amount of adsorbed Zn²⁺ onto soil minerals. The adsorption equilibrium data showed that adsorption behavior of Zn²⁺ could be described more reasonably by Langmuir adsorption isotherm than Freundlich isotherm in the absence and presence of humic acid. Pseudo first and pseudo second order models were used to evaluate the kinetic data and the rate constants. The results indicated that the adsorption of Zn²⁺ on hematite and kaolinite in the absence and presence of humic acid is more conforming to pseudo second order kinetics.

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1. Introduction

Heavy metals are natural components of the Earth's crust. It is known that heavy metals can be bioaccumulated through crops, which have potential risks to human health via consumption of these contaminated food crops (Ali *et al.*, 2004, Zhuang *et al.*, 2009). Since they cannot be biodegraded, various methods such as hydrometallurgical technologies, ion exchange, electrodialysis, reverse osmosis, precipitation and adsorption have been used for heavy metal removal from environmental various solutions (Hizal and Apak, 2006). Many metal ions are essential as trace elements, but at higher concentrations, they become toxic.

Zinc occurs in natural soils as a result of weathering of the soil parent material, and total Zn contents in soils in average ranges from 40 to 120 mg kg⁻¹ depending on their lithology (Kabata-Pendias, 2001). However, Zn is an essential nutrient for plants and soils are often deficient in it (Kochian, 2000), the Zn content of agricultural soils is usually higher than that of natural soils mainly due to the addition of commercial fertilizers, liming materials or manures (Senesi, 1999). Moreover, pesticides and fungicides containing Zn also contribute to its presence in agricultural soils (Komarek, 2010). Zn can accumulate in agricultural soils, achieving values considerably higher than its optimum concentration as a nutrient, and it may be toxic to soil organisms (Alloway, 2005). A recent review on heavy metal toxicity in plants supplies more information on the effects of Zn toxicity (Nagajyoti, 2010).

The mobility of toxic metals in soils or sediments is of great concern to scientists and environmentalists and directly affects the bioavailability of metals to plants and their movement to surface and ground waters. Kaolinite and hematite are among the most important sorbents for metals cations in soil and sediments, which is due to their high abundance, large specific surface area, negative surface charge and reactive surface hydroxyl groups (Parks, 1965, Wang *et al.*, 2003).

Humic acid (HA) molecules, which adsorbed onto the surface of soil minerals, would increase the adsorption capacity of metallic cations because HA has strong complexing sites. Besides, the complexation capacities of humic acid are significantly higher than that of the usually reported for the adsorption capacities of soil minerals (Abate, and Masini, 2005). Therefore, soil minerals and humic acid play a very important role in the chemical reaction, occurring in soil which influences the movement, and retention of contaminants, metals and nutrients in the soil. The kinetic study of heavy metals adsorption on soil minerals is a significant factor in determining heavy metals retention in aquatic and soil environments.

Equilibrium and the kinetic study for the adsorption of Zn²⁺ onto soil minerals in the presence of humic acid and different types of background electrolyte have been poorly studied. Accordingly, the aim of this study is to investigate the influence of humic acid on the rate of adsorption of zinc cations onto soil minerals under different laboratory

conditions (e.g. ionic strength, pH and solution cations).

2. Material and methods

2.1. Materials

Humate salt was obtained from Sigma-Aldrich. Humate salt used to prepare humic acid as follows (Swift, 1996): briefly, humate salts dissolved in deionized water, and precipitated by acidification to a pH (2). The precipitate was redissolved in deionized water. This precipitation and dissolution was repeated 10 times. This pretreatment procedure eliminated significant levels of metals such as Al, Fe, Ca and Mg from HA.

Kaolinite and hematite are commonly abundant minerals in soils. Kaolinite was obtained from standard of Ward's natural science Established (No. 3Bieoh pit Maccon, Georgia). Kaolinite fraction, < 1- μ m diameter particles, was separated by sedimentation techniques.

Hematite colloids were synthesized using a modified method reported elsewhere (Sugimoto *et al*, 1993). A concentrated Fe(OH)₃ gel was prepared by mixing 100 mL of 2 mol dm⁻³ FeCl₃ with 100 mL of 6 mol dm⁻³ NaOH. The gel was aged in an oven at 100 \pm 1 °C for 8 days, and allowed to cool to room temperature for 72 h. Then hematite colloids were redispersed in deionized water to remove the excess salts by using centrifuge. Complete precipitation of the salts was checked up in supernatant by the AgCl test. The surface area of the hematite and kaolinite particles was measured by BET surface area analysis.

2.2. Methods

2.2.1 Preparation of soil minerals suspensions, HA and Zn²⁺ solutions

Kaolinite or hematite suspensions (5 g/L) stock solutions were prepared in order to obtain consistent solid concentrations in the equilibrium adsorption experiments. These suspensions were prepared in 0.001 and 0.01 mol dm⁻³ of KCl or CaCl₂ for the HA and Zn²⁺ adsorption isotherms at pHs (5, 6 and 7) over a period of 14 days.

Stock HA solutions were prepared by dissolving HA in an aqueous solution of NaOH (0.05 mol dm⁻³) with shaking for 1 hour. HCl or NaOH was then added to adjust its pH at 5, 6 and 7. Amounts of KCl or CaCl₂ were added to HA solutions to adjust to the desired ionic strength (0.01 and 0.001 mol dm⁻³). Finally humic acid concentration reached 2 g/L.

Stock solutions of Zn²⁺ were prepared with a concentration of 75 mg/L from zinc chloride and adjusted at different pH values (5, 6 and 7) and different ionic strength (0.001 and 0.01 mol dm⁻³ of KCl or CaCl₂).

2.2.2 Adsorption of humic acid and zinc onto soil minerals

2.2.2.1 Humic acid adsorption

A fraction of the well-mixed (kaolinite or Hematite) suspension (at the desired pH and ionic strength values) was pipetted into series of HA solutions at concentration (416 mg/L to obtain on maximum adsorption capacity as described in pervious study (Shaker *et al*, 2012)) to give the final volume of 30 ml in 50-ml polyethylene centrifugation tubes. The suspensions were shaken for 24 h on a horizontal shaker (junior orbit shaker, Lab line Instruments, Melrose Park, IL, USA) to reach equilibrium. The final (kaolinite or hematite) concentrations for all adsorption experiments was 2.5 g/L. Preliminary experiments verified that after 4 h no measurable change occurred in the adsorbed amount. Each sample was centrifuged for 5 min at 20 000 rpm Damon/IEC Division Model HT High - Speed Centrifuge. The HA / kaolinite (HA - Ka) or HA / hematite (HA -He) complexes were resuspended for 24 h in the horizontal shaker. This washing step was repeated four times to exclude the free HA from the solution in case of hematite and three times in case of kaolinite. The aspirated supernatant of each washing step was stored for HA measurement. The stock HA / (kaolinite or hematite) suspensions were stored in the dark at 3°C.

2.2.2.2 Adsorption of Zn²⁺ onto soil minerals

The adsorption experiments were performed exactly as in the case of HA adsorption experiments (as described in 2.2.2.1). The total added concentration of Zn²⁺ generally varied from 8.3 to 75mg/l.

2.2.3 Zinc adsorption onto HA / kaolinite or HA / hematite complexes

The HA / kaolinite and HA/ hematite complexes were prepared as described in 2.2.1. After centrifugation for all samples, five ml of supernatant (at the desired pH and ionic strength value) was taken then replaced with series of Zn²⁺ portions at differently varying concentrations to give the final volume of 10 ml in 16-ml polyethylene centrifugation tubes. The Zn²⁺ stock solution used was pre-adjusted at the same pH and ionic strength. The suspensions were shaken for 24 h in an overhead shaker (Melrose Park). The samples were centrifuged for 5 minutes at 20 000 rpm Damon/IEC Division Model HT High - Speed Centrifuge. The Zn²⁺ adsorbed amount was calculated from the difference between the initial concentration of the Zn²⁺ and the Zn²⁺ equilibrium concentration in the supernatant by using the Atomic Absorption Spectrophotometer technique (Perkin Elmer).

2.2.4 Kinetic experiment

Kinetics experiments were carried out by shaking certain amounts of adsorbents (kaolinite, hematite, HA - Ka or HA - He) with 50 mL solution containing

Zn²⁺ (to achieve 50 mg/L concentration) at 25 °C. At pre-determined time intervals, portions of the mixture were drawn by a syringe, and then centrifuged and Zn²⁺ concentration was determined as described before in 2.2.3.

In adsorption kinetics the amount of adsorption at time t , q_t (mg/g) was calculated by the following formula:

$$q_t = (C_i - C_t) V/w \quad (1)$$

Where C_i is the initial concentration of Zn²⁺ solutions (mg/L), C_t is the concentration at any time t (mg/L), V is the volume of solution used in the adsorption experiment (L), and w is the dry weight of adsorbent (g).

3. Results and discussion

3.1 Characteristics of HA and soil minerals

Figure 1 shows IR spectrophotometer results of humic acid. Clearly, a large peak was observed at 1640-1588 cm⁻¹, associated with the carbonyl of the carboxylic acid group, and a broad peak at 3416.6 cm⁻¹, associated with carboxylates, phenols and alcohols.

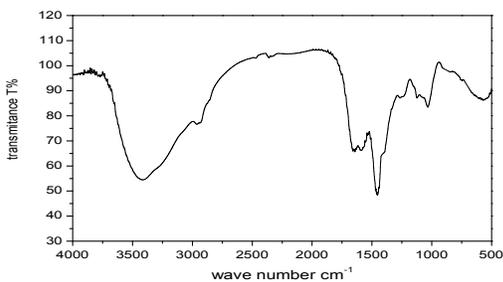


Fig 1. FT-IR spectra of Aldrich humic acid.

The chemical composition of kaolinite is O 64.16%, Na 0.27%, Mg 0.09%, Al 16.94%, Si 17.61%, K 0.08%, Ca 0.03%, Ti 0.83%. Figure 2 displays the EDAX chart of kaolinite.

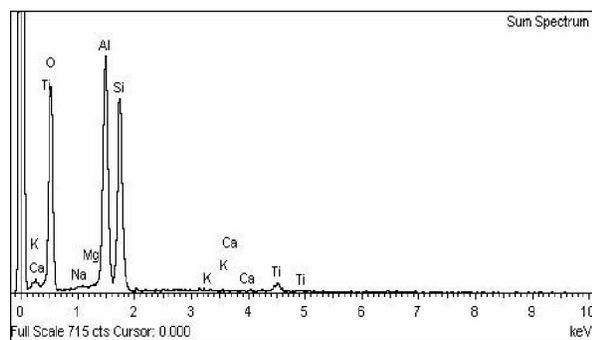


Fig 2. Kaolinite elemental analysis by EDAX

Table 1 shows that kaolinite and hematite particles are on Nano scale, *i.e.* they passed through a 1- μ m pore size sieve. Clearly, results of BET surface area indicated that hematite is greater than kaolinite. Also, BET surface area is the measure of the accessible surface area per unit mass of soil minerals and equals to the sum of internal and external surface area. It is an inverse function of the particle size.

Table 1: properties of soil minerals

	Hematite	Kaolinite
N ² -BET surface area (m ² /g)	35.81	17.2
Particles diameter	< 1- μ m	< 1- μ m

Stephen Brunauer, Paul Hugh Emmett, and Edward Teller (BET) surface area analysis.

3.2 Influence of pH, ionic strength and solution cations on Zn²⁺ adsorption

The adsorption amount q_e of Zn²⁺ solutions were calculated from the mass balance equation for each isotherm bottle using Eq. (2):

$$q_e = (C_i - C_e) V/w \quad (2)$$

Where V is the volume of solution used in the adsorption experiment (L), C_i and C_e are the initial and equilibrium concentrations of the Zn²⁺ solution (mg/L), respectively, and w is the dry weight of the adsorbent (g).

The effect of pH on Zn²⁺ adsorption onto kaolinite, hematite, HA- Ka and HA- He was studied by using different initial pH values (5, 6 and 7), *cf.* Table 2, figs 3, 4. The pH value of the solution has an important role in the adsorption process. The adsorption of Zn²⁺ onto hematite, kaolinite, HA- Ka and HA- He increases significantly with increasing pH. This behaviour refers to the competition of H⁺ with Zn²⁺ at lower pH medium by sorption sites of adsorbent (Jiang *et al*, 2010, Caliskan *et al*, 2011). In addition, it could be interpreted that, with increasing pH, sorption site (>SOH) of soil minerals could be progressively deprotonated to form (>SO⁻) speciation, which could develop the negative charge density on soil minerals surface. There is a strong electrostatic attractive force between negative charge density on soil minerals and positive charge speciation of Zn²⁺ in the observed pH range of 5-7 (Li *et al*, 2011).

The adsorption of Zn²⁺ onto hematite and kaolinite would be affected by background electrolyte. In this study, the ionic strength of solutions was adjusted at 0.001 and 0.01 mol dm⁻³ KCl or CaCl₂. The results in Table 2 showed that the rate and amount of Zn²⁺ adsorption onto kaolinite, hematite, HA- Ka and HA- He decreased with increasing ionic strength. This behaviour would be explained by highly competition of Ca²⁺ or K⁺ with Zn²⁺ to sorption sites of adsorbents

surfaces. Thus, the results suggest that ion exchange is very important process governing Zn^{2+} sorption under experimental conditions studied (Jiang *et al*, 2010, Gu and Evans, 2008). It also suggested that increasing electrolyte concentration can cause screening of surface negative charges by electrolyte ions leading to a drop in the adsorption of the metal ions (Coles and Yong, 2002). In addition, the

adsorption of Zn^{2+} onto kaolinite, hematite, HA - Ka and HA - He was also affected by solution cations. The presence of Ca^{2+} as background electrolyte decreased the adsorption onto adsorbents rather than the presence of K^+ , *cf.* Fig.5. This behaviour may refer to that Ca^{2+} as divalent cations are less dissociative than monovalent K^+ leading to increase the competition with Zn^{2+} ions.

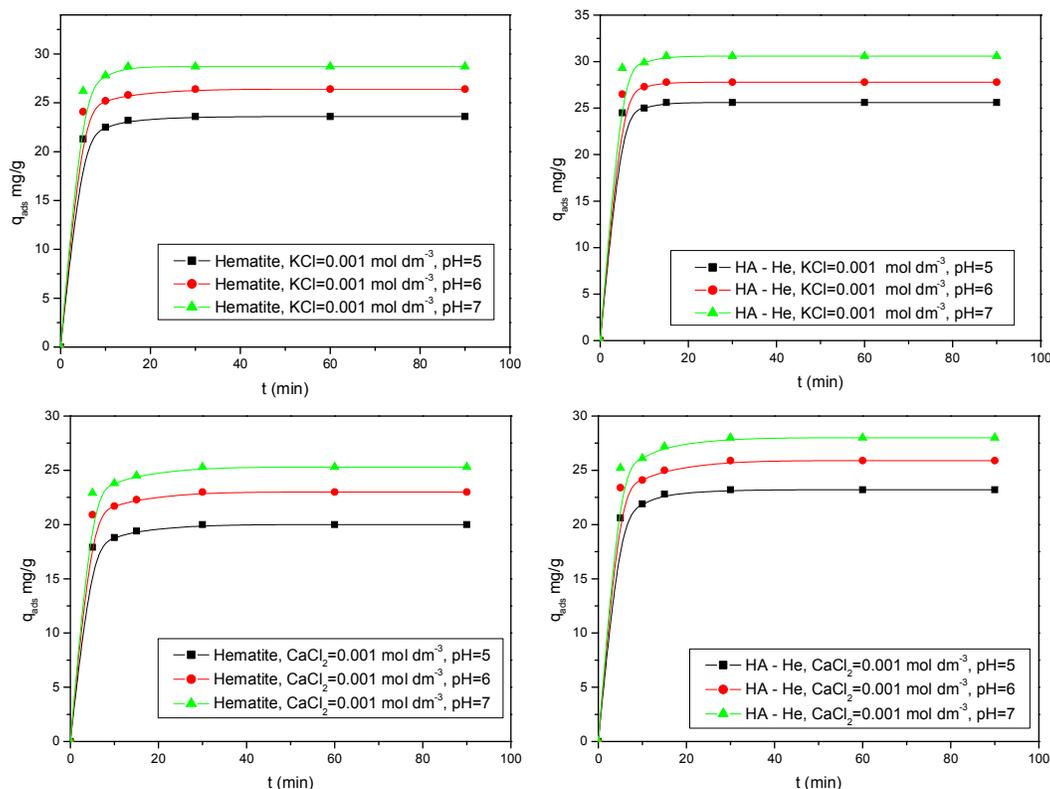


Fig. 3 Adsorption of Zn^{2+} on hematite and humic acid – hematite complex at different pHs

Table 2. Relation between maximum adsorption of Zn^{2+} and k_{obs} (observed rate constant) values.

Adsorbents	Ionic strength (mol dm ⁻³)	Max C_{ads} mg/g			K_{obs}			
		pH			pH			
		5	6	7	5	6	7	
Hematite	[KCl]	0.01	20.9	23.5	24.8	0.069	0.077	0.091
		0.001	23.6	26.4	28.7	0.081	0.082	0.84
	[CaCl ₂]	0.01	18.5	21.8	23.2	0.058	0.062	0.065
		0.001	20	23.2	25.9	0.076	0.078	0.09
Kaolinite	[KCl]	0.01	17.8	19	22	0.045	0.047	0.049
		0.001	20.6	22.5	24.6	0.058	0.061	0.066
	[CaCl ₂]	0.01	15.4	17.8	19.8	0.041	0.043	0.045
		0.001	18.8	21.2	22.9	0.047	0.049	0.052
HA – He complex	[KCl]	0.01	22.7	25.2	27.4	0.072	0.094	0.098
		0.001	25.6	27.8	30.6	0.11	0.12	0.13
	[CaCl ₂]	0.01	20.5	22.6	25	0.071	0.091	0.095
		0.001	23.2	25.9	28	0.095	0.097	0.1
HA – Ka complex	[KCl]	0.01	20	21.5	23.4	0.047	0.049	0.051
		0.001	23	25.2	27.4	0.06	0.063	0.068
	[CaCl ₂]	0.01	18	20.2	21.8	0.045	0.048	0.049
		0.001	21.5	23.5	24.9	0.052	0.055	0.057

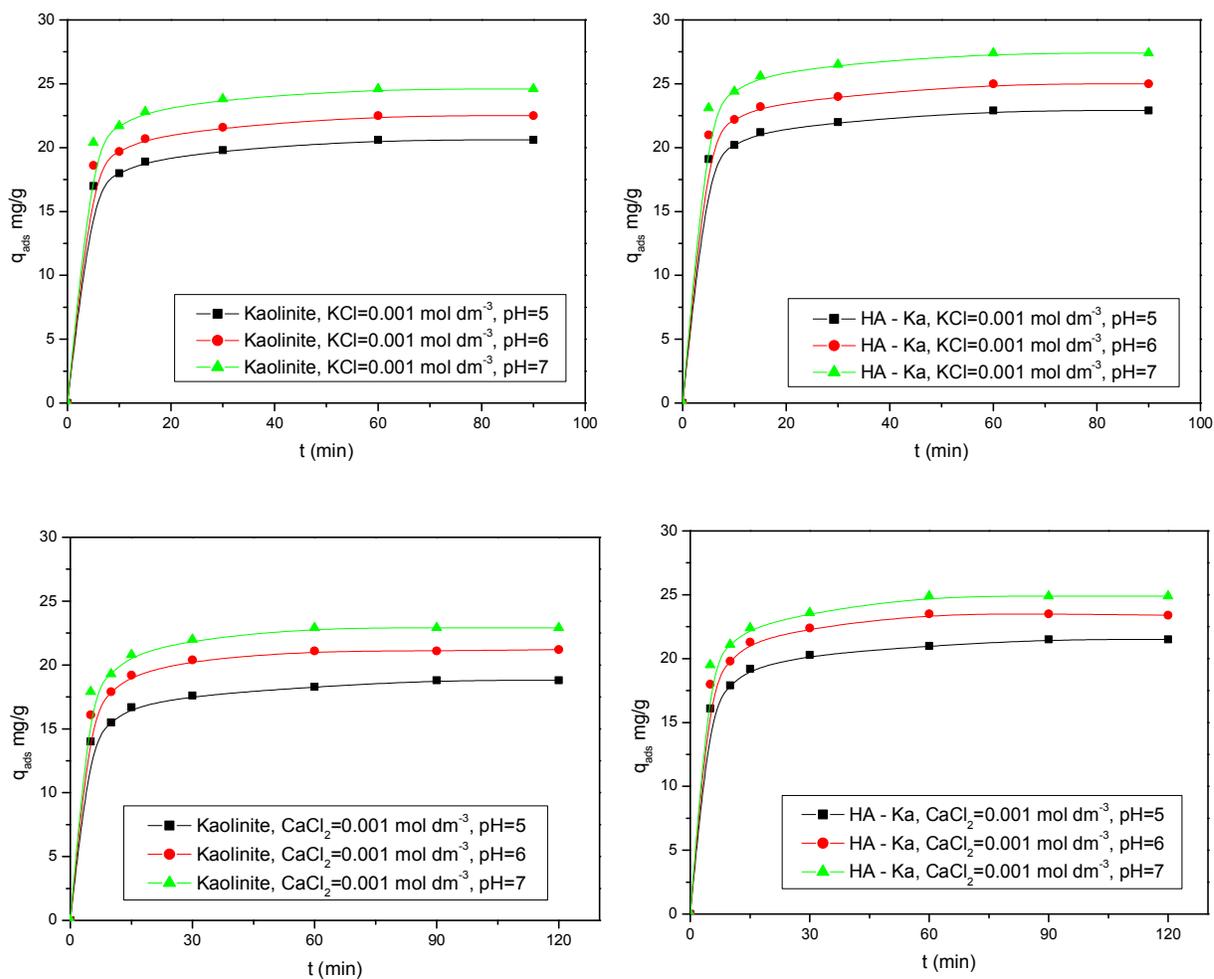


Fig 4. Adsorption of Zn^{2+} on kaolinite and humic acid – kaolinite complex at different pHs.

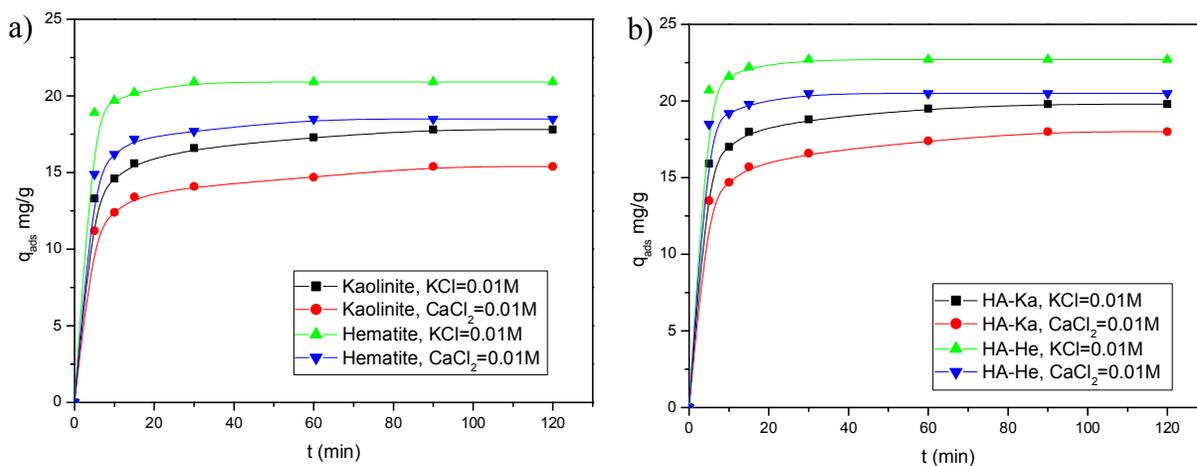


Fig 5. Adsorption of Zn^{2+} at pH= 5 onto a) Kaolinite and Hematite b) HA - Ka- and HA - He.

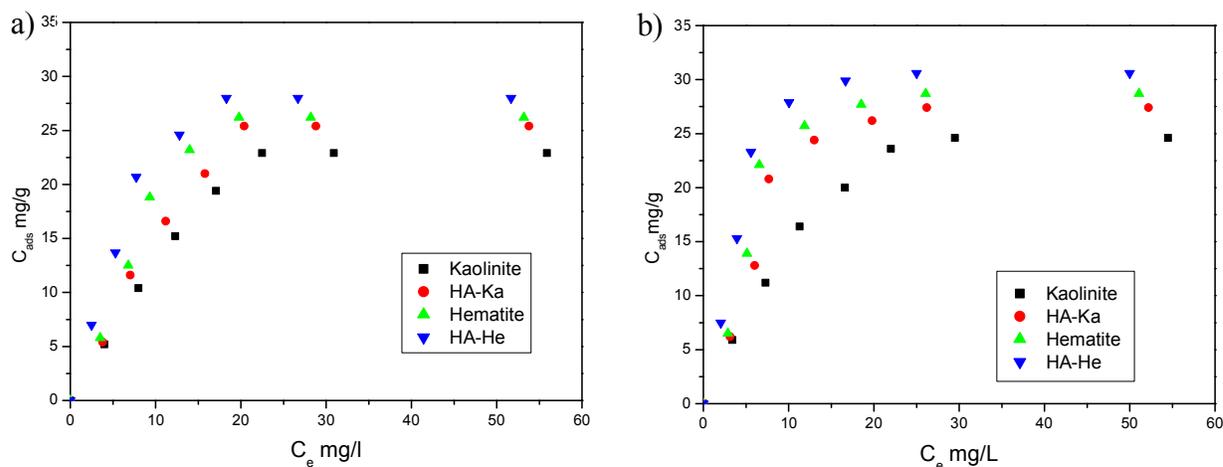


Fig 6. Adsorption of Zn^{2+} on kaolinite, hematite, HA - Ka and HA - He at pH=7 at a) $CaCl_2=0.001 \text{ mol dm}^{-3}$, b) $KCl=0.001 \text{ mol dm}^{-3}$

The maximum capacity of Zn^{2+} adsorption onto hematite and kaolinite in the absence and presence of HA has been obtained at higher pH (pH=7), lower ionic strength ($0.001 \text{ mol dm}^{-3}$) and monovalent cations (K^+) as background electrolyte (as shown in Table 2). The maximum adsorption capacity of Zn^{2+} was determined as 28.7 mg/g and 24.6 mg/g on hematite and kaolinite respectively and 30.6 mg/g and 27.4 mg/g onto HA - He and HA - Ka complexes respectively, cf. Table 2. Also, it is appeared from figure 6 that the amount of Zn^{2+} adsorbed on hematite is greater than that on kaolinite. Based on the adsorption results, it is assumed that a surface reaction adsorption mechanism may take place as a result of an interaction, specifically, between negatively charged groups of soil minerals and the positively charged metal ions (Zn^{2+}). High maximum adsorption of hematite than kaolinite is attributed to surface area and cation exchange capacity for hematite are higher than those for kaolinite. The presence of HA led to increase Zn^{2+} adsorption onto hematite and kaolinite (Liang *et al*, 2011, Singh *et al*, 2011). The relatively higher adsorption of Zn^{2+} onto soil minerals in the presence of humic acid refers to that the ion exchange process plays an important role in the adsorption mechanism (strongly electrostatic in nature) and may be a consequence of Zn^{2+} complexation by the carboxylic and phenolic groups.

3.3 Adsorption isotherm studies

The obtained experimental equilibrium adsorption data, cf. Fig.6, were compared with the adsorption isotherm models. Two models of Langmuir

(Langmuir, 1916) and Freundlich (Freundlich, 1906) in their related linearized expressions have been used as Eqs. (3) and (4) respectively.

$$\frac{1}{q_e} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} \quad (3)$$

Where C_e is the concentration of adsorbate (mg/L) at equilibrium in solution, q_e the amount of adsorbate at equilibrium (mg/g), a_L (L/mg) and K_L (L/g), are constants

$$\log q_e = \log K_f + \frac{\log C_e}{n} \quad (4)$$

Where K_f ($(\text{mg/g})(\text{mg/L})^{-1/n}$) and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. If n is close to 1, the surface heterogeneity could be assumed to be less significant and as n approaches 10 the impact of surface heterogeneity becomes more significant (Noroozi *et al*, 2007).

The parameters related to each isotherm were determined by using linear regression analysis and the square of the correlation coefficients (R^2) were also calculated. Lists of the parameters obtained along with R^2 values are predicted in Table 3 for the Zn^{2+} adsorption onto kaolinite, hematite, HA- Ka and HA- He. The results indicated that the Langmuir model fitted to the experimental data better than the Freundlich model under various conditions (Arias and Sen, 2009). Langmuir equation describes the adsorption on strongly homogeneous surfaces (Maghoodloo *et al*, 2011).

Table 3: Zinc adsorption fitting by Langmuir and Freundlich equation

Adsorbents	Ionic strength (mol dm ⁻³)	Langmuir			Freundlich		
		R ²	K _L (L/g)	a _L (L/mg)	R ²	K _F (mg/g)(mg/L) ^{-1/n}	n
Hematite	[CaCl ₂]=0.001	0.98	0.19	0.004	0.88	2.9	1.36
	[KCl]=0.001	0.97	0.18	0.003	0.90	4.7	1.6
HA - He	[CaCl ₂]=0.001	0.98	0.17	0.002	0.88	4.8	1.7
	[KCl]=0.001	0.98	0.13	0.002	0.90	6.7	1.88
Kaolinite	[CaCl ₂]=0.001	0.99	0.22	0.005	0.95	1.99	1.3
	[KCl]=0.001	0.98	0.21	0.004	0.97	2.8	1.47
HA - Ka	[CaCl ₂]=0.001	0.97	0.18	0.003	0.96	2.2	1.2
	[KCl]=0.001	0.97	0.16	0.001	0.85	3.7	1.48

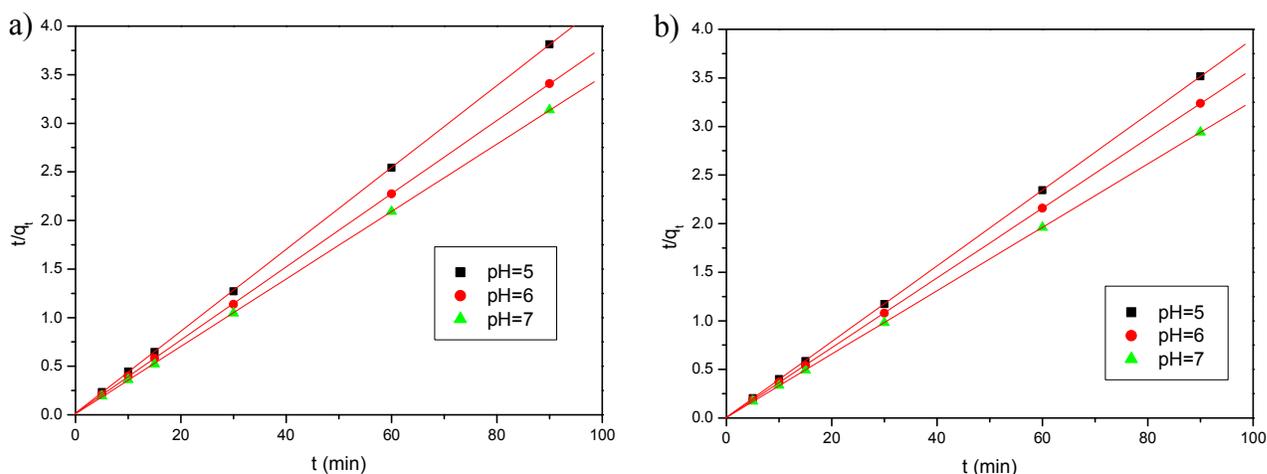
3.2.3. Kinetic models

The kinetic mechanism is important in adsorption processes because it determines the uptake rate and controls the residual time of the entire process. The observed rate constant values (k_{obs}) of Zn²⁺ adsorption onto soil minerals in the absence and presence of HA increased with increasing pH. The

obtained experimental data, *cf.* Table 2, were compared with two models. Linear and Polynomial models have been used (Newman *et al*, 2004). The results in table 4 explained that the Polynomial model fitted to the experimental data more than the linear model. This behavior indicated that the change in k_{obs} values with pH are not gradually.

Table 4: Relation between k_{obs} and pH fitting by Linear and Polynomial models

Adsorbents	Ionic strength (mol dm ⁻³)	Fit Linear	Fit Polynomial
		R ²	R ²
Hematite	[KCl]	0.01	0.98
		0.001	0.96
	[CaCl ₂]	0.01	0.98
		0.001	0.84
HA - He	[KCl]	0.01	0.80
		0.001	1
	[CaCl ₂]	0.01	0.86
		0.001	0.98
Kaolinite	[KCl]	0.01	0.85
		0.001	0.80
	[CaCl ₂]	0.01	1
		0.001	0.98
HA - Ka	[KCl]	0.01	1
		0.001	0.98
	[CaCl ₂]	0.01	0.92
		0.001	0.98

**Fig 7.** pseudo second order fitting for adsorption of Zn²⁺ on a) hematite b) HA- He at KCl= 0.001 mol dm⁻³.

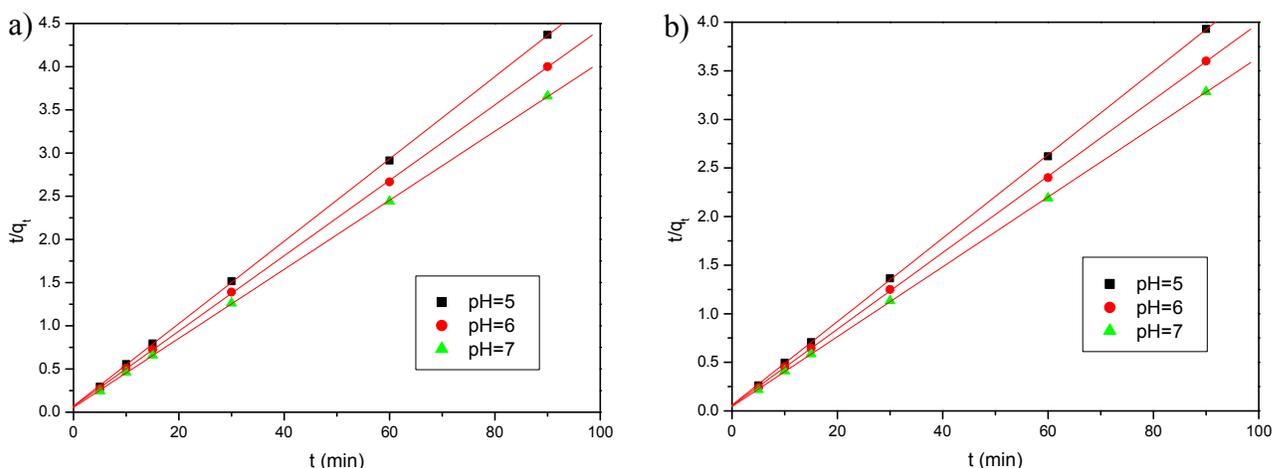


Fig 8. pseudo second order fitting for adsorption of Zn^{2+} on a) kaolinite b) HA- Ka at $KCl = 0.001 \text{ mol dm}^{-3}$.

The kinetic adsorption data were collected to understand the dynamics of the adsorption reaction in terms of the order of the rate constant. Batch experiments were conducted to explore the rate of Zn^{2+} adsorption by kaolinite, hematite, HA - Ka and HA - He as described in Section 2.2.4 at different pH, ionic strength and solution cations. The adsorbed amount of Zn^{2+} on hematite, kaolinite, HA - He and HA - Ka increased with increasing in contact time (Jeon *et al*, 2003) and reached the equilibrium within 15 - 60 min and 60 - 90 min for hematite and kaolinite respectively, due to the studied conditions. Two kinetic models were applied to the adsorption kinetic data in order to investigate the behavior of adsorption process of Zn^{2+} onto the adsorbents. These models include the irreversible pseudo-first-order kinetics (Chang and Juang, 2005) and the pseudo-second-order (Wu *et al*, 2010). Linear form of irreversible pseudo-first-order model can be formulated as:

$$\ln\left(\frac{C_i}{C_t}\right) = k_1 \times t \quad (5)$$

Where C_i (mg/L) is the initial concentration and C_t (mg/L) is the equilibrium concentration at time t of Zn^{2+} , and k_1 (min^{-1}) is the first order rate constant. The values of k_1 and correlation coefficients were determined from linear plots of $\ln(C_i/C_t)$ versus time for various solution conditions and shown in Table 5. The linear pseudo-second-order kinetics can be formulated as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_e and q_t are surface loading of Zn^{2+} at equilibrium and time t respectively, and k_2 (g/mg min) is the second-order rate constant. The linear plots of t/q_t as a function of t provided not only the rate constant k_2 , but also an independent evaluation of q_e .

Table 5: comparison of the pseudo first order and pseudo second order kinetic models for the adsorption of Zn^{2+} onto, kaolinite, hematite, HA- Ka and HA- He at various solution conditions at 25°C.

Adsorbents	Ionic strength (mol dm^{-3})	pH	Pseudo first order		Pseudo second order			
			k_1 (min^{-1})	R^2	q_e (mg/g)(q_{exp})	k_2 (g/min mg)	R^2	
Hematite	[CaCl ₂]	0.01	5	0.001	0.76	18.8 (18.5)	0.035	0.99
			6	0.0015	0.80	22.2(21.8)	0.03	0.99
			7	0.0016	0.75	23.6(23.2)	0.031	0.99
		0.001	5	0.0018	0.87	20.2(20)	0.089	0.99
			6	0.002	0.91	23.2 (23.2)	0.084	0.99
			7	0.0025	0.91	25.5(25.9)	0.07	0.99
	[KCl]	0.01	5	0.0018	0.92	21.2 (20.9)	0.088	0.99
			6	0.002	0.95	23.7(23.5)	0.08	0.99
			7	0.0025	0.94	25(24.8)	0.068	0.99
		0.001	5	0.002	0.75	23.8(23.7)	0.098	0.99
			6	0.0023	0.82	26.5(26.56)	0.088	0.99
			7	0.003	0.77	28.8(28.7)	0.12	0.99
HA- He	[CaCl ₂]	0.01	5	0.0018	0.92	20.7(20.5)	0.085	0.99

		0.001	6	0.0023	0.90	22.8(22.6)	0.073	0.99		
			7	0.0026	0.91	25.2(25)	0.068	0.99		
			5	0.0024	0.76	23.4(23.2)	0.086	0.99		
			6	0.0027	0.94	26.1(25.9)	0.064	0.99		
			7	0.0032	0.89	28.2(28)	0.062	0.99		
			5	0.0019	0.85	22.8(22.7)	0.1	0.99		
		[KCl]	0.01	6	0.0026	0.91	25.5(25.2)	0.07	0.99	
				7	0.0029	0.92	27.6(27.4)	0.065	0.99	
				5	0.003	0.98	25.7(25.6)	0.24	1	
		0.001	6	0.004	0.98	27.9(27.8)	0.24	1		
				7	0.0044	0.98	30.7(30.6)	0.21	1	
				5	0.0008	0.81	16.04 (15.8)	0.018	0.99	
		Kaolinite	[CaCl ₂]	0.01	6	0.0009	0.79	18.1(17.8)	0.023	0.99
					7	0.001	0.83	20.2(19.8)	0.021	0.99
5	0.001				0.76	19.2(18.8)	0.022	0.99		
0.001	6			0.0011	0.67	21.5(21.2)	0.026	0.99		
				7	0.0013	0.72	23.3(22.9)	0.025	0.99	
				5	0.001	0.79	18.16 (17.8)	0.022	0.99	
[KCl]	0.01			6	0.0011	0.84	19.4(19)	0.02	0.99	
				7	0.0012	0.73	22.4(22)	0.023	0.99	
				5	0.0014	0.84	21(20.6)	0.032	0.99	
0.001	6			0.0016	0.84	22.9(22.5)	0.029	0.99		
				7	0.0018	0.83	25(24.6)	0.028	0.99	
				5	0.001	0.82	18.4(18)	0.021	0.99	
HA- Ka	[CaCl ₂]			0.01	6	0.0011	0.80	20.6(20.2)	0.022	0.99
					7	0.0012	0.88	22.2(21.8)	0.019	0.99
		5	0.0013		0.74	21.9(21.5)	0.021	0.99		
		0.001	6	0.0014	0.72	23.8(23.5)	0.025	0.99		
				7	0.0015	0.76	25.3(24.9)	0.022	0.99	
				5	0.001	0.79	20.3(20)	0.025	0.99	
		[KCl]	0.01	6	0.0012	0.83	21.8(21.5)	0.027	0.99	
				7	0.0013	0.79	23.6(23.4)	0.033	0.99	
				5	0.0016	0.83	23.4(23)	0.028	0.99	
		0.001	6	0.0017	0.84	25.5(25.2)	0.027	0.99		
				7	0.0019	0.81	27.9(27.4)	0.026	0.99	

The fitting of experimental data to the pseudo first order and pseudo second order equations (*cf.* Table 5 and Figs. 7 and 8) and the calculated correlation coefficient (R^2) showed that Zn^{2+} adsorption onto kaolinite, hematite, HA - Ka and HA - He was more conformity to pseudo second order (Olu-Owolabi *et al.*, 2010, Sheela *et al.*, 2012). Also, q_e values agree with the experimental data at different solution conditions. This means that the adsorption of Zn^{2+} onto hematite, kaolinite, HA - He and HA - Ka is mainly chemisorption. The initial adsorption rate, $K_2q_e^2$, for HA - He is greater than hematite and for HA - Ka is greater than kaolinite at different solution chemistry. This can be explained the greater adsorption of Zn^{2+} on hematite and kaolinite in the presence of HA than in the absence of HA under various conditions.

4. Conclusion

Equilibrium and kinetics of Zn^{2+} adsorption onto soil minerals (kaolinite and hematite) in the absence and presence of humic acid has been investigated under various conditions. The maximum adsorption

capacity of Zn^{2+} onto soil minerals was increased by the addition of humic acid. The adsorbed amount of Zn^{2+} increased with increasing pH and decreasing ionic strength. The adsorption of Zn^{2+} onto kaolinite, hematite, HA- Ka and HA- He also affected by solution cations. The presence of K^+ enhances the adsorption of Zn^{2+} onto kaolinite, hematite, HA- Ka and HA- He than the presence of Ca^{2+} .

The equilibrium data have been explored by Freundlich and Langmuir models. The results indicated that the Langmuir model fitted to the experimental data better than the Freundlich model under various conditions. The adsorbed amount of Zn^{2+} onto kaolinite, hematite, HA- Ka and HA- He increased with increase in contact time. The kinetics of Zn^{2+} adsorption was studied by using pseudo first and pseudo second order models. The results explained that Zn^{2+} adsorption onto kaolinite, hematite, HA- Ka and HA- He was more conformity to pseudo second order. This means that the adsorption of Zn^{2+} onto adsorbent surfaces is mainly chemisorptions.

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Nomenclature

a_L	Constant in Langmuir isotherm model (L/mg)
C_e	Equilibrium concentration of the adsorbate (mg/L)
C_i	Initial concentration of the adsorbate (mg/L)
C_t	Equilibrium concentration of the adsorbate at time t (mg/L)
EDAX	Energy Disperse Analysis X-ray
FTIR	Fourier transform infrared
HA	Humic acid
HA – He	humic acid / hematite complex
HA – Ka	humic acid / kaolinite complex
k_1	Rate constant of irreversible pseudo first-order kinetic (min^{-1})
k_2	Rate constant of pseudo second-order kinetic (g/min mg)
K_f	Constant of Freundlich isotherm (mg/g)/(mg/L) ^{1/n}
K_L	Constant in Langmuir isotherm model (L/g)
k_{obs}	rate constant
n	Constant of Freundlich isotherm
q_{ads}	Amount of solute adsorbed
q_e	Amount of solute adsorbed at equilibrium (mg/g)
q_{exp}	Amount of solute adsorbed at equilibrium (mg/g) practically
q_t	Amount of solute adsorbed at time t (mg/g)
R^2	Square of the correlation coefficient
SEM	Scanning electron microscopy
V (L)	Volume of solution used in the adsorption experiment (L)
W	Dry weight of adsorbent (g)

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