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WATER PURIFICATION FROM HUMIC ACIDS BY CLINOPTILOLITE-RICH TUFF

Extended abstract

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Background

Humic substances (HS) are natural polymers produced by biological decomposition of plants and other organisms (Abate and Masini, 2003) and accounting for 50–80% of natural organic matter in water, soil and sediment. HS are generally subdivided into humin, humic acids (HA) and fulvic acids (FA) based on their solubility under acidic or alkaline conditions in aqueous solution. Among numerous methods developed for HA removal from water, adsorption is the most promising approach. Adsorption by low-cost materials, either natural or by-products of industrial activity, has become the focus of intensive investigation (Leone et al., 2012). Previous work (Capasso et al., 2007a; Capasso et al., 2007b) has shown that the Neapolitan yellow tuff (NYT), a volcanic rock rich in phillipsite/chabazite zeolites, binds HA through the action of surface extra-framework exchangeable cations, whereas HA molecules are too big to enter the system of channels and cages of zeolite crystals. The binding ability is markedly enhanced when the zeolitic material is enriched with divalent cations, especially Ca^{2+}, that act as micro-bridges between negative charges on the zeolite surface framework and HA carboxylic groups. Moreover, it has been shown that HA adsorption by natural zeolites is a relatively long-lasting process with kinetic curves characteristic of a two-stage adsorption process (Ambrosone et al., 2013; Capasso et al., 2007b). Here we report a study on the HA adsorption onto a clinoptilolite-rich tuff. The influence of calcium ions and particle sizes were analyzed.

Objectives

Adsorption of humic acids in water solution onto a clinoptilolite-rich tuff from New Mexico (USA) was investigated with the batch technique, with attention to the effects of adsorbent-bound Ca2+ and adsorbent particle size. Kinetic analysis showed that the adsorption process takes several days and follows a two-step pattern. In this study, two of the most established isotherm models were used for fitting the experimental data: the Langmuir and the Freundlich equation. Interestingly, the statistical parameters show that the Langmuir equation describes the experimental data more accurately for two of the three samples analyzed. The q_m parameter did not change significantly with particle sizes and calcium concentration; the K parameter, which reflects energy interactions between the adsorbate and adsorbing sites, increased with calcium amount and decreased with particle size. The results point to the tuff investigated, a low-cost natural material, as a potentially useful adsorbent for water purification from humic acids.

Methods

1. Clinoptilolite rich tuff (CCT)

The clinoptilolite-rich tuff (CCT) used in the present investigation was extracted from a quarry in New Mexico (USA) and supplied by Coyote Cliff LLC Company. The mineralogical composition was determined by the company: clinoptilolite 89%, quartz 5% smectite <1%, feldspar <5%. The raw material was provided in two particle

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size ranges: 0.5–1.0 and 1.0–2.0 mm. Before sorption experiments, the samples were repeatedly washed with Milliq water (50 mL water for 1g tuff) until the rinse water showed no increase in the conductivity after 1 day contact with tuff. Finally the samples were dried at 40°C.

2. *Enriching tuff samples by Ca^{2+}*

Two hundred and fifty grams of CCT for each particle size were put in a chromatographic column and eluted with 2.0 L of 1.0 M $CaCl_2$ solution, then washed with Milliq water. The exchangeable calcium content was determined by the ammonium acetate method. 15.0 mL of 1.0 M ammonium acetate were added to 1.0 g of Ca-CCT sample. The mixture was stored at room temperature for 1 day on a shaker at one oscillation per second.

Afterwards the mixture was centrifuged and the amount of Ca^{2+} cation in the water phase determined by atomic absorption spectrophotometer (Perkin Elmer, AA analyst 100). The extraction with ammonium acetate was repeated until the metal concentration was coincident with that present as impurity in the starting solution).

3. *Humic acids purification*

Humic acids (HA) were obtained from Aldrich. Ten grams HA were suspended in 1 L of Milliq water containing 10.0 mL concentrated HF and 10.0 mL concentrated HCl. After vigorous stirring for 1 day, the mixture was filtered, the precipitate washed with 1.0 M HCl, followed by Milliq water and finally re-suspended in 0.8 L of water. An appropriate volume of 1.0 M NaOH was added to the suspension to bring pH to 10.

The mixture was then stirred for 1 day, filtered, brought to pH 1.5 by concentrated HCl, and stored in a refrigerator for 1 week. Afterwards, the HA precipitate was collected by centrifugation, water-washed repeatedly, and dialyzed (molar mass cutoff = 3500 Da) against Milliq water until no significant change was observed in the conductance of bath water (<100 µS cm-1 per day). Finally, the purified HA was collected by lyophilisation and dried in oven at 40°C. The elemental contents were determined using a CHN analyzer. The ash content was determined by keeping the sample in oven at 600°C for 6 h.

4. *Adsorption batch experiments*

All experiments were conducted using a stock HA solution of 200 mg L-1, prepared by dissolving 0.20 g of purified humic acids in 1000 mL of 0.01 mol L-1 Tris/TrisHCl buffer [Tris = 2-amino-2-(hydroxymethyl)-1,3-propandiol], 0.04 mol L-1 KCl solution, pH 7.4, and vigorously stirred for 1 day. pH was periodically tested and, when required, adjusted with a few drops of 1.0 M Tris base solution. The HA solution was then filtered through a RC 0.45 µm membrane (Chemtek). This stock solution was then diluted with 0.01 mol L-1 Tris/TrisHCl buffer [Tris = 2-amino-2-(hydroxymethyl)-1,3-propandiol], 0.04 mol L-1 KCl solution, pH 7.4 to prepare the different concentrations of HA to be used in the tests. Batch adsorption experiments were conducted using vials of 50 mL. The following particle sizes were used: 0.5-1.0 mm or 1.0 – 2.0 mm for Ca-CCT, 0.5-1.0 mm for CCT. At programmed intervals the supernatants were centrifuged at 13,000 rpm for 15 minutes and analyzed by VIS-spectrometry at 450 nm, using the extinction coefficient $\varepsilon = 0.0072414$ mg–1 l cm–1 determined from the concentration–absorbance linear plot. The adsorption capacity at time t was calculated using the following equation (Eq. 1):

$$q_t = (C_0 - C_t * V) / m \qquad (1)$$

where: q_t is the adsorption capacity at time t (mg kg^{-1}), C_0 the initial HA concentration (mg L^{-1}), C_t is HA concentration (mg L^{-1}) at time t, V the volume of HA solution in the vials (L), m the adsorbing mass (kg).

2.4.1. Kinetics

Fifty mL aliquots of 140 mg L^{-1} HA solutions were put in vials containing 200 mg of clinoptilolite rich tuff enriched in calcium ions (Ca-CCT) or row tuff (CCT). The vials were kept at room temperature on a rotating shaker, one oscillation per second and HA concentration in solution was determined at selected times.

2.4.2. Adsorption isotherms

Fifty mL aliquots of HA solutions prepared as reported above, concentration range 28 - 200 mg L^{-1}, were added to 100 mg of adsorbing (Ca-CCT or CCT) in vials and kept at room temperature on a shaker at one oscillation per second. After 20 days, aliquots were analyzed; few experiments carried out after longer times showed no significant further changes in HA concentration.

Results and discussion

1. Kinetic study

Fig. 1a shows the sorption kinetics of HA onto row clinoptilolite rich tuff (CCT) and Ca^{2+}-enriched sample (Ca-CCT), while Fig. 1b compares the sorption kinetics of HA on Ca-CCT with different particle sizes. For all kinetic runs the adsorption process lasted several days. The data reported in Fig. 1b, obtained at a higher HA/tuff ratio than that for Fig. 1a, show a two-step adsorption kinetics, in line with results of previous studies on HA adsorption on zeolitic tuff (Ambrosone et al., 2013, Capasso et al., 2007b): after an initial phase of fast adsorption lasting a few days, the adsorption rate decreased appreciably but subsequently it raised again up to the equilibrium state.

It has been shown (Ambrosone et al., 2013) that this behaviour is described by the following equation (Eq 2):

$$q_t = q_1 [1 - e\hat{}(-t/\tau_1)] + q_2 [1 - e\hat{}(- (t/\tau_2)\hat{}m)] \qquad (2)$$

where: q_t is the amount adsorbed at time t.

The fist term of the second member is the pseudo-first order adsorption kinetic equation and describes the first step of the adsorption; q1 is the pseudo plateau at the beginning of the kinetic run. The second term is similar to the so-called Johnson–Mehl–Avrami function with m as exponential (Johnson and Mehl, 1939; Avrami, 1941). This relation suggests a rearrangement of HA molecules on tuff surface during adsorption, possibly through a process of nucleation. The sum $q_1 + q_2$ is the amount adsorbed at equilibrium. The parameters τ_1 and τ_2 are the times required to reach the corresponding plateau. The parameter values obtained by least square fits for the adsorption of HA (50 mL of 140 mg L^{-1} HA solution) on 100 mg Ca^{2+}-enriched clinoptilolite-rich tuff with two particle size ranges was τ_1=0.95 ± 0.26 and τ_2=15.09 ± 1.64 for particle size 0.5-1.0 mm and τ_1=0.89 ± 0.35 and τ_2=12.4 ± 1.32 for particle size 1.0-2.0 mm. Within the errors, the only difference between the two sets of values is pertained to the parameter qi found to be higher for the size range 0.5-1.0 mm. This probably reflects the increase in the adsorbing surface consequent to a reduction in the average size of adsorbing particles. The curves in Fig. 1b were drawn using eq. (2). The parameters obtained by the curves in Fig. 1a were drawn fitting the experimental data with a pseudo-first order kinetic equation (the first term of the second member of eq. 2). The parameters obtained by the fits for the adsorption of HA (50 mL of 140 mg L^{-1} HA solution) on 200 mg row (CCT) was τ_1=7.36 ± 0.50 and for Ca^{2+}-enriched clinoptilolite-rich tuff (Ca-CCT) was τ_1=3.04 ± 0.20.

2. *Isotherms study*

Mathematical descriptions of equilibrium adsorption isotherms permit a reliable prediction of adsorption parameters and afford quantitative comparison of the behaviour of different adsorption systems (Anirudhan and Ramachandran, 2007). The equation parameters of these models often provide useful insights into the adsorption mechanism, surface properties and affinity of the adsorbing. In this study, two of the most established isotherm models were used for fitting the experimental data: the Langmuir and the Freundlich equations. The Langmuir model supposes that the adsorbing sites are energetically equivalent and that at equilibrium the adsorbed molecules are arranged in monolayers. The Langmuir model is represented as follows (Eq 3):

$$q_e=(q_m \,.\, K \,.\, C_e)/(1+(K \,.\, C_e)) \qquad (3)$$

where q_e is the amount of HA adsorbed per unit weight of adsorbing material at equilibrium, C_e the equilibrium adsorbate concentration in solution, q_m the amount of solute adsorbed, and K the Langmuir adsorption equilibrium constant, related to the adsorption energy (Rawajfih and Nsour, 2006).

The Freundlich equation (Eq. 4) is based on the assumption that the adsorbing has a heterogeneous surface with different types of adsorption sites. Adsorption on each class of sites follows the Langmuir isotherm. The Freundlich equation has the form of:

$$q_e = K_f \,.\, C_e\hat{}(1/n) \qquad (4)$$

where: K_f and n are parameters.

Fig. 2 shows the sorption isotherms of HA onto clinoptilolite tuff. The parameters of the Freudlich and Langmuir adsorption equations are reported in Table 1.

The statistical parameters show that the Langmuir equation describes the experimental data more accurately for two of the three samples analyzed.

Moreover, we observe that there is no significant difference among the q_m values of the Langmuir equation. In contrast K_L, a parameter related to the interaction energy between the solid phase and the adsorbate, is higher for the Ca-enriched samples and increases with decreasing particle size.

The qm values reported here are higher than the values determined for a similar tuff (79% clinoptilolite) from Turkey under the same experimental conditions (Capasso et al., 2007b). Interestingly, markedly higher qm values have been reported for phillipsite and chabazite-rich tuff from Naples (Italy) (Capasso et al., 2007b), although this material had a lower zeolite amount (54%) than the clinoptilolite-rich tuff examined in the present study and that from Turkey.

Up to now the Neapolitan yellow tuff is zeolitic tuff with the higher humic-acids adsorbing capacity.

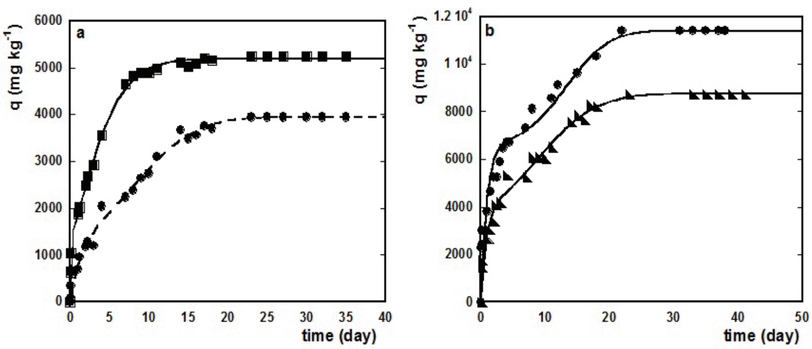

Fig. 1. Sorption kinetics of HA 140 mg L^{-1} on a) 200 mg row (●) or Ca^{2+}-enriched clinoptilolite-rich tuff (■), particle size 0.5-1.0 mm; b) 100 mg Ca^{2+}-enriched clinoptilolite-rich tuff, particle size 1.0-0.5 mm (●) or 1.0-2.0 mm (▲)

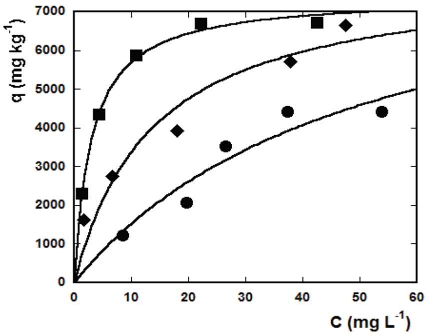

Fig. 2. Sorption isotherms of HA (50 mL of 140 mg L^{-1} HA solution) onto 100 mg row clinoptilolite-rich tuff, particle size 0.5-1.0mm (●), and Ca^{2+}-enriched clinoptilolite-rich tuff , particle size 0.5-1.0mm (■) or 1.0-2.0mm (♦)

Table 1. Isotherms parameters for HA sorption onto: row (CCT) and Ca-CCT

	CCT ***particle size 0.5-1.0 mm***	***Ca-CCT*** ***particle size 0.5-1.0 mm***	***Ca-CCT*** ***particle size 1.0-2.0 mm***
Freudlich model			
K_F	360.26±223.64	2851.7±543.26	1163.9±129.48
1/n	0.6529±0.1715	0.2527±0.0634	0.4434±0.0319
R^2	0.878	0.876	0.991
Langmuir model			
q_m	9246.1±3764.7	7402.5±160.21	8018.5±1286.7
K_L	0.0197±0.0136	0.3322±0.0307	0.0727±0.0339
R^2	0.908	0.994	0.930

Concluding remarks

Our results show that clinoptilolite rich tuff, a low-cost natural material, is a potentially useful adsorbing for water purification from humic acids, although it does not entirely match the Neapolitan yellow tuff. In line with previous work, samples rich in calcium are characterized by a higher energy of interaction. Moreover, under selected experimental conditions, the amount adsorbed versus time follows a two-step kinetics, suggesting a rearrangement of HA molecules on tuff surfaces during the adsorption process.

Keywords: clinoptilolite, humic acids, kinetics, sorption, zeolitic tuff

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