Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.934732

56 (2015) 55–62
September

Taylor & Francis
Taylor & Francis Group

Sorption of non-ionic organic pollutants onto immobilized humic acid

Pasquale Iovino*, Vincenzo Leone, Stefano Salvestrini, Sante Capasso

Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Second University of Naples, Via Vivaldi 43, 81100 Caserta, Italy, Tel. +39 0 823 275111; Fax: +39 0 823 274605; email: pasquale.iovino@unina2.it (P. Iovino), Tel. +39 0 823 274148; email: vincenzo.leone@unina2.it (V. Leone), Tel. +39 0 823 274639; email: stefano.salvestrini@unina2.it (S. Salvestrini), Tel. +39 0 823 274623; email: sante.capasso@unina2.it (S. Capasso)

Received 27 December 2013; Accepted 1 June 2014

ABSTRACT

Sorption isotherms from water solution onto immobilized humic acid have been determined at 4, 14, 24, and 34˚C for toluene, cyclohexane, o-xylene, benzyl alcohol, phenol, and cyclohexanol. The experimental data were well described by the Freundlich sorption equation. The higher values of K constant were obtained for the two aromatic hydrocarbon compounds, toluene (924 $\text{mmol}^{n-1}\,\text{L}^{n}\,\text{kg}^{-1}$) and o-xylene (1,350 $\text{mmol}^{n-1}\,\text{L}^{n}\,\text{kg}^{-1}$). The isosteric sorption enthalpy ($\Delta_{ist}H$) and the standard enthalpy were negative for all compounds analyzed, and the absolute values of $\Delta_{ist}H$ decreased with increasing sorbate loading. Comparisons with data for a humic acid-zeolitic tuff adduct supports the conclusion that the sorption properties of combined materials may not be the sum of the components, thus strengthening the rationale for research of novel adducts.

Keywords: Water treatment; Zeolitic tuff; Calcium humate; Thermodynamic parameters; Isosteric heat

1. Introduction

The main sources of water contamination are industrialization, civilization, and agricultural activities. Few hundred organic pollutants have been found contaminating water resources. Adsorption is considered as the best wastewater treatment method due to its universal nature, inexpensiveness, and ease of operation. Adsorption has been used for the removal of a variety of organic pollutants from various contaminated water sources [1,2]. Basically, adsorption is the accumulation of a substance at a surface or interface. In case of water treatment, the process occurs at an interface between solid adsorbent and contaminated water. Different methods and protocols have been developed for water treatment by adsorption using low-cost adsorbents [3,4].

Humic acid (HA) is a class of organic macromolecules with high structural complexity and multiple reactivity properties, produced by biological decomposition of dead organic matter and widespread in soils, sediments, and water systems. HA consists of a skeleton of aromatic blocks and alkyl chains with a diversity of functional groups, notably carboxyl, phenol, hydroxyl, and quinone groups [5]. In operational terms HA is defined as the fraction of humic substance soluble in alkaline and neutral solutions, and insoluble in acidic solutions.

HA reversibly binds cations, prevalently by electrostatic interaction with deprotonated carboxyl and phenol groups, as well as non-ionic compounds

---

*Corresponding author.

including several common pollutants by means of hydrogen bonds, dipole interactions, and hydrophobic effects [6]. Because of these binding properties, HA may affect the distribution of pollutants in soil and water systems and is extensively investigated for applications in water purification plants. The water solubility of HA can be markedly reduced by heating at high temperature, possibly due to a partial loss of –COOH and –OH groups [7]. Heat-treated HA retains the ability to adsorb cations [8] and organic pollutants [9]. Recent work has revealed that the sorption of hydrocarbon compounds onto a HA-zeolitic tuff adduct is endothermic, whereas sorption of hydroxy compounds is exothermic [10]. Consequently, a temperature rise increases sorption efficiency (i.e. the amount of sorbate bound per unit mass of sorbent at the equilibrium) for hydroxyl compounds, but decreases sorption efficiency for hydrocarbon compounds. This property has potential application for the development of more effective protocols of water purification and sorbent recycling.

Here, we report a study of equilibrium sorption of some non-ionic organic pollutants onto HA immobilized by thermal treatment. A specific goal of this study was to determine whether sorption onto heat-immobilized HA displays a similar thermodynamics as observed for a formerly investigated HA-zeolitic tuff adduct [10] or diverges from this model in some respect. Information on this topic is pivotal in research of novel sorbing materials.

2. Experimental

2.1. Materials

HA was purchased from Sigma-Aldrich and purified as previously reported [11]: dissolution at basic pH, precipitation at acidic pH, and dialysis against deionised water (nominal molecular cut-off 3,500 Da). Analytical-grade benzyl alcohol, toluene, phenol, cyclohexanol, cyclohexane, and o-xylene were purchased from Fluka (Germany).

2.2. Preparation of immobilized HA

A few milliliters of a 1.0 mol L^{-1} $CaCl_2$ solution were added to a 100 mg L^{-1} HA solution, pH 7.4 (obtained by Tris buffer) until complete precipitation of humic substances as calcium humate (Ca-HA). After one day, the precipitate was collected by centrifugation, rinsed with deionized water, dried at 40℃, and finally kept in an oven at 330℃ for 1.5 h [7], thus producing an insoluble form of the HA salt (ImCaHA) [7]. The material was characterized by IR spectra and C, H, N determination at the Taibah University Microanalytical Center.

2.3. Adsorption experiments in batch

The selected compounds were dissolved in water at different concentration levels ranging from 10 to 150 mg L^{-1}, containing 1.0×10^{-3} mol dm^{-3} TrisHCl/Tris buffer, pH 6.0, and 1.0×10^{-2} mol dm^{-3} KCl. For cyclohexane, because of its lower solubility in water, the higher concentration tested was 50 mg L^{-1}. Twenty-mL aliquots of each solution were mixed with 50 mg of ImCaHA in glass containers with a butyl/PTFE cap (of the type usually used for space head analyses) and kept in a thermostat at 4, 14, 24, or 34℃ and periodically shaken. After seven days, an aliquot of the solution was taken through the cap and analyzed by gas-chromatography. Analyses carried out after longer times gave much the same results as after seven-day incubation, hence this was adopted as the protocol procedure.

2.4. Analytical procedures

The IR spectra were recorded in the range of 500–4,000 cm^{-1} using pellets of 0.5 mg of ImCaHA in 100 mg KBr. Measurements were carried out on a Perkin Elmer Spectrum GX (FT-IR System). The amount of calcium was determined by heating 100 mg of ImCaHA at 690℃ for 3 h; the powder residue was solubilized with a HNO_3:HCl mixture (1:3) and analyzed by Dionex DX-120 ionic chromatography.

Free sorbate concentration in solution was determined by a Dani GC 1000 gas chromatographer equipped with a split/splitless capillary inlet system and a FID detector. Samples (1.0 μL) were injected in the split mode with a split ratio of 1:20 and analyzed on an ELITE 1 capillary column (60 m × 0.32 mm I.D., 5 mm film thickness; Perkin Elmer, USA). The GC-FID analysis was performed according to the following temperature program: inlet, $T = 200$℃; detector $T = 300$℃; oven, 60℃ (1 min), 8℃/min–280℃ (2 min); flow N_2, 2 mL min^{-1}.

3. Results and discussion

Fig. 1 reports the IR spectra of calcium humate before (CaHA) and after (ImCaHA) thermal treatment.

The two spectra are closely similar, both showing typical features of HA. Notably, both materials displayed a broad absorption band in the spectral region 3,600–2,800 cm^{-1} (diagnostic for OH groups), several IR bands near 1,700 cm^{-1} (characteristic of carbonyl

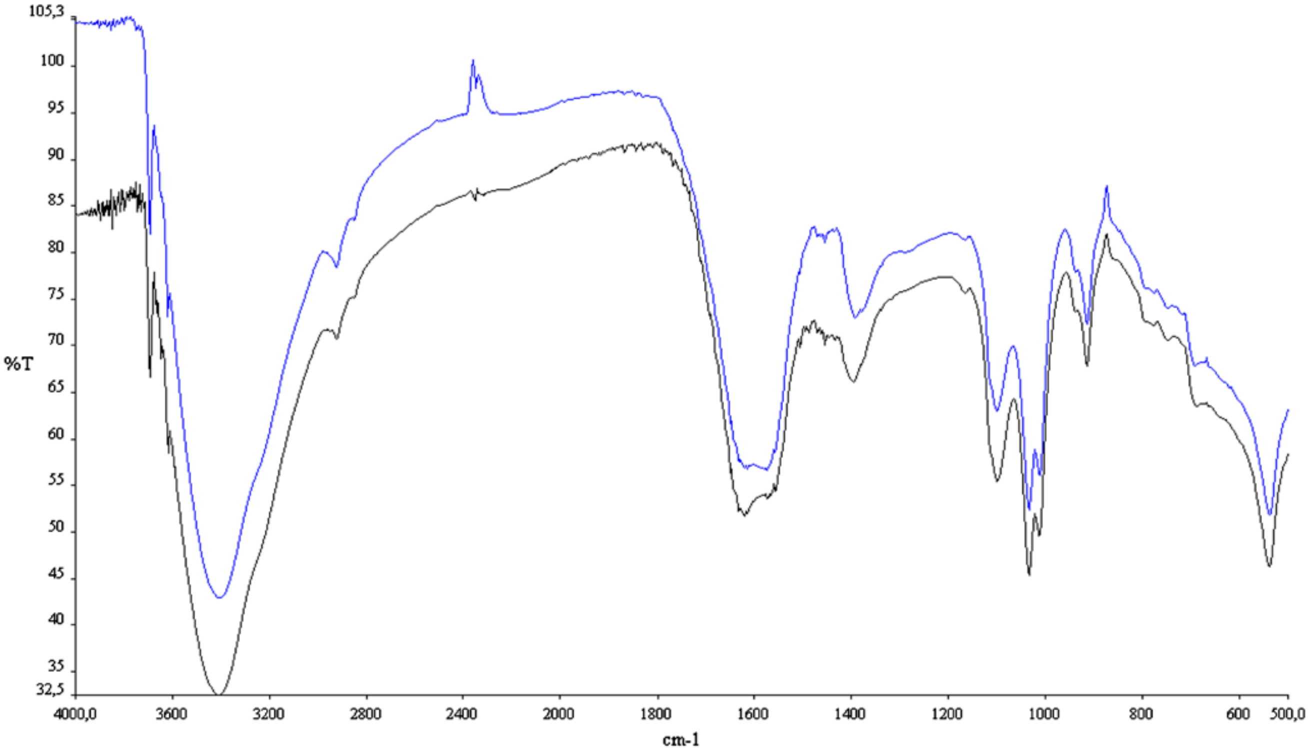

Fig. 1. IR spectra of Ca-HA (upper curve) and ImCaHA (lower curve).

groups), and bands at about 1,400 and 1,000 cm^{-1} (indicative of CH_3 and CH_2 groups and of aromatic ethers) [12]. The elemental analysis of ImCaHA gave 71.30 mg g^{-1} Ca, and 45, 15, and 4% for C, H, and N, respectively, hence being fully consistent with the elemental composition of the HA used in this work [13]. The results indicate that the thermal treatment applied caused no major alteration in the chemistry of the material.

The sorption isotherms determined at four different temperatures for each compound are reported in Fig. 2.

The curves in Fig. 2 were obtained by fitting the experimental data with the Freundlich equation [14]:

$$q_e = KC_e^{\frac{1}{n}} \tag{1}$$

where q_e and C_e are, respectively, the amount of sorbate adsorbed and the concentration in solution at the equilibrium; K and n are parameters. The parameter values obtained from the fitting procedure are reported in Table 1 along with statistical parameters.

With few exceptions, the parameter n was above 1, indicating that the sorption isotherms were of the favorable type. As expected, because of the chemical heterogeneity of the sorbates analyzed, no simple relation was found between the parameters K and $\log K_{ow}$. The higher K values were obtained for the aromatic hydrocarbons toluene and o-xylene, probably due to π-staking interactions [15] between the aromatic ring of these compounds and those present in the molecule of HA. It is worth noting that the K value obtained from the Freundlich equation is equal to the amount sorbed onto the solid phase in equilibrium with a solution of unitary concentration (in our experiments 1 mmol L^{-1}). The K and n values recorded for toluene at 24°C are consistent with values recorded by Iovino [16] for the same molecule sorbed onto activated carbon (Filtrasob 400). Considering that our humic acid adduct costs much less than activated carbon and arguably has a lower environmental impact, it appears to be by far a more convenient choice. Moreover, at least for the compounds analyzed in the present study, the sorption capacity of ImCaHA decreased with temperature (Fig. 2), indicating that the sorption process was exothermic.

The isosteric enthalpy of adsorption (H_{ist}), that is the enthalpy change for sorption at constant amount of sorbed, is given by

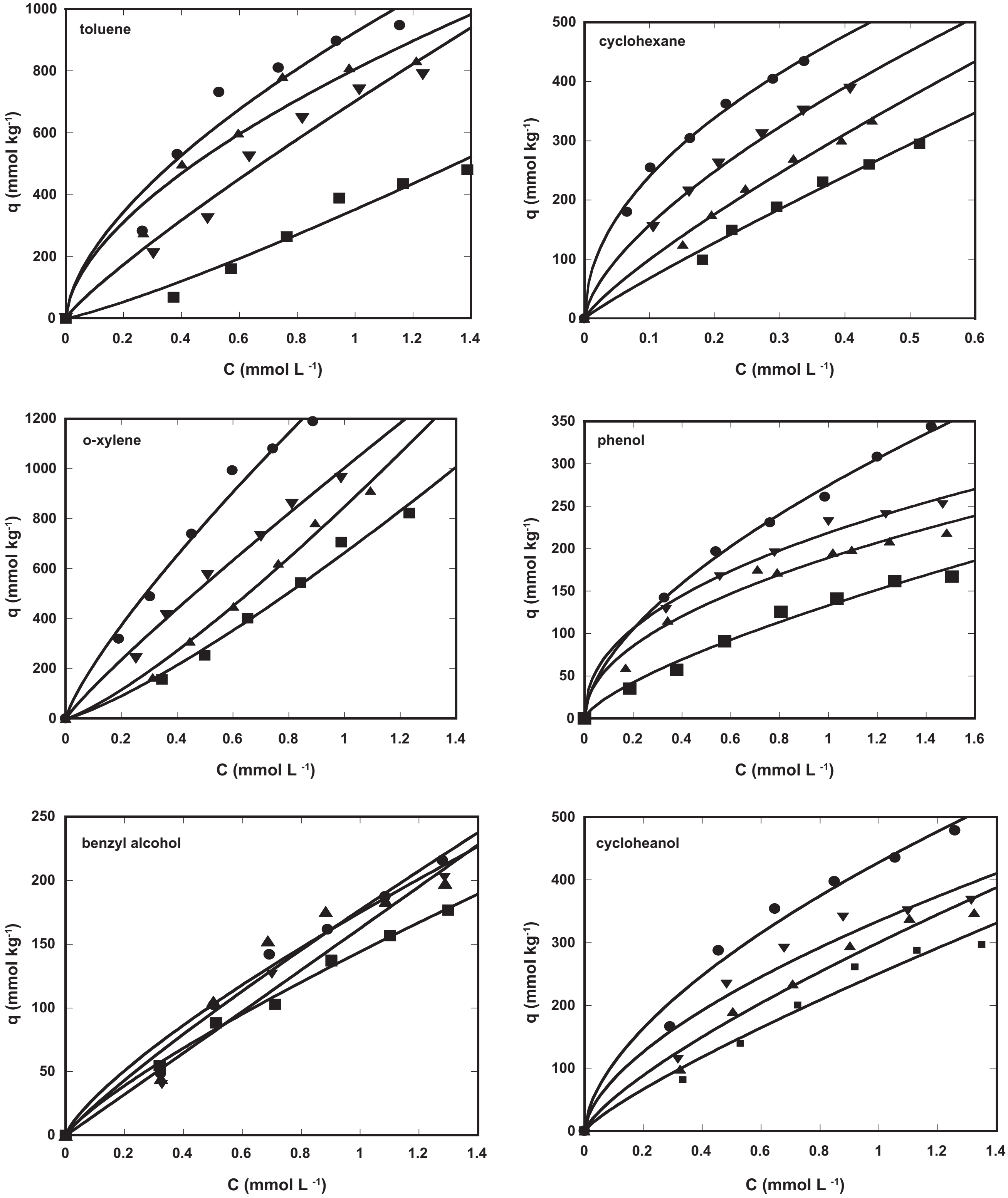

Fig. 2. Sorption isotherms for toluene, cyclohexane, cyclohexanol, benzyl alcohol, phenol, and o-xylene onto ImCaHA at 4°C (●), 14°C (▲), 24°C (▼), and 34°C (■).

Table 1
Parameters of the Freundlich equation for sorption onto ImCaHA

Adsorbent	Temperature (°C)	K (mmol^{n-1} L^{n} kg^{-1})	ΔK (±)	n	Δn (±)	R^2
Toluene ($\log K_{ow} = 2.73$)	4	924	49	1.8	0.3	0.955
	14	805	40	1.7	0.3	0.957
	24	702	27	1.2	0.1	0.973
	34	352	17	0.85	0.1	0.965
o-Xylene ($\log K_{ow} = 3.12$)	4	1,350	50	1.2	0.1	0.988
	14	1,000	30	1.1	0.1	0.993
	24	849	20	0.81	0.04	0.993
	34	663	19	0.81	0.06	0.984
Cyclohexanol ($\log K_{ow} = 3.15$)	4	428	12	1.7	0.2	0.984
	14	335	16	1.6	0.3	0.951
	24	300	10	1.3	0.2	0.979
	34	251	10	1.2	0.2	0.974
Cyclohexane ($\log K_{ow} = 3.44$)	4	750	30	2.0	0.1	0.996
	14	710	30	1.5	0.1	0.994
	24	660	30	1.2	0.1	0.993
	34	550	40	1.1	0.1	0.980
Phenol ($\log K_{ow} = 1.46$)	4	275	3	1.7	0.1	0.997
	14	219	4	2.2	0,2	0.977
	24	189	4	2.0	0.2	0.982
	34	133	3	1.4	0.1	0.985
Benzyl alcohol ($\log K_{ow} = 1.81$)	4	177	5	0.87	0.08	0.985
	14	162	5	1.0	0.1	0.983
	24	175	9	0.7	0.1	0.948
	34	144	2	0.81	0.04	0.948
Cyclohexanol ($\log K_{ow} = 3.15$)	4	428	12	1.7	0.2	0.984
	14	335	16	1.6	0.3	0.951
	24	300	10	1.3	0.2	0.979
	34	251	10	1.2	0.2	0.974

$$H_{ist} = -RT^2 \frac{d \ln C_e}{dT} \tag{2}$$

where R and T, are, respectively the gas constant and absolute temperature.

Integration of this equation, assuming that H_{ist} does not change over the temperature range analyzed, gives:

$$\ln C_e = \frac{H_{ist}}{R} \frac{1}{T} + Con \tag{3}$$

where Con is an integration constant.

Accordingly, plots of the logarithm of the equilibrium concentrations of sorbate in solution against $1/T$ at constant amount of bound sorbate (Fig. 3) give the isosteric enthalpies of sorption [17]. The values for the sorption onto ImCaHA are reported in Table 2.

As expected from the temperature dependence of sorption isotherms, the isosteric sorption enthalpy $\Delta_{ist}H$ was negative for all the compounds analyzed and its absolute value decreased with sorption degree, thereby indicating that ImCaHA contains sorption sites with different sorption energy. Table 3 reports the change of the standard enthalpy ($\Delta_{ads}H^\circ$) for the sorption process analyzed. The values have been obtained by extrapolation [18] of $\Delta_{ist}H$ values at zero sorption loading (plots not shown). $\Delta_{ads}H^\circ$ is one of the thermodynamic parameters more widely used in current literature to describe thermal properties of sorption.

Negative values of $\Delta_{ads}H^\circ$ have been reported for the sorption of phenol from water onto agro-based carbons [19] and onto a hypercrosslinked polymeric sorbent [20]. In contrast, positive $\Delta_{ads}H^\circ$ values have been reported for phenol sorption onto surfactant-modified bentonite- and kaolinite-rich clays, [21]. Apparently, the nature of the sorbing material has a predominant role in determining the value of $\Delta_{ads}H^\circ$. Positive values of $\Delta_{ads}H^\circ$ have also been reported for the sorption of toluene, ethylbenzene, and xylene onto

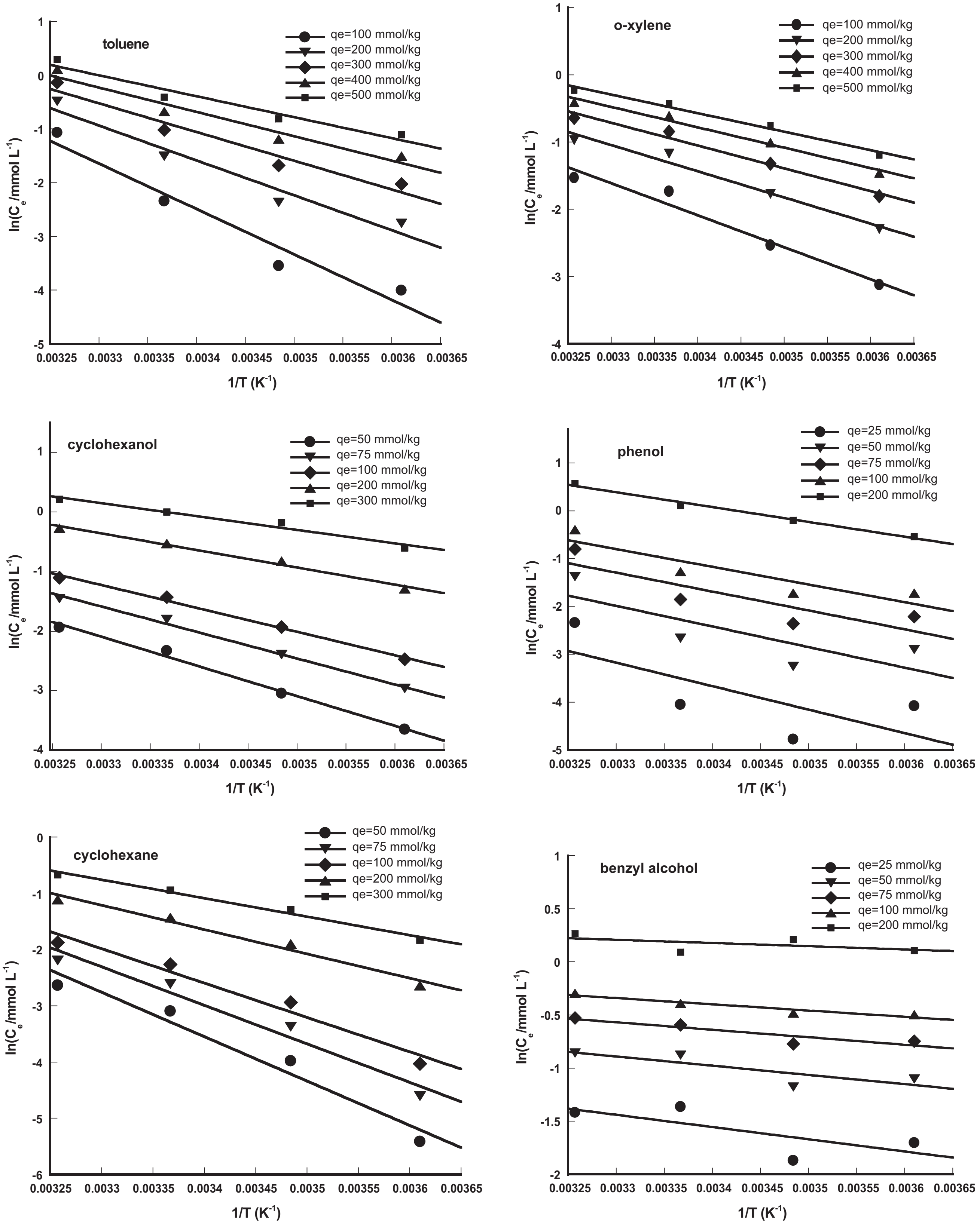

Fig. 3. Plots of logarithms of the equilibrium concentrations (C_e) of toluene, cyclohexane, benzyl alcohol, cyclohexanol, phenol, and o-xylene sorbed to ImCaHA for four constant amounts of bound sorbate (q_e), against the reciprocal of temperature.

Table 2
Values of isosteric enthalpies of sorption ($\Delta_{ist}H$) of toluene, cyclohexane, benzyl alcohol, cyclohexanol, phenol, and o-xylene onto ImCaHA, at various degrees of sorption

Sorbate	Sorption degree (mmol kg^{-1})	$\Delta_{ist}H$ (kJ mol^{-1})	R^2
Toluene	100	−70 ± 17	0.952
	200	−54 ± 14	0.953
	300	−44 ± 13	0.953
	400	−38 ± 11	0.951
	500	−32 ± 5	0.948
o-Xylene	100	−40 ± 9	0.964
	200	−32 ± 7	0.974
	300	−28 ± 6	0.979
	400	−25 ± 5	0.982
	500	−23 ± 2	0.984
Cyclohexanol	50	−41 ± 4	0.992
	75	−36 ± 3	0.993
	100	−33 ± 2	0.994
	200	−24 ± 2	0.986
	300	−19 ± 2	0.967
Phenol	25	−41 ± 6	0.517
	50	−36 ± 3	0.635
	75	−33 ± 2	0.731
	100	−31 ± 1	0.811
	200	−26 ± 2	0.987
Cyclohexane	50	66 ± 28	0.959
	75	−57 ± 19	0.963
	100	−51 ± 14	0.966
	200	−36 ± 10	0.976
	300	−27 ± 2	0.985
Benzyl alcohol	25	−10 ± 6	0.532
	50	−7 ± 3	0.680
	75	−6 ± 2	0.823
	100	−5 ± 1	0.911
	200	−3 ± 3	0.306

Table 3
Standard enthalpy ($\Delta_{ads}H^{\circ}$) for the sorption of organic pollutants onto ImCaHA

Adsorbate	$\Delta_{ads}H^{\circ}$ (kJ mol^{-1})	R^2
Toluene	−88 ± 3	0.997
o-Xylene	−47 ± 1	0.997
Cyclohexanol	−50 ± 2	0.995
Phenol	− 45 ± 1	0.994
Cyclohexane	−79 ± 3	0.995
Benzyl alcohol	−12 ± 0.5	0.994

montmorillonite modified with polyethylene glycol [22]. At the best of our knowledge, no $\Delta_{ads}H$ values are available in the literature for the sorption of cyclohexane, benzyl alcohol, and cyclohexanol. Remarkably, the sign of $\Delta_{ist}H$ for sorption onto a HA-zeolitic tuff adduct changes according to the presence/absence of hydroxyl groups in the sorbate [23]. In combination with the results of the present study, this indicates that the sorption properties of the HA-zeolitic tuff adduct are not the sum of its components.

4. Conclusion

In the immobilized form obtained by controlled heating, the HA resulted to be a good sorbent for organic pollutants. The sorbitivity of HA immobilized decreased with increasing sorbate loading and increasing temperature for all compounds tested. In line with qualitative temperature dependence, $\Delta_{ads}H$ was always negative and independent of the water-octanol partition coefficient of the sorbate. The divergence between the $\Delta_{ads}H$ values recorded in the present studies and those recorded for the sorption of the same compounds onto a HA-zeolitic tuff adduct suggests that the thermodynamic properties of sorbing materials are prone to significant change depending on the nature of the materials combined and the type of treatment applied. This is a strong rationale for the development of more effective and manageable adducts.

References

[1] I. Ali, M. Asim, T.A. Khan, Low cost adsorbents for the removal of organic pollutants from wastewater, J. Environ. Manage. 113 (2012) 170–183.

[2] S. Salvestrini, P. Sagliano, P. Iovino, S. Capasso, C. Colella, Atrazine adsorption by acid-activated zeolite-rich tuffs, Appl. Clay Sci. 49(3) (2010) 330–335.

[3] I. Ali, V.K. Gupta, Advances in water treatment by adsorption technology, Nat. Protoc. 1(6) (2006) 2661–2667.

[4] S. Capasso, C. Colella, E. Coppola, P. Iovino, S. Salvestrini, Removal of humic substances from water by means of calcium-ion-enriched natural zeolites, Water Environ. Res. 79(3) (2007) 305–309.

[5] V. Leone, S. Canzano, P. Iovino, S. Capasso, Sorption of humic acids by a zeolite-feldspar-bearing tuff in batch and fixed-bed column, J. Porous Mater. 19 (2012) 449–453.

[6] J.C. Joo, C.D. Shackelford, K.F. Reardon, Sorption of nonpolar neutral organic compounds to humic acid-coated sands: Contributions of organic and mineral components, Chemosphere 70 (2008) 1290–1297.

[7] H. Seki, A. Suzuki, Adsorption of heavy metal ions onto insolubilized humic acid, J. Colloid Interface Sci. 171 (1995) 490–494.

[8] O. Celebi, A. Kilikli, H.N. Erten, Sorption of radioactive cesium and barium ions onto solid humic acid, J. Hazard. Mater. 168 (2009) 695–703.

[9] M. Klavins, L. Eglite, A. Zicmanis, Immobilized humic substances as sorbents, Chemosphere 62 (2006) 1500–1506.

[10] V. Leone, P. Iovino, S. Salvestrini, S. Capasso, Sorption of non-ionic organic pollutants onto a humic acids-zeolitic tuff adduct: Thermodynamic aspects, Chemosphere 95 (2013) 75–80.

[11] S. Capasso, E. Coppola, P. Iovino, S. Salvestrini, C. Colella, Sorption of humic acids on zeolitic tuffs, Microporous Mesoporous Mater. 105 (2007) 324–328.

[12] J. Polak, M. Bartoszek, M. Żądło, A. Kos, The spectroscopic studies of humic acid extracted from sediment collected at different seasons, Chemosphere 84 (2011) 1548–1555.

[13] T. Tanaka, Functional groups and reactivity of size-fractionated Aldrich humic acid, Thermochim. Acta 532 (2012) 60–64.

[14] A.W. Adamson, A.P. Gast, Physical Chemistry of Surfaces, sixth ed., John Willey & Sons Inc, New York, NY, 1997.

[15] X. Cheng, Y. Peng, C. Gao, Y. Yan, J. Huang, Studying of 1-D assemblies in anionic azo dyes and cationic surfactants mixed systems, Colloids Surf., A 422 (2013) 10–18.

[16] P. Iovino, S. Canzano, S. Capasso, M. Di Natale, A. Erto, A. Lama, D. Musmarra, Single and competitive adsorption of toluene and naphthalene onto activated carbon, Chem. Eng. Trans. 32 (2013) 67–72.

[17] A. Erto, R. Andreozzi, F. Di Natale, A. Lancia, D. Musmarra, Experimental and isotherm-models analysis on TCE and PCE adsorption onto activated carbon, Chem. Eng. Trans. 17 (2009) 293–298.

[18] S. Salvestrini, V. Leone, P. Iovino, S. Canzano, S. Capasso, Considerations about the correct evaluation of sorption thermodynamic parameters from equilibrium isotherms, J. Chem. Thermodyn. 68 (2014) 310–316.

[19] V. Srihari, A. Das, The kinetic and thermodynamic studies of phenol-sorption onto three agro-based carbons, Desalination 225 (2008) 220–234.

[20] A. Li, Q. Zhang, G. Zhang, J. Chen, Z. Fei, F. Liu, Adsorption of phenolic compounds from aqueous solutions by a water-compatible hypercrosslinked polymeric adsorbent, Chemosphere 47 (2002) 981–989.

[21] U.F. Alkaram, A.A. Mukhlis, A.H. Al-Dujaili, The removal of phenol from aqueous solutions by adsorption using surfactant-modified bentonite and kaolinite, J. Hazard. Mater. 169 (2009) 324–332.

[22] H. Nourmoradi, M. Nikaeen, M. Khiadani (Hajian), Removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solutions by montmorillonite modified with nonionic surfactant: Equilibrium, kinetic and thermodynamic study, Chem. Eng. J. 191 (2012) 341–348.

[23] V. Leone, S. Canzano, P. Iovino, S. Salvestrini, S. Capasso, A novel organo-zeolite adduct for environmental applications: Sorption of phenol, Chemosphere 91 (2013) 415–420.