

Adsorption of humic acid on bentonite

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Abstract

Isotherms of adsorption of Azraq humic acid (HA) onto Azraq bentonite were studied at different pH (3.0–6.0) and temperature values. The Langmuir monolayer adsorption capacity (q_m) was found to be 53 mg HA/g raw bentonite at pH=3.0 and 25 °C, $\Delta H^\circ = 54.8$ kJ/mol, $\Delta S^\circ = 220$ J/mol deg which were approximate to those reported for the adsorption of HA on kaolinite. In the case of bentonite, the q_m and Langmuir constant (K_L) values are significantly greater than those reported for zeolite. These results indicate the importance of sheet structure of bentonite in the adsorption process. Treatment of raw bentonite with NaCl, CH₃COOH and HCOOH does not affect adsorptivity (q_m and K_L) of HA on bentonite, while treatment with HCl causes great decrease in adsorptivity. The adsorptivity of HA on bentonite was found to be inversely proportional to the increase in pH because of the increase in repulsion between HA and bentonite.

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1. Introduction

Soil organic matter (SOM) refers to the sum total of all organic carbon containing substances in soils (Hayes, 1998). SOM is usually subdivided into (a) nonhumic and (b) humic substances (HS). Nonhumic substances include those with recognizable chemical characteristics such as carbohydrates, proteins, peptides, amino acids, fatty acids, waxes and other low-molecular mass organic substances. The bulk of SOM, however, consists of HS. HS no longer exhibit specific chemical and physical characteristics normally associ-

ated with well defined organic compounds but are more resistant to chemical and biological degradation (Hayes, 1998). The distinctions between different types of HS are based on their solubility in acid or alkali. Humic acid (HA) is soluble in alkali and insoluble in acid or water (Schnitzer, 1991).

The interaction of HS with clay takes place in soils, sediments and aqueous environments (Balke et al., 2002). The Adsorption of HS on clay prevents HS from being washed away and decreases their rate of decomposition (Ghabbour et al., 1998). Furthermore, adsorption of HS onto clay is important in relation to speciation and mobility of pollutants in the environment (Chorover et al., 1999; Guzman et al., 2003).

A number of studies have been carried out on Azraq HA at the University of Jordan. The Azraq oasis lies 100 km east of Amman — the capital of Jordan.

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The complexation of dissolved Azraq HA with Pb(II), Cd(II), Cu(II), Ni(II) and Zn(II) was previously investigated at different pH and temperature values (Baker and Khalili, 2003, 2005). Furthermore, the adsorption behavior of Cu(II) and Ni(II) onto solid Azraq HA was recently investigated at $\text{pH} < 4$ (El-Eswed and Khalili, 2006); the results reveal that solid HA is an effective adsorbent. However, HA has much higher affinity for metal ions at $\text{pH} > 4$, but the solubility of HA limits the use of HA as a solid adsorbent at $\text{pH} > 4$. The insolubilization of HA by loading it onto clays and minerals seems to be a promising idea to solve this problem. Thus, the adsorption behavior of HA on these surfaces is of great interest. The adsorption of HA on zeolitic tuff (Capasso et al., 2005) and clay kaolinite (Ghabbour et al., 1998) was previously investigated. It has been shown that HA/kaolinite complex is stable in the range from 3.5 to 13.0 (Ghabbour et al., 1998).

This paper reports the results of adsorption of Azraq HA on Azraq bentonite from solutions adjusted to $\text{pH} = 3.0, 4.0, 5.0$ and 6.0 and at different temperatures. The effect of acid treatment of Azraq bentonite on the adsorptivity of HA on bentonite was also investigated. The data was analyzed in terms of Langmuir model in order to make it possible to compare the present results with the reported Langmuir parameters for the adsorption of HA on kaolinite and zeolite.

2. Materials and methods

2.1. Materials

Sodium chloride (analytical grade) used in the present study was from Reidel-deHaen. Acetic acid (99.6%) and formic acid (99%) were from GCC.

Samples of Jordanian bentonite were kindly supplied by the Natural Resource Authority from well number BT-25, came from Ain Al-Baida at Azraq area (Jordan).

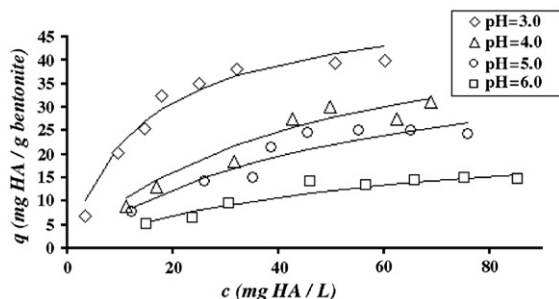


Fig. 1. A plot of amount of HA adsorbed on raw bentonite (q) versus equilibrium concentration (c) at different pH values and $25\text{ }^{\circ}\text{C}$ (fitted, continuous line; experimental, points), parameters of fitting are given in Table 1.

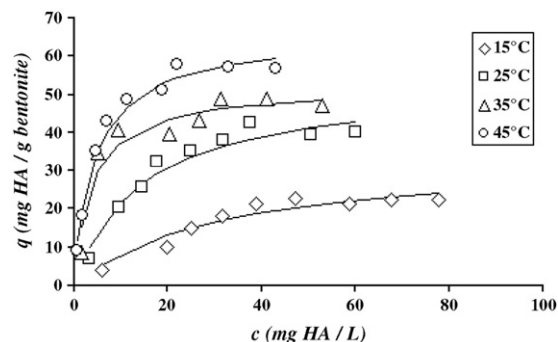


Fig. 2. A plot of amount of HA adsorbed on raw bentonite (q) versus equilibrium concentration (c) at different temperature values and $\text{pH} = 3.0$ (fitted, continuous line; experimental, points), parameters of fitting are given in Table 2.

Humic acid samples used in this investigation were extracted from a soil sample collected from the A0 (top layer) horizon which lies cross the street from Qasr Al-Azraq next to the water pump lake (North Azraq–Jordan). Azraq HA was extracted from the Azraq soil using the recommended procedure by the International Humic Substance Society (Swift, 1996). The characteristics of Azraq HA have been reported previously (El-Eswed and Khalili, 2006).

2.2. Equipments

A Shimadzu analytical balance model AW 120 was used (± 0.0001 g). A Memmert WB 22 water bath-shaker equipped with a digital thermostat was used in batch adsorption experiments. A Metrohm pH meter model 525A was used for pH measurements. HA concentration was determined using a double beam Carry 100 UV–Visible spectrophotometer at 400 nm. X-ray diffraction was performed on Philips 2KW model X-radiation ($\text{CuK}\alpha$ 1.5418 \AA). The chemical composition of bentonite samples were determined using X-ray fluorescence spectrometer (Philips PW 1404).

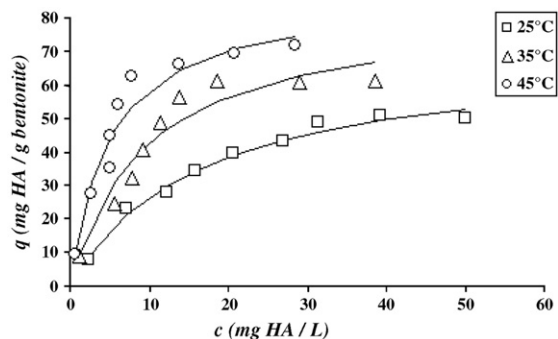


Fig. 3. A plot of amount of HA adsorbed on purified bentonite (q) versus equilibrium concentration (c) at different temperature values and $\text{pH} = 3.0$ (fitted, continuous line; experimental, points), parameters of fitting are given in Table 3.

Table 1

The effect of pH on the adsorption of HA on raw bentonite at 25.0 °C

pH	q_m	K_L	Sum of square residuals	Standard error ^a
3.0	53	7.0×10^{-2}	56	2.68
4.0	52	2.3×10^{-2}	65	3.25
5.0	45	1.9×10^{-2}	39	2.52
6.0	26	1.7×10^{-2}	9	1.21

^a Standard error = $\{\sum(y_i - \hat{y}_i)^2 / n - 2\}^{0.5}$, y_i : experimental, \hat{y}_i : predicted.

2.3. Procedures

2.3.1. Treatments of raw bentonite samples

Acid treatments of raw bentonite samples were performed using the following acids: 8 M HCl, 8 M CH₃COOH and 8 M HCOOH. A 60.0 mL portion of the acid was added with stirring to 10.0 g of raw bentonite in round-bottom flask fitted with a condenser. After heating for 5 h in a water bath at 95 °C, the mixture was allowed to cool at room temperature and then washed with distilled water and centrifuged for several times until the supernatant was acid free. The solid was dried overnight in an oven at 110 °C, and kept in a desiccator.

2.3.2. Purification of bentonites

Purification of raw bentonite was done by removal of quartz. This includes repeating the following steps (Khoury, 2000): first, mixing raw bentonite with water. Second, centrifugation at 750 rpm. Third, decanting into a large bottle. The decanted suspensions were collected, filtered and dried overnight at 110 °C, and kept in a desiccator.

2.3.3. Adsorption procedure

A stock solution, which was 1000 ppm of AZHA, was prepared by dissolving 1.0 g of AZHA in 1.0 L of 0.01 M NaOH solution. The stock solution was diluted with 0.01 M NaOH solution for the purpose of preparing of more diluted solutions.

An accurate mass of 0.02 g of bentonite which was measured to the nearest 0.0001 g was shaken with 20.0 mL of 10.0–150.0 ppm HA solutions for 24 h at different pH (3.0, 4.0, 5.0, 6.0) and temperature (15.0, 25.0, 35.0, 45.0 °C) values. Aliquot of solution was then centrifuged and analyzed by UV–Visible spectrophotometer at 400 nm to measure the concentration of dissolved free HA. Calibration curves were determined using standard samples prepared from HA at each pH value.

Table 2

The effect of temperature on the adsorption of HA on raw bentonite at pH=3.0

Temperature (°C)	q_m	K_L	Sum of square residuals	Standard error
15.0	34	3.1×10^{-2}	31	2.03
25.0	53	7.0×10^{-2}	56	2.69
35.0	52	2.6×10^{-2}	113	4.16
45.0	66	2.2×10^{-2}	48	2.46

Table 3

The effect of temperature on the adsorption of HA on purified bentonite at pH=3.0

Temperature (°C)	q_m	K_L	Sum of square residuals	Standard error
15.0	74	1.6×10^{-2}	136	4.34
25.0	70	6.1×10^{-2}	26	1.90
35.0	83	1.1×10^{-2}	199	5.28
45.0	87	2.0×10^{-2}	223	5.63

2.4. Desorption of HA from bentonite loaded with HA

A sample of 5 g of purified bentonite was shaken with 200 mL solution of 10 g/L HA for 72 h at 45 °C and pH=3.0. The solid product was filtered, washed and dried at 110 °C. Samples of 0.10 g of HA/bentonite complex were shaken for 24 h with 100 ml of deionized water at 25 °C at different pH values (7.0–13.0). Then aliquots were filtered and analyzed by UV–Visible spectrophotometer at 400 nm.

2.5. Isotherm data analysis

The adsorption data was fitted to Langmuir equation using nonlinear least square regression by means of Microsoft Excel programme:

$$q = K_L q_m C / (1 + K_L C)$$

Where q and q_m are the equilibrium and the maximum adsorbable amount of HA (mg HA/g bentonite), respectively. C is the equilibrium concentration of free HA (mg HA/L). K_L is the affinity constant which is related to the binding strength between HA and bentonite measured in L/mg HA. The resultant fitting curves are given in Figs. 1–3 and the fitted parameters of q_m and K_L are given in Tables 1–4.

3. Results and discussion

3.1. Properties of bentonite adsorbents

The chemical composition of raw, purified and treated bentonite samples are given in Table 5, as determined by X-ray fluorescence technique. The

Table 4

The effect of treatment of bentonite on the adsorption of HA on bentonite at pH=5.0 and 25 °C

Bentonite treated with	q_m	K_L	Sum of square residuals	Standard error
Raw	45	1.9×10^{-2}	39	2.52
NaCl	40	1.9×10^{-2}	24	1.74
HCl	15	5.6×10^{-3}	1	0.44
CH ₃ COOH	33	1.9×10^{-2}	44	2.52
HCOOH	46	1.9×10^{-2}	27	1.76

Table 5
The chemical composition (% w/w) of bentonite samples

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	CaO	MgO	K ₂ O	Na ₂ O	Lost on ignition
Raw	59.60	13.70	8.34	1.61	0.05	1.15	2.33	2.07	0.68	10.47
Purified	52.06	15.80	12.15	1.41	0.06	0.63	3.04	2.53	1.12	11.20
Treated with NaCl	58.43	11.25	10.37	0.54	0.13	0.13	0.24	2.13	3.16	13.62
Treated with HCl	67.51	8.83	3.01	0.82	0.11	0.52	0.93	1.81	0.77	14.68
Treated with CH ₃ COOH	60.03	13.96	8.55	1.15	0.21	0.63	1.23	2.16	0.62	11.46
Treated with HCOOH	62.28	12.16	5.84	0.75	0.15	0.61	1.13	1.63	0.77	14.68

purified bentonite is characterized by a lower % SiO₂ and higher % Al₂O₃, % Fe₂O₃ and % MgO than raw and treated bentonite. Bentonite treated with HCl is characterized by the highest % SiO₂ and the lowest % Al₂O₃ and % Fe₂O₃ among the other bentonite samples.

The XRD patterns of raw, purified and treated bentonite samples were similar. The bentonite samples contains quartz ($2\theta=26.7$) as major and montmorillonite ($2\theta=6.0, 19.9$) as minor.

3.2. Equilibration time

As shown in Fig. 4, the time needed for the adsorption of HA on bentonite to reach equilibrium is about 24 h. The relatively long time needed, may be due to the difficulty for large size HA molecules to enter between the bentonite layers. Furthermore, this may indicate that there is no complexation between HA and metal ions on the surface of bentonite because these complexation processes are usually very fast as indicated by complexation studies of HA with metal ions (Kerndorff and Schnitzer, 1980; El-Eswed and Khalili, 2006).

3.3. Adsorption of HA onto raw bentonite

As given in Table 1, the estimated maximum HA amount taken up by the untreated raw bentonite (q_m) at pH=3.0 and 25 °C was 53 mg HA/g bentonite. This value is approximate to that reported for kaolinite at

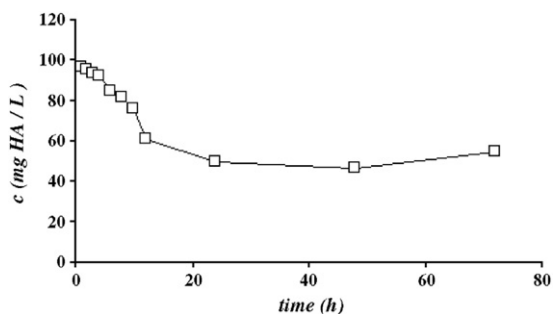


Fig. 4. A plot of equilibrium concentration c as a function of time in the adsorption of HA on raw bentonite at pH=3.0 and 25 °C.

pH=3.5 and 25 °C (45 mg HA/g kaolinite) (Ghabbour et al., 1998), while it is higher than that reported for zeolite at pH=2.7 and 25 °C (8.5 mg HA/g zeolite) (Capasso et al., 2005). This may indicate that the sheets interlayer gaps of kaolinite and bentonites are more effective than zeolitic pores in the adsorption of HA.

On the other hand, the Langmuir constant for the adsorption of HA on bentonite ($K_L=0.070$ L/mg HA, Table 1 at pH=3.0 and 25 °C) is lower than that of kaolinite (0.585 L/mg HA at pH=3.5 and 25 °C) (Ghabbour et al., 1998) and much higher than that of zeolite (1.08×10^{-5} L/mg HA at pH=2.7 and 25 °C) (Capasso et al., 2005).

3.4. The effect of purification on the adsorptivity of HA on bentonite

As shown from the comparison of the values in Tables 2 and 3, purification of raw bentonite results in an increase of q_m values. The increase of q_m values may result from the enrichment of bentonite clay and the increase of % Al₂O₃ content (Table 5) upon purification of raw bentonite.

3.5. The effect of treatment on the adsorptivity of HA on bentonite

As shown in Table 4, treatment of raw bentonite with NaCl, CH₃COOH and HCOOH does not have significant

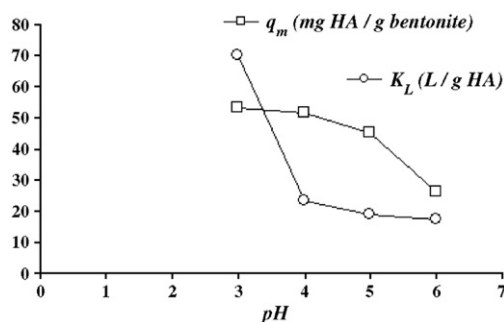


Fig. 5. A plot of Langmuir parameters as a function of pH.

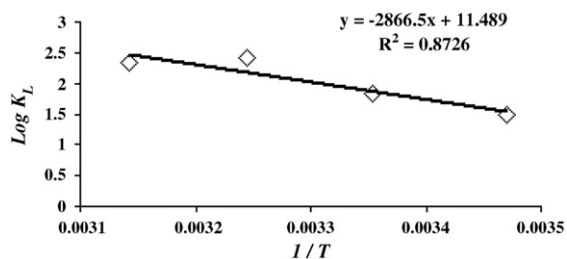


Fig. 6. A plot of $\log K_L$ for the adsorption of HA on raw bentonite as a function of inverse of temperature (K^{-1}).

effect on the adsorptivity of HA (q_m and K_L values). However, these reagents are expected to affect surface ions of bentonite. This may support the assumption that surface metal ions are not included in the adsorption of HA.

On the other hand, treatment with HCl, which decreases the % Al_2O_3 and % Fe_2O_3 content (Table 5), results in a significant decrease of the adsorptivity of HA on bentonite. It seems that the adsorptivity of HA on bentonite is directly proportional to the % Al_2O_3 (Section 3.4).

3.6. The effect of pH on HA adsorption on bentonite

As shown in Table 1 and Figs. 1 and 5, the adsorptivity of HA decreases as pH increases. This is due to the increase of repulsion between negatively charged HA and bentonite, and/or repulsion between competitively adsorbed HA molecules.

3.7. The effect of temperature on HA adsorption on bentonite

Adsorption isotherms of HA on raw and purified bentonite at different temperature values are given in Figs. 2 and 3, while q_m and K_L obtained from fitting are given in Tables 2 and 3. The adsorption process is

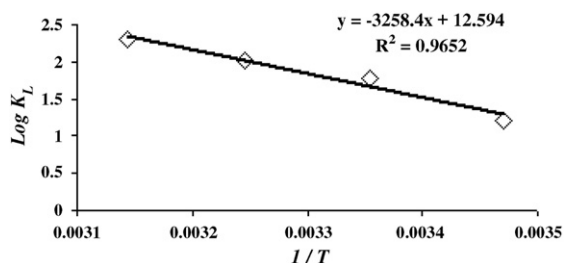


Fig. 7. A plot of $\log K_L$ for the adsorption of HA on purified bentonite as a function of inverse of temperature (K^{-1}).

Table 6
Thermodynamic data for adsorption of HA on bentonite

Adsorbent	ΔH° (kJ/mol)	ΔS° (J/mol deg)
Raw bentonite	54.8	220
Purified bentonite	62.4	241
Kaolinite	39.7	188

endothermic, since the q_m and K_L values increases with increasing temperature. A plot of $\log K_L$ versus $1/T$ is given in Figs. 6 and 7 and the resultant ΔH° and ΔS° are given in Table 6. The results indicate that the process is endothermic and thus the adsorption of HA on bentonite is entropy driven. This is in contrast to the fact that an entropy decrease is expected for adsorption of dissolved solutes on solid surfaces. However, two factors may contribute to the increase of entropy; first: dehydration of interacting HA sorbate molecules, second: disaggregation of HA aggregates.

As shown in Table 6, the values of ΔH° and ΔS° for the adsorption of HA on bentonite are close to those reported for kaolinite. The fact that both bentonite and kaolinite have similar ΔH° , ΔS° and q_m values suggests that the adsorption behavior of HA on these surfaces is similar.

3.8. Desorption of HA from bentonite loaded with HA

The percentage amounts of HA desorbed from HA/bentonite complex as a function of pH are given in Table 7. There was no significant amount of HA desorbed from bentonite in the pH range from 7.0 to 11.0. Thus, bentonite has a dramatic effect on the solubility of HA.

Table 7
The percentage amount of HA desorbed from HA/bentonite complex as a function of pH^a

pH	The percentage amount of HA desorbed (%) ^b	pH	The percentage amount of HA desorbed (%)
7.0	/	10.0	6.1
7.5	1.6	10.5	9.0
8.0	2.4	11.0	12
8.5	2.5	11.5	37
9.0	3.9	12.0	63
9.5	5.3	12.5	61

^a The maximum adsorption capacity of HA on purified bentonite is 87 mg HA/g bentonite at pH=3.0 and 45 °C.

^b The percentage amount desorbed = $(C_{des} \times \text{volume of solution} \times 100\%) / (\text{mass of bentonite loaded with HA} \times q_m)$ Where C_{des} is the concentration of humic acid desorbed into solution in ppm, and $q_m = 87$ mg HA/g bentonite. The volume of solution in liter and the mass of bentonite in gram.

4. Conclusion

The interlayer structure rather than surface metal ions may be the limiting factor that affects adsorption of HA on bentonite. The adsorption behavior of HA on bentonite is similar to that on kaolinite but different from that on zeolite. Purified bentonite has greater adsorptivity than raw bentonite. However, treatment of raw bentonite with NaCl, CH₃COOH and HCOOH does not affect adsorptivity (q_m and K_L) of HA on bentonite, while treatment with HCl causes great decrease in adsorptivity. The adsorptivity of HA on bentonite was found to be inversely proportional to the increase of pH which results in an increase of repulsion between HA and bentonite. The calculated ΔH° and ΔS° values indicates that the adsorption process is endothermic and thus entropy driven.

Acknowledgement

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