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Research article

Kinetic study of humic acid adsorption onto smectite: The role of individual and blend background electrolyte

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Abstract: Many factors can affect the natural organic matter adsorption on clay, such as pH and ionic strength. Blended background electrolyte could be causing better simulation to natural effects. Therefore, kinetic study of humic acid (HA) adsorption onto smectite has been studied under various conditions. Impact of pH and individual and blend background electrolyte with different ionic strength concentration on the rate of adsorption has been investigated. The rate and amount of adsorbed HA on smectite improved with raised background electrolyte concentration, declining pH, and in existence Ca^{2+}. The rate of adsorption order was in the presence of $CaCl_2$ > blend ($CaCl_2$ and KCl) > KCl. The adsorption isotherm was L-shap in the presence of $CaCl_2$ and KCl while was S-shap in presence blend ($CaCl_2$ and KCl). Moreover, the data revealed that the adsorption behavior of HA might be pronounced more obviously by Freundlich model than Langmuir. Two kinetic models were applied to assess the rate constants and kinetic data. The results clarified that HA adsorption on smectite was following to pseudo second order model under various conditions.

Keywords: kinetics; humic acid; smectite; adsorption; background electrolyte

1. Introduction

Smectite is phyllosilicate minerals [1,2] characterized as a 2:1 (Si:Al) layer structure. Smectite clays have a changeable net negative charge, that is stabled by metal cations such as Na, Ca, Mg and H

sorbed outwardly on interlamellar surfaces. The building, chemical structure, replaceable ions nature and small crystal size of smectite is responsible for the numerous of unique properties, as well as a highly active surface area, a high cation exchange capacity, uncommon hydration features, and the facility change powerfully the movement behavior of solutions [3–6]. Furthermore, saturated clays with Al^{3+} has a strong polarity of water linked with Al^{3+}, and cause reveals strong H-bonding with insecticides cause better adsorption [6]. Otherwise, some hydrated metal cations as Ca^{2+} and Mg^{2+} surrounding with water molecules reduced the ion-dipole connections by preventing the straight contact among the polar functional groups and exchangeable cations [7,8]. Moreover, nonpolar organic compounds can interact with siloxane surfaces of smectite [9,10]. While, saturated clays with weakly hydrated cations as NH_4^+, K^+, increased the size of adsorptive spheres among replaceable cations therefore improving the adsorption of organic compound. Moreover, some academics have illustrious that organic compound adsorption onto siloxane surfaces of clay rise by reducing the charge density of clay surface [11–13].

One of the most prevalent components of humic substances is humic acid, which is polyelectrolyte made by secondary synthesis reactions through the decay progression of soil organic matter that undergoes microbial transformation [14]. The HAs are heterogeneous agglomerations containing varying functionalities ranging from nonpolar poly methylene chains to highly polar carboxylic acid fractions [15]. Due to greater aromaticity, poly functionality and hydrophobicity, HAs are more likely to adsorb on soil minerals than other humic substances [16]. Adsorption of HA by mineral surfaces is influenced mostly by solution pH, ionic strength, and the type of exchangeable cations. These factors also affect the structure conformation of HA [17]. Complexes of HA and clay contribute to soil structure and water-holding capacity, and are involved in reductive and oxidative reactions, playing a major role in the cycling of various nutrients and pollutants [18]. Interactions between HA and clay have been studied widely, and the reporting mechanisms include ligand exchange, cation and water bridging, Van der Waals forces, and entropy-driven hydrophobic interactions. The ligand exchange mechanism is considered one of the furthermost significant HA sorption mechanisms [19]. Ligand exchange occurs between polar organic functional groups of HA and mineral hydroxyls. Ligand exchange is significant mainly on Fe and Al oxides or on smectite where an abundance of hydroxyl edge surface sites exists in adsorption [20].

The HA adsorption on smectite occurs mainly on the large basal surfaces; electrostatic interactions and interactions such as hydrogen bonding and cation bridging account for the formation of organic coatings on the clay particles [21]. The dominant interactions are, on the one hand, determined by the nature of the HA molecules and, on the other, by the properties of the mineral surfaces.

Hence, the object of this paper was to explore the isotherm and kinetics of HA adsorption onto smectite under various solution conditions.

2. Materials and methods

2.1. Materials

2.1.1. Smectite

Smectite was gotten from Sabga in the North West region of Cameroon with geographical

coordinates: latitude 6° N and longitude 10°19 E [22].

Smectite was dried and ground into fine powder. Then smectite was sieved to get geometrical sizes of 1 μm, that reserved in an oven at 110 °C a period of 24 h, removed and cooled as described elsewhere [23]. After being dried, Smectite was ground and sieved. The smectite was characterized and identified by qualitative X-ray powder diffractometry (XRD) and the BET surface area of smectite was determined.

2.1.2. Humic acid

Humate salt was gotten from Sigma-Aldrich. Humic acid was prepared from humate salt as follows [24], humate salt has been dissolved in deionized water, and precipitated by acidification to a pH of 2 as described elsewhere [25]. Humic acid was described by FTIR spectra, elemental analysis, potentiometric titrations.

2.2. Methods

2.2.1. FT-IR spectroscopy

Smectite and HA samples were kept in a desiccator and the KBr was dried in an oven at 105 °C for 48 h until the measurements were made. The FTIR spectra were obtained according to the Stevenson methodology [14], using a Perkin Elmer FTIR spectrometer frontier spectrophotometer, in duplicate. All individual FTIR spectra were recorded in the range 4000 to 400 cm^{-1} and were composed by 64 scans with a spectral resolution of 4 cm^{-1}.

2.2.2. Potentiometric titration of HA

Potentiometric titration on Aldrich HA complexes was performed to the suspension of 100 mg dry weight of HA in 100 mL deionized water (ionic strength to 0.001 KCl) to determine the carboxylic and phenolic groups in the pH ranges of 3–8 and 8–12 [25], respectively. A steam of purified and presaturated nitrogen gas was bubbled through the system in order to exclude CO_2 and O_2 dissolved gases as well as to avoid any evaporation of the sample at constant temperature 25 °C.

2.2.3. Preparation of smectite

Smectite suspension (2.5 g/L) stock solution was equipped as a solid concentration for the equilibrium adsorption experiments. This suspension was set in 0.001 and 0.01 mol/L of KCl, $CaCl_2$ or blend ($CaCl_2$ and KCl) background electrolyte.

2.2.4. Adsorption of HA

A well-mixed smectite suspension (under study conditions) was pipetted into a series of HA solutions at changing concentrations (66.7 and 400.2 mg/L) to bounce the absolute volume of 30 mL in 50 mL tubes. The suspensions were shaken for 24 h on a shaker to reach equilibrium. Smectite concentration for all adsorption experiments was 10 g/L. Each tube was centrifuged for 5 min

at 20000 rpm. The supernatant was transferred to separate bottles. The amount of the adsorbed HA was calculated from the following Eq 1,

The amount of adsorption q_e was calculated from the mass balance equation for each isotherm:

$$q_e = \frac{(C_i - C_e)V}{w} \tag{1}$$

where V is the volume of solution used in the adsorption experiment (L), C_i and C_e are the initial and the equilibrium concentrations of the HA solutions (mg/L), respectively at 400 nm, and w is the dry weight of the adsorbent (g).

2.2.5. Kinetic experiment

Kinetic tests were done by shaker a certain amounts of adsorbents with 40 ml of solution contain humic acid (to reach 240 mg/L concentration) at 25 °C. At pre-determined time intervals, fractions of the mixture were pulled by a syringe and then centrifuged and HA concentration was evaluated as described before. The pH value checked up through the experimental life time. The adsorption amount at time t, q_t (mg/g) was determined by the next Eq 2,

$$q_t = \frac{(C_i - C_t)V}{w} \tag{2}$$

where C_i is HA initial concentration (mg/L), C_t is the concentration at any time t (mg/L), V is the adsorption experiment volume (L), and w is the adsorbent dry weight (g).

3. Result and discussion

3.1. Humic acid, smectite, smectite-humic complex properties

The XRD pattern of smectite (Figure 1) showed that the dominant phase is the smectite with ratio 96% and with the presence of quartz and kaolinite as impurities. The mineralogical composition determined was expressed in clay fraction and ranged from high content of smectite with very low of other clay minerals as kaolinite and quartz. The method is based on identifying the pattern of basal peaks and their corresponding relative intensity values occurring in the X-ray diffraction pattern [26] which corresponded to a typical montmorillonite pattern. The quantitative analysis of clay minerals in soils involves working out of peak intensity (area or height) ratios based on standard powder diffraction of the international powder diffraction file.

The elemental analysis of Aldrich HA was 40.06, 4.57, 0.79, 0.73 and 53.83 for carbon, hydrogen, nitrogen, sulfur and oxygen percentage respectively. The results of potentiometric titration (Figure 2) showed that the total carboxyl and phenolic groups contents were 6.01 mmol/g in presence KCl, $CaCl_2$ and blind (KCl and $CaCl_2$) electrolyte. Furthermore, carboxylic group and phenolic group contents of Aldrich HA were 3.68 and 2.33 mmol/g respectively in the presence of $CaCl_2$ and blend electrolyte of Aldrich HA while, in the presence of KCl, carboxylic group and phenolic group contents of Aldrich HA were 4.1 and 1.91 mmol/g respectively. Moreover, the potentiometric study of Aldrich HA has been significant affected by background electrolyte cations.

The EDAX results display that the chemical composition of smectite (O 69.41%, Na 1.44%, Mg

1.86%, Al 8.93%, Si 16.19%, K 1.3%, Ca 0.52%, Ti 0.35%). The elemental analysis for smectite demonstrate that the Si:Al ratio is approximately 2:1.
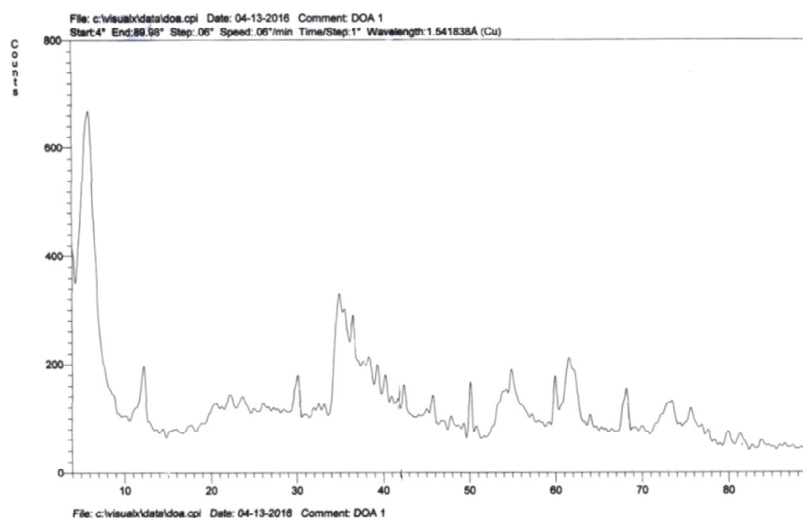

Figure 1. XRD pattern of smectite.
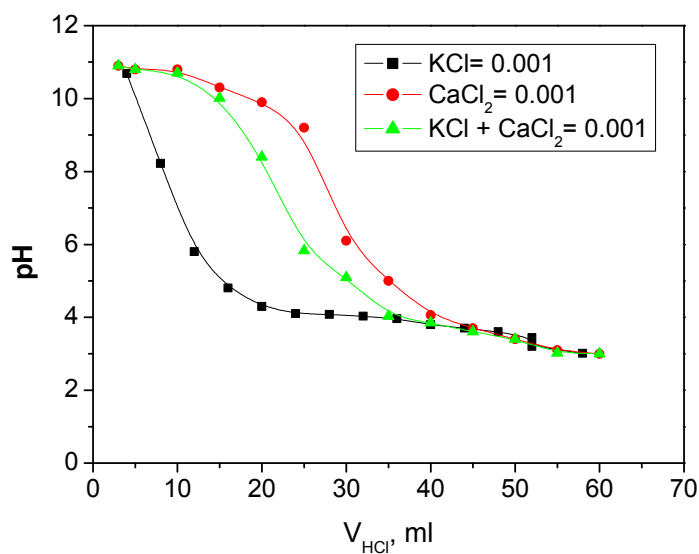
Figure 2. Curves of the potentiometric titration of Aldrich humic acid with a solution of HCl.

Figure 3 represented the FTIR spectra of HA, smectite and smectite-humic acid complex. Humic acid spectra had two major peaks observed at 1640–1588 cm^{-1} associated to the carbonyl with the carboxylic acid group, and a broad peak at 3417 cm^{-1} associated to carboxylates, phenols, and alcohols.

The obtained FTIR spectra of the smectite showed the absorption band at 3618 cm^{-1} found in the spectra of smectite is typical for dioctahedral smectite and is due to stretching vibrations of structural OH groups of smectite [27]. The band at 3694 cm^{-1} observed in smectite is characteristic for kaolinite

which is present as impurity in the sample and is frequently used for identification of kaolinites in raw materials. This band is well separated by absorption bands of most other minerals, which allows identification of very low amounts of kaolinites [28]. The broadband near 393 cm^{-1}, observed in the spectra of all samples is due to O–H stretching vibrations of adsorbed water, while the bending vibration of water observed at 1634 cm^{-1} [29]. The IR spectra of dioctahedral smectite show a broad band in the 1227–1371 cm^{-1} region due to Si–O stretching vibrations. The bands at 908 and 983 cm^{-1} are attributed to Al–Al–OH bends vibration, while the 455 cm^{-1} bands to the Si–O–Si bending vibration which is characteristic for smectites [29].
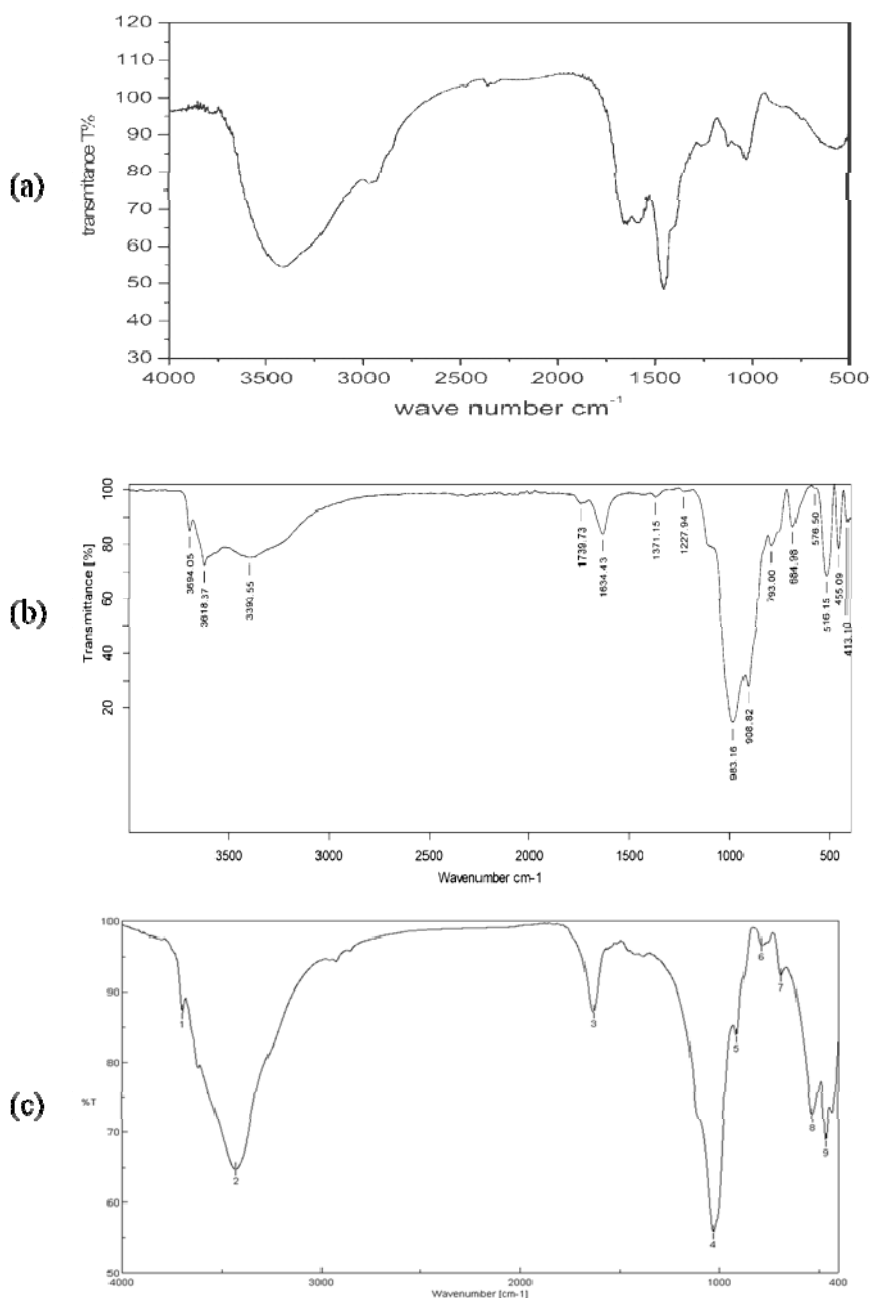
Figure 3. FTIR spectra of the (a) humic acid, (b) smectite and (c) humic-smectite complex.

FTIR spectroscopic analysis of smectite-humic acid complex showed major changes of the absorbance band at 914 and 789 cm^{-1} for O–Al–OH vibrations and increased absorption in the 1031 and 1633 cm^{-1} regions for Si–O and COO– stretching vibrations, respectively. The absorption band for Si–O was retained by the IR spectrum of the high molecular weight fraction of HA, and the O–Al–OH absorption by that of low molecular weight HA. The latter showed in addition the strong band for COO– stretching vibrations. These effects indicate that sorption on Smectite is carried out through COO– functional groups [30]. This is considered strong evidence for ligand exchange mechanism.

To quantify changes in specific infrared absorption bands, we employed potassium thiocyanate (KSCN) as an internal standard [31], added at a constant 1:5 (w/w) KSCN/HA-clay complex ratio. Difference spectra for clay-HA complexes were obtained by subtracting the spectra of analogously treated HA-free clay samples of clay-HA complexes using a subtraction factor of ~1 to match the 3696 cm^{-1} peaks due to the clay structure OH [32]. The heights of peaks of interest were normalized to that of the C–N stretching, vibration (C–N) at 789–790 cm^{-1} from KSCN [30].

Smectite particles are on the nanoscale due to its particles distributed through a 1 μm pore size sieve. The BET surface area value of smectite was 31.18 m^2/g whilst the BET surface area value of smectite-humic complex was 35.34 m^2/g and this refers to the high contents of carboxylic and phenolic groups of HA.

3.2. Adsorption of HA on smectite
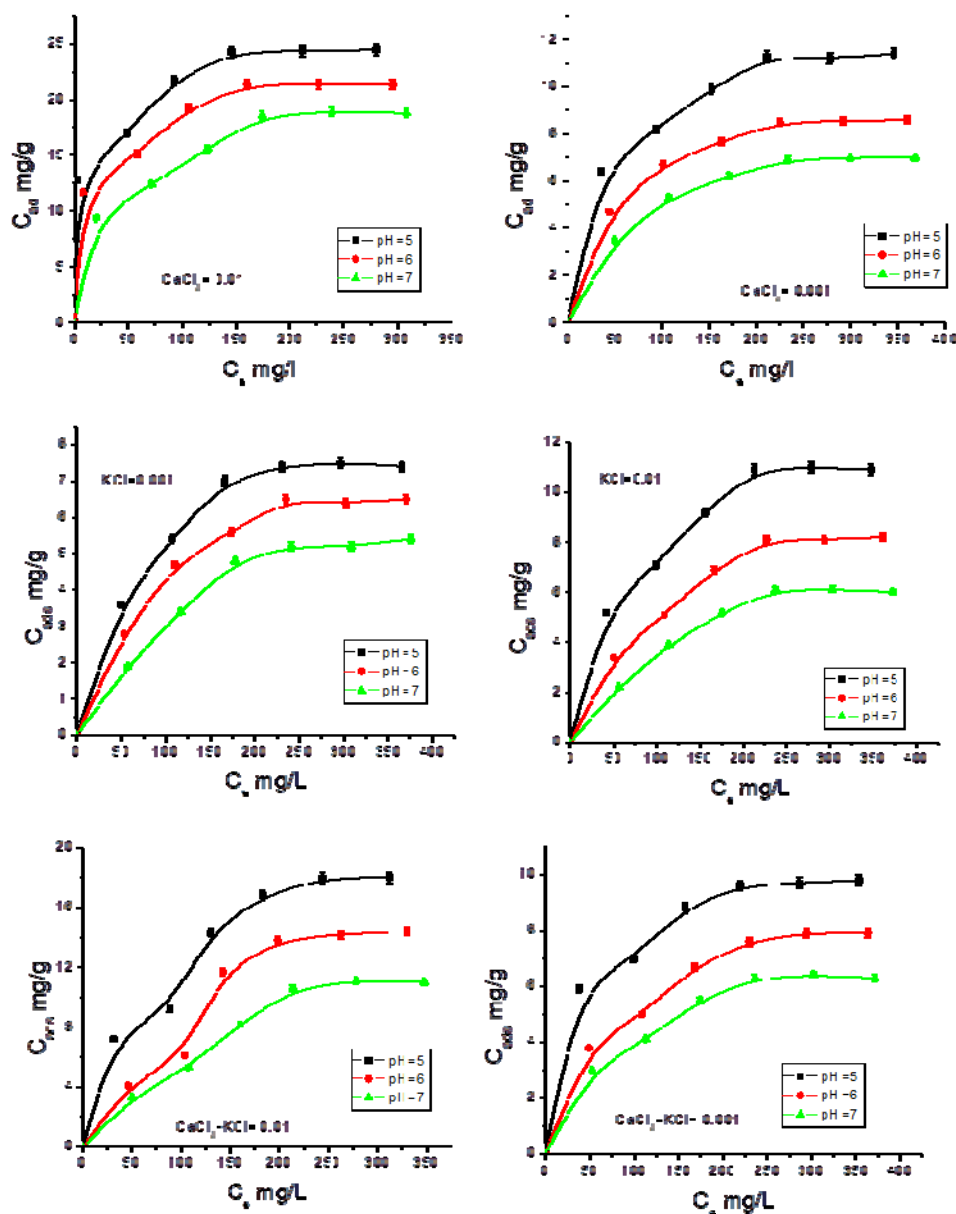
3.2.1. Adsorption isotherm studies

The HA maximum ability adsorption on smectite obtained at 240 mg/L of HA initial concentration. The more adding of HA concentrations didn't display any future change. Adsorption data are most normally signified by an adsorption isotherm [33], which is a scheme of the capacity of adsorptive reserved by a solid (the adsorbate) as a function of the concentration of that adsorbate in the bathing liquid stage that is at equilibrium with the solid. The shape of this isotherm route proposes information about the adsorbate-adsorbent (organic-surface) interaction; to this end, isotherms have been classified into four types, S-type, L-type, H-type and C-type. The adsorption isotherm data explored that the adsorption isotherm was more pronounced as L-type under various condition while was more pronounced as S-type at blended background electrolyte (CaCl$_2$ and KCl) under different pH and ionic strength concentrations Figure 4. This means that dsorbate-adsorbate interface is stronger than the adsorbate-adsorbent interface at mixed background electrolyte. This situation favours the "clustering" of adsorbate molecules at the surface because they bond strongly with one another than with the surface.

Moreover, Langmuir [34] and Freundlich [35] models in their associated linearized terms as represented in Eqs 3 and 4, respectively are used to analysis the adsorption data.

$$\frac{1}{q_e} = \frac{1}{k_L \, c_e} + \frac{a_L}{k_L} \qquad (3)$$

where C_e is the concentration of adsorbate (mg/L) at equilibrium, q_e the amount of adsorbate at equilibrium (mg/g), and a_L (L/mg) and k_L (L/g) are constants.

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

Figure 4. Adsorption isotherm of humic acid adsorption on smectite under different conditions (with error bar).

Where K_f $((mg/g)(mg/L)^{-1/n})$ and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. If n is near to 1, the surface heterogeneity could be supposed to be less significant and as n approximation 10, the influence of surface heterogeneity became more significant [36] The factors linked to each isotherm were investigated by using linear regression analysis and the square of the correlation coefficients (R^2) was also calculated. Lists of the constant obtained along with R^2 values are predicted in Table 1 for the HA adsorption onto smectite. The results observe that the data pointed out that the Freundlich model fits the experimental data more than the Langmuir. On the other way, many factors effect on HA adsorption and behavior, where n values of the Freundlich equation are near to 1 for smectite and the surface heterogeneity might be supposed to be less significant [37,38].

Table 1. Humic acid adsorption fitting by Langmuir and Freundlich equations.

Ionic strength (mol/L)		pH	Langmuir			Freundlich		
			R^2	k_L (L/g)	a_L (L/mg)	R^2	K_f ((mg/g)(mg/L)$^{-1/n}$)	n
CaCl$_2$	0.01	5	0.98	1.145	0.042	0.97	2.82	6.7
		6	0.98	0.79	0.032	0.96	2.45	5.4
		7	0.97	0.42	0.018	0.96	1.85	3.6
	0.001	5	0.99	0.20	0.02	0.94	1.24	3.4
		6	0.97	0.37	0.03	0.96	1.48	3.70
		7	0.99	0.11	0.013	0.93	0.98	2.83
Blend	0.01	5	0.93	0.34	0.017	0.92	1.19	2.24
		6	0.96	0.099	0.003	0.90	0.57	1.4
		7	0.99	0.076	0.0046	0.95	0.53	1.15
	0.001	5	0.96	0.13	0.013	0.96	0.92	2.53
		6	0.92	0.35	0.03	0.95	1.45	4.03
		7	0.97	0.089	0.011	0.94	0.8	2.41
KCl	0.01	5	0.98	0.205	0.015	0.95	1.12	2.63
		6	0.99	0.096	0.008	0.95	0.78	2.11
		7	0.99	0.050	0.0035	0.92	0.562	1.80
	0.001	5	0.98	0.08	0.008	0.91	0.77	2.30
		6	0.98	0.12	0.01	0.91	0.96	2.7
		7	0.98	0.04	0.004	0.91	0.52	1.78

3.3. Adsorption kinetics

3.3.1.   Influence of pH on HA adsorption on semectite

The impact of pH on HA adsorption onto smectite was studied under different pH (5–7). The HA adsorption onto smectite rises meaningfully with declining pH Figure 5 [39,40]. The adsorption of HA on smectite increases significantly with decreasing pH. This behavior refers to the fact that carboxylic groups of humic acid become less negative charged at low pH [41]. The electrostatic repulsion decreases between HA and smectite. The electrical double layer on the adsorbent also affects the adsorption process by changing the polarity from positive to negative as the pH changes from acidic to basic media.
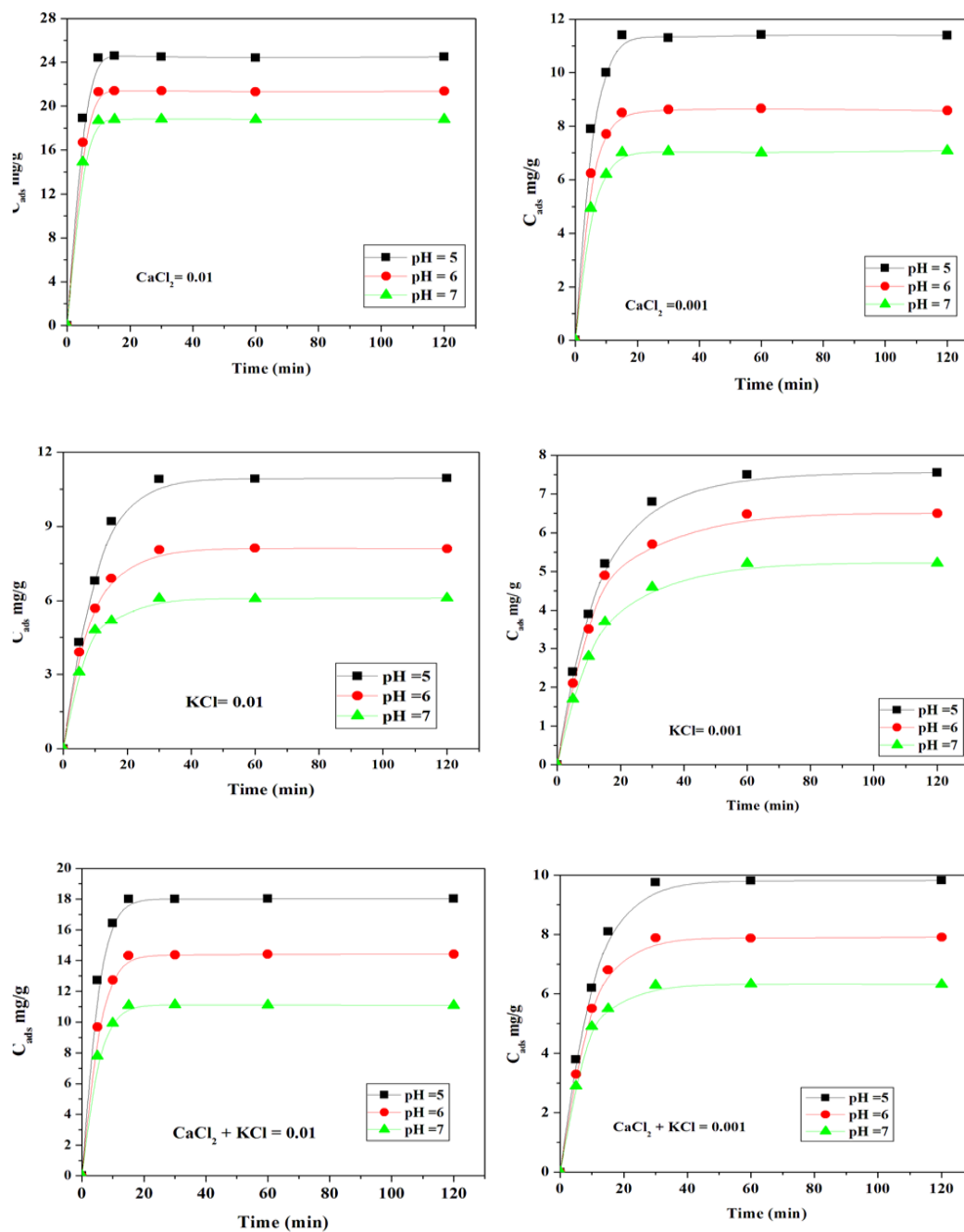
Figure 5. Adsorption humic acid on smectite under different conditions.

3.3.2.   Influence of ionic strength on HA adsorption on smectite

Background electrolyte effect on the rate and capacity of adsorbed HA onto smectite. The concentrations of ionic strength solutions were set at 0.001 and 0.01 mol/L KCl, CaCl$_2$ or blend background electrolyte (KCl and CaCl$_2$). The results of HA adsorption clarified that sorption of HA onto smectite improved with increasing ionic strength. The results might be clarified by many mechanisms (1) reduce HA molecular size, due to minimization of the repulsion between ionized carboxylic groups through rise the ionic strength, which simplifies the adsorption process [42]; (2) at

upper ionic strength, HA disperses quicker than at minor ionic strength refer to HA coiled structure; (3) wideness of diffuse double layer become more reduced at higher ionic strength; (4) metals ions in solution interact with water molecules and competition with HA on the active site of smectite at low level.

3.3.3. Influence of solution cations on the adsorption of HA on smectite.

The solution cations effect on the rate and quantity of sorbed HA onto smectite. The existence of Ca^{2+} improves the binding between mineral surface and HA. The Ca^{2+} is more influential than K^+ at linking the repulsive charges between smectite surface and ionizied HA groups. Furthermore, The Ca^{2+} ions effect on and reduce the HA solubility [43]. All previous studies on HA sorption by clays performed utilizing homoionic clays and few studies conducted to study the sorption by clays with more than one type of exchangeable cation. Thence, The HA adsorption to the mixtures of homoionic K^+- and Ca^{2+}-saturated smectite has been studied and found that the adsorption improved with fraction K-clay present but not linearly [44]. Thus, the HA adsorption mechanism onto smectite could be a combination between two or more of the following mechanisms: ligand exchange, Van der Waals, water bridging, anion exchange, cation bridge and hydrogen binding [45]. The actual mix depends on the HA composition and solution cations. Therefore, the ligand exchange mechanism could be the specific and the predominant mechanism in the presence of KCl and cation bridge mechanism could be specific and predominant mechanism in the presence $CaCl_2$ while in the presence of blended solution cations (K^+ and Ca^{2+}) the ligand exchange and cation bridge mechanisms could be predominant mechanisms.

3.3.4. Kinetics study

The kinetic data were calculated to more understanding the adsorption dynamics and the rate constant order. As described before the rate of HA adsorption on smectite was explored at different pH, ionic strength, and solution cations (Figure 4). In order to examine the performance of the adsorption process of HA on the adsorbents, two kinetic models were used for fitting the adsorption kinetic data. These two models in the linear form were the irreversible pseudo first order and the pseudo second order kinetics and could be expressed as Eq 5,

$$\ln\left(\frac{c_i}{c_t}\right) = k_1 t \tag{5}$$

where C_i and C_t (mg/L) are the initial and equilibrium HA concentration at time t, respectively, and k_1 (min^{-1}) is the rate constant. The correlation coefficients k and values under different various solution conditions are represented in Table 2.

The linear pseudo second order kinetics model could be expressed Eq 6,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where q_t and q_e are the adsorption amount of HA at time t, and equilibrium, respectively, and k_2 (g/mg min) is the rate constant.

The results in Table 2 observed that the pseudo second order was more fitted to the data than the

pseudo first order equation. Moreover, the results evaluated the rate constant (k_2) and the amount of adsorption at equilibrium (q_e) values. Furthermore, the results of the correlation coefficient (R^2) clarified that the HA adsorption on smectite had more conformity to pseudo second order [38,46]. In addition, the theoretical values of q_e are matched and agreed with the experimental data. Hence, HA adsorption on smectite is predominantly chemisorption [47].

Table 2. Kinetic models for humic acid adsorption on smectite.

Ionic strength (mol/L)		pH	Pseudo first order		Pseudo second order		
			k_1 (min^{-1})	R^2	q_e (mg/g) (q_{exp})	k_2 (g/mg min)	R^2
CaCl$_2$	0.01	5	0.0024	0.38	24.63 (24.5)	0.117	0.99
		6	0.0019	0.38	21.45 (21.36)	0.105	0.99
		7	0.0016	0.39	18.90 (18.8)	0.128	0.99
	0.001	5	0.0017	0.53	11.49 (11.37)	0.076	0.99
		6	0.0012	0.53	8.69 (8.58)	0.128	0.99
		7	0.001	0.54	7.19 (7.08)	0.113	0.99
Blend	0.01	5	0.0027	0.5	18.24 (18.03)	0.056	0.99
		6	0.0024	0.53	14.61 (14.42)	0.055	0.99
		7	0.00159	0.51	11.23 (11.08)	0.091	0.99
	0.001	5	0.0038	0.67	10.41 (9.82)	0.017	0.99
		6	0.0027	0.64	8.26 (7.91)	0.027	0.99
		7	0.0018	0.62	6.57 (6.32)	0.044	0.99
KCl	0.01	5	0.0042	0.66	11.62 (10.95)	0.016	0.99
		6	0.0026	0.67	8.47 (8.1)	0.030	0.99
		7	0.0017	0.64	6.32 (6.11)	0.051	0.99
	0.001	5	0.0036	0.77	8.26 (7.55)	0.012	0.99
		6	0.0029	0.75	7.09 (6.50)	0.016	0.99
		7	0.0024	0.77	5.71 (5.22)	0.019	0.99

4. Conclusion

Solution cations and mixed background electrolyte effect on the adsorption of HA on semectite as well as such as pH and ionic strength. The results explained the great effect of blend background electrolyte on the kinetics and adsorption isotherm of HA adsorption on smectite. The adsorption isotherm was L-shap in the presence of CaCl$_2$ and KCl, while was S-shap in the presence of blend background electrolyte (CaCl$_2$ and KCl). Moreover, the data revealed that the adsorption behavior of HA might be pronounced more obviously by Freundlich model than Langmiur. Furthermore, the rate and amount of adsorbed HA on smectite improved with raised background electrolyte concentration, declining pH, and in existence Ca^{2+}. The rate of adsorption order was in the presence of CaCl$_2$ > blend (CaCl$_2$ and KCl) > KCl. In addition, the results clarified that HA adsorption on Smectite was following to pseudo second order model under various conditions.

Conflict of interests

The authors declare no conflict of interests.

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