BTX abatement using Chilean natural zeolite: the role of Brønsted acid sites

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ABSTRACT

In wastewater treatment facilities, air quality is not only affected by conventional unpleasant odour compounds; toxic volatile organic compounds (VOCs) are also found. In this study, the adsorptive capacity of Chilean natural zeolite toward VOC removal was evaluated. Moreover, the influence of zeolite chemical surface properties on VOC elimination was also investigated. Three modified zeolite samples were prepared from a natural Chilean zeolite (53% clinoptilolite, 40% mordenite and 7% quartz). Natural and modified zeolite samples were characterised by nitrogen adsorption at 77 K, elemental analyses and X-ray fluorescence (XRF). Chemical modifications of natural zeolite showed the important role of Brønsted acid sites on the abatement of VOCs. The presence of humidity has a negative effect on zeolite adsorption capacity. Natural zeolites could be an interesting option for benzene, toluene and xylene vapour emission abatement.

Key words | Benzene, brønsted acid sites, Lewis acid sites, natural zeolite, toluene, xylene

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INTRODUCTION

Waste air treatment at wastewater treatment facilities is usually planned for odour nuisance reduction, but waste air also contains a variety of volatile organic compounds (VOCs), usually at low concentrations (Iranpour *et al.* 2005). In recent years, toxic organic contaminants in industrial emissions have been recognised as an issue of growing importance (Luo & Lindsey 2006). In Chile, the Ministry of Health adopted internationally recommended standards for occupational exposure limits for about 200 airborne chemicals (MINSAL DS 594 1999), including VOCs. In Europe, more and more drastic regulations have been set new standards for 20 years. Conventional techniques for controlling odours and VOCs include incineration, scrubbing, chemical oxidation and condensation (Mudliar *et al.* 2010). Sorption processes have been widely used as feasible methods for VOC removal. Among adsorbents, activated carbon is normally preferred. However, activated carbons are not stable at high temperatures and could be flammable. Great effort has been dedicated to testing efficiencies of aluminosilicate materials (Monneyron *et al.* 2003; Ghiaci *et al.* 2004). Recently, researchers have focused their attention on natural zeolites. Natural zeolites have been applied for sulfur dioxide and VOC removal (Kuleyin 2007; Allen *et al.* 2009). In this work, the influence of chemical surface characteristics of natural zeolite on VOCs abatement was studied. The effect of air humidity on VOCs removal efficiency was also assessed.

METHODS

Materials

Chilean natural zeolite (53% clinoptilolite, 40% mordenite and 7% quartz) was provided by Minera Formas™. A zeolite sample was ground and sieved to 0.3–0.425 mm; then was rinsed with ultrapure water, oven-dried at 398 K for 24 h, and stored in a desiccator until further use. Benzene (B), toluene (T), and xylene (X) were selected here as model aromatic VOCs, as these pose serious occupational health and environmental risks, particularly in cases of chronic exposure. B, T and X were provided by Merck with 99.8% purity. Ultrapure water was obtained from an EASY pure® RF II system.

Chemical modification of natural zeolite

Three zeolite samples with different chemical surface properties were prepared from natural zeolite (NZ). Two kinds of treatment were applied: de-alumination and ion-exchange according to the procedure described elsewhere (Alejandro *et al.* 2011). De-alumination treatment was carried out using HCl (2.4 mol dm^{-3}) and ion exchange was conducted using an ammonium sulfate solution (0.1 mol dm^{-3}). Modified zeolites with HCl and ammonium sulfate were named ZH2.4 and NH4Z1, respectively. Another ammonium-exchanged zeolite sample (2NH4Z1) was prepared by conducting an ion exchange procedure, as described in previous work (Alejandro *et al.* 2011).

Physical–chemical characterisation of zeolite samples

Natural and modified zeolite samples were characterised by different techniques. X-ray powder diffraction (XRD) was applied to natural and modified zeolite samples in order to evaluate mineralogical and structural changes. XRD was performed with a Bruker AXS Model D4 ENDEAVOR diffractometer, equipped with a cupper X-ray tube and Ni filter. Nitrogen adsorption isotherms at 77 K were obtained on a Micromeritics Gemini 3175 and elemental analyses in a LECO CHN 2000 apparatus as described elsewhere (Alejandro *et al.* 2011). X-ray fluorescence (XRF) allowed determination of bulk chemical composition of natural and modified zeolites by using a RIGAKU Model 3072 spectrometer (Valdés *et al.* 2009). Zeolite samples were also characterised by NH_3-TPD using a temperature-programmed desorption/reaction (TPD/TPR) 2900 Micromeritics system, coupled with a thermal conductivity detector (TCD). More details are given in a previous communication (Alejandro *et al.* 2011). Infrared spectra of VOC saturated-zeolite samples were recorded using a Nicolet NEXUS spectrometer. Spectra were collected at an average of 64 scans and a resolution of 4 cm^{-1} using a pressed disc containing 1 mg of zeolite sample and 100 mg of KBr.

Experimental system

Experiments were carried out in a quartz U-shaped fixed-bed flow contactor (4 mm ID) at 293 K and 101 kPa (see Figure 1). Zeolite samples were out-gassed in Ar flow (0.1 dm^3 min^{-1}) for 2 h at 623 K or 823 K (heating rate 10 K min^{-1}) before the adsorption experiments. Inlet VOC concentration (C_{Vint}) was fixed by bubbling argon in a temperature controlled saturator with the selected VOC (*B*, *T* or *X*) and was diluted by mixing with another fresh argon stream. Mass flow controllers (Aalborg) were used and the volumetric flow rate was measured at the experimental system exit, using a calibrated soap bubble flow meter. Once the inlet concentration of the selected VOC was stabilised, the VOC stream was redirected to the zeolite contactor containing 0.15 g of the selected zeolite sample. VOC concentration in the outlet stream (C_{Vout}) was monitored on-line as a function of time by gas chromatography (GC), using a Perkin Elmer Clarus 500 Gas Chromatograph equipped with a FID detector; until the zeolite sample reached the VOC saturation. Data were recorded every 6 min and processed with TotalChrom Navigator Clarus 500 software.

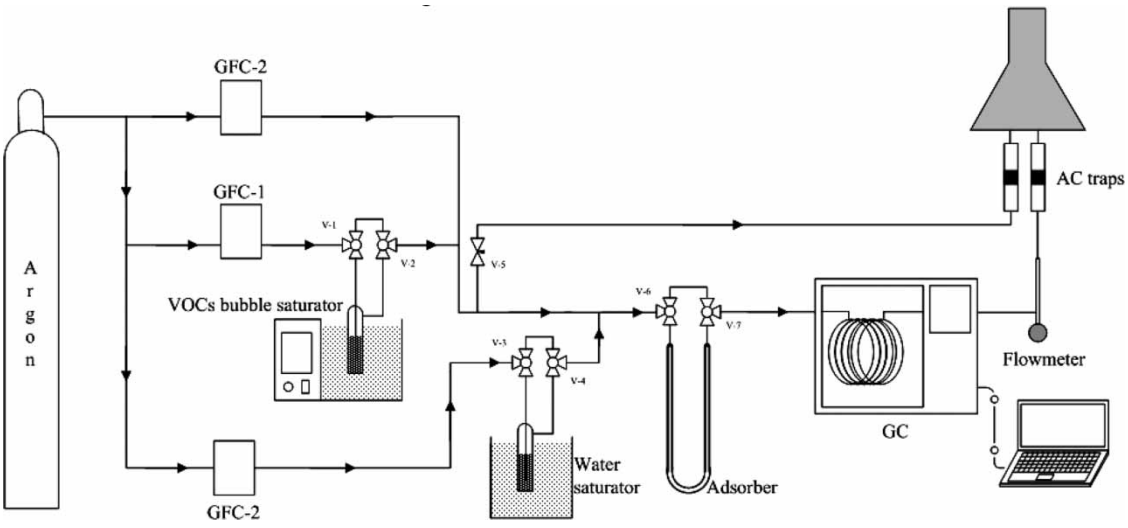

Figure 1 | Experimental set-up.

Adsorption capacities of zeolite samples toward the selected VOC (*B*, *T*, or *X*) were determined by calculating the areas from breakthrough curves using Equation (1). All experiments reported here were conducted in triplicate.

$$q = \frac{\int_0^{t_s} (\dot{n}_0 - \dot{n}_t)\, \mathrm{d}t}{W \cdot S} \quad (1)$$

where q is the amount of the adsorbed VOC (*B*, *T*, or *X*) on the zeolite sample at equilibrium [mmol m^{-2}], $\dot{n}_o$ is the VOC (*B*, *T*, or *X*) inlet molar flow [mmol s^{-1}], $\dot{n}_t$ is the VOC (*B*, *T*, or *X*) molar flow [mmol s^{-1}] obtained for each point of the breakthrough curves, t_s is the time needed to reach the saturation, W is the zeolite mass [g], and S is the zeolite surface area [$m^2\,g^{-1}$].

The effect of humidity on VOC adsorption was investigated by bubbling argon (0.02 $dm^3\,min^{-1}$) in a water saturator at 293 K, and mixing this humid stream with the VOC stream at the adsorber inlet.

RESULTS AND DISCUSSION

Characterisation of zeolite samples

XRD patterns (results not shown) indicated that zeolite samples are highly crystalline. Chemical modification treatments of natural zeolite do not show any significant changes in the zeolite crystalline structure. Table 1 summarises the physical–chemical characterisation results of natural and modified zeolite samples. It can be seen that acid treatment increased the surface area and Si/Al ratio, as a result of a decationisation and de-alumination mechanism (Barrer 1964). The highest value of ZH2.4 surface area could be related to the amorphous material dissolution that could block zeolite structure channels, generating new pores (Allen *et al.* 2009).

Temperature programmed desorption-mass spectrometry (TPD-MS) profiles were obtained in a previous work (Alejandro *et al.* 2011), for natural and modified samples previously oven dried at 398 K for 24 h. The results showed the transformation of adsorbed NH_4^+ into H^+ when temperature was raised, releasing ammonia and contributing to 'bridging hydroxyl groups' formation (Alejandro *et al.* 2011). These 'bridging hydroxyl groups' are also known as Brønsted acid sites. At around 823 K water signal intensity was increased, evidencing Brønsted acid sites transformation into new Lewis acid sites on the zeolite surface (Valdés *et al.* 2011).

Table 1 | Physical–chemical characterisation of zeolite samples

Sample	S [$m^2\,g^{-1}$]	V_{micro}[$cm^3\,g^{-1}$]	Si/Al ratio[a]	N_2[b]
NZ	205	47.08	5.34	0.13
ZH2.4	434	99.67	7.1	0.14
NH4Z1	181	41.51	5.32	1.78
2NH4Z1	171	36.92	5.34	2.16

[a]By XRF (% w/w).
[b]By elemental analyses (% w/w).

Effect of zeolite chemical surface properties on the adsorption of VOCs

Figure 2 shows the adsorption isotherms of the selected VOCs at 293 K on natural and modified zeolite samples after the outgassing step at 623 and 823 K. Adsorption equilibrium data are represented as the amount of adsorbed VOC (*B*, *T*, or *X*) per zeolite surface [$mmol_{adsorbed\,VOC} \cdot m^{-2}_{zeolite}$].

Experimental results were fitted to the Langmuir adsorption model (Langmuir 1916) as indicated by Equation (2):

$$q_L = \frac{q_m b C_{VOC}}{1 + b C_{VOC}} \quad (2)$$

where q_L is the amount of adsorbed VOC (*B, T*, or *X*) on the zeolite surface at equilibrium [mmol m^{-2}], C_{VOC} is the equilibrium concentration [μmol dm^{-3}], q_m is the maximum adsorption capacity [mmol m^{-2}], and b is the adsorption intensity or Langmuir coefficient [$dm^3\,\mu mol^{-1}$]. The Langmuir sorption model has been applied to VOC adsorption on synthetic zeolites (Brosillon *et al.* 2001; Monneyron *et al.* 2003). The values of different parameters of the Langmuir adsorption model at 293 K for the selected VOC on natural and modified zeolite samples are summarised in Table 2.

Results obtained for out-gassed natural and modified zeolite samples at 623 K indicate that the lowest VOC elimination is obtained when natural zeolite (NZ) is used. The adsorption capacity of NZ toward *B, T,* and *X* is lower than modified zeolite samples out-gassed at 623 K. In the case of benzene adsorption on out-gassed zeolite samples at 623 K, a better result is reached when 2NH4Z1 is used. Under such out-gassing conditions, a high content of Brønsted acid sites are generated on this sample as a consequence of ammonium-exchange followed by thermal treatment. Thus, Brønsted acid sites might be responsible for the highest observed benzene removal. However, for toluene and xylene adsorption on out-gassed samples at

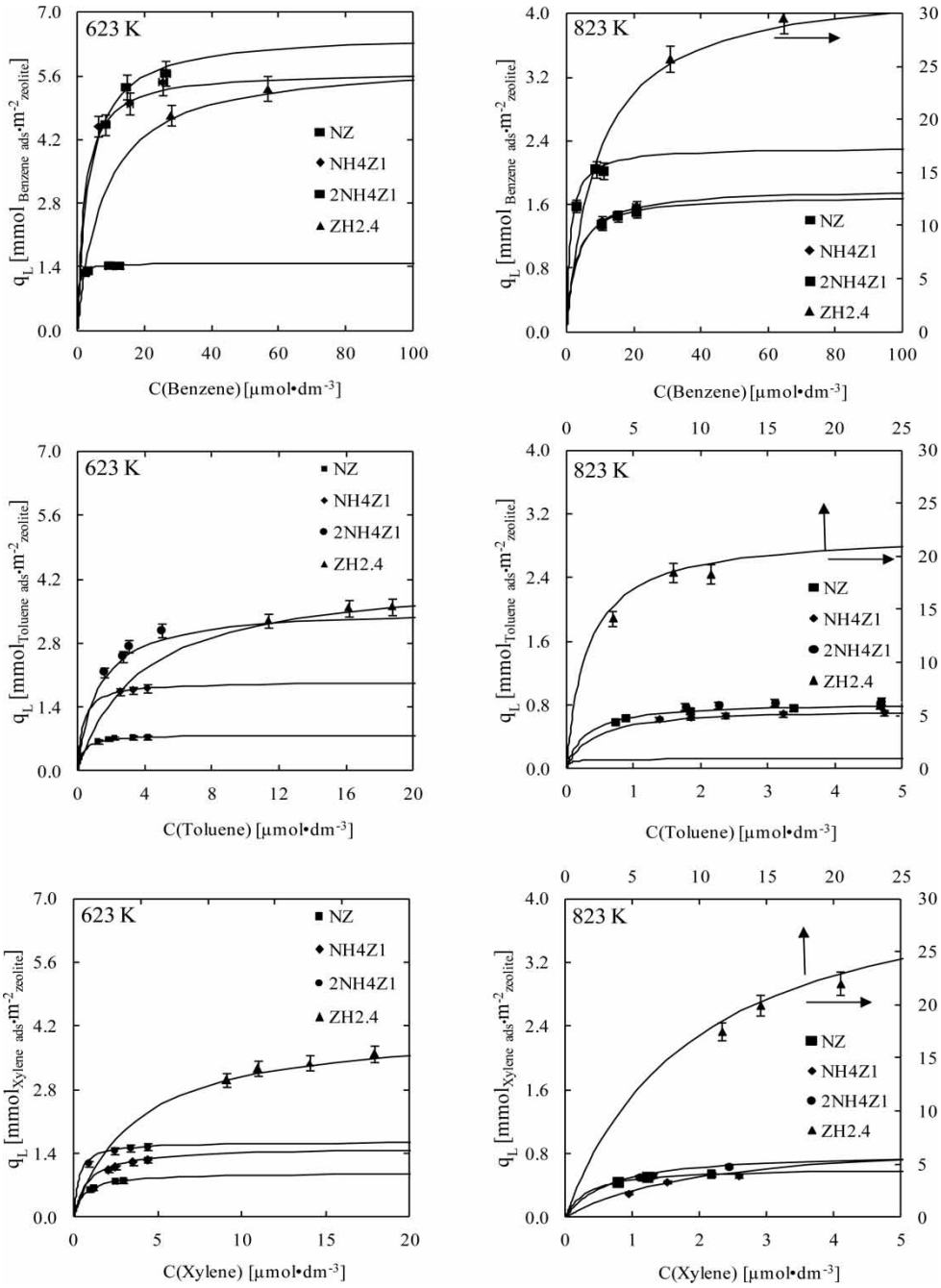

Figure 2 | Effect of zeolite chemical surface properties on the adsorption of VOCs (*B*, *T*, or *X*). (■) NZ, (▲) ZH2.4, (◆) NH4Z1, (•) 2NH4Z1, (—) represents the fit to Langmuir adsorption model. Experimental conditions: 0.15 g of zeolite, 0.05 dm^3 min^{-1}, 101 kPa, 293 K.

623 K, the highest adsorption capacity is achieved by the ZH2.4 sample. VOC adsorption experiments on out-gassed natural and modified zeolite samples at 823 K show that ZH2.4 adsorption capacity is higher than other samples used here. This behaviour is probably due to the presence of new pores in the ZH2.4 sample, as a result of the applied acid treatment. The adsorption of the selected VOC could also increase because more than a monolayer might be formed on the ZH2.4 surface.

The acidity of natural and modified zeolite samples was previously investigated by (NH_3-TPD) (Alejandro *et al*. 2011). The higher amount of desorbed ammonia (13.6%) in the mid-temperature range (373–463 K) was obtained by the out-gassed NZ at 623 K. However, the ZH2.4 demonstrated

Table 2 | Adsorption model parameters

			Langmuir		
VOCs	**Sample**	**Outgassing temperature**	q_m [mmol m^{-2}]	b [dm^3 μmol^{-1}]	R^2
Benzene (*B*)	NZ	623 K	1.48	3.29	0.98
	ZH2.4		5.93	0.13	0.99
	NH4Z1		5.71	0.48	0.94
	2NH4Z1		6.54	0.30	0.97
	NZ	823 K	2.32	0.85	0.98
	ZH2.4		32.96	0.11	0.97
	NH4Z1		1.79	0.32	0.95
	2NH4Z1		1.71	0.37	0.99
Toluene (*T*)	NZ	623 K	0.79	3.07	0.98
	ZH2.4		4.29	0.27	0.97
	NH4Z1		1.95	3.15	0.96
	2NH4Z1		3.57	0.82	0.95
	NZ	823 K	0.83	3.55	0.99
	ZH2.4		22.21	0.63	0.97
	NH4Z1		0.75	2.65	0.99
	2NH4Z1		0.90	4.27	0.99
Xylene (*X*)	NZ	623 K	0.97	1.67	0.99
	ZH2.4		4.21	0.27	0.95
	NH4Z1		1.53	1.20	0.99
	2NH4Z1		1.66	3.53	0.98
	NZ	823 K	0.62	3.18	0.99
	ZH2.4		33.68	0.10	0.97
	NH4Z1		1.02	0.49	0.99
	2NH4Z1		0.82	1.56	0.95

the highest acid strength as the amount of desorbed ammonia in the high temperature region was larger than the other out-gassed samples at 623 K. NH_3-TPD showed two characteristic peaks, the first one in the range of 400–500 K, which was related to Lewis acid sites and the second (550–900 K) to Brønsted acid sites. It was observed that as the out-gassing temperature was increased, Brønsted acid surface site concentration decreased as a consequence of its transformation into Lewis acid sites at around 823 K. The presence of Brønsted acid sites could be the main cause of the observed removal enhancements for the out-gassed samples at 623 K. As can be seen in Figure 2, the results of *B*, *T*, and *X* abatements using out-gassed samples at 823 K are lower than those obtained when out-gassed samples at 623 K are applied. It appears that Lewis acid sites are not as active as Brønsted acid sites toward *B*, *T*, and *X* adsorption. Adsorbate molecules within the zeolite framework are subjected to acid–base interactions with zeolite Brønsted acid sites (Roque-Malherbe 2000). Furthermore, the relative basicities for benzene, toluene and xylene are 0.61, 0.92 and 1.26, respectively (Barthomeuf & De Mallmann 1990). Consequently, the three VOCs assessed here (*B*, *T*, and *X*) exhibit different levels of interactions toward the Brønsted acid sites of natural and modified zeolite samples. However, xylene with the highest relative basicity shows the lowest abatement. These results could be associated with an adsorption reduction within the zeolite smaller micropores. Xylene molecule cross-sectional area (0.54 nm^2) is higher than toluene (0.47 nm^2) and benzene (0.43 nm^2) (McClellan & Harnsberger 1967). On the other hand, benzene with the lowest basicity and cross-sectional area could be easily accommodated inside natural and modified zeolite zeolite frameworks, resulting in a higher abatement.

Influence of humidity on the adsorption of VOCs on natural zeolite

Breakthrough curves of the adsorption of VOCs (*B*, *T*, and *X*) on natural zeolite (out-gassed at 623 K) in the presence and absence of humidity are shown in Figure 3.

The results show that the presence of humidity (40%), strongly affects the adsorptive capacity of out-gassed natural zeolite at 623 K. The zeolite adsorption capacity toward *B*, *T* and *X* is reduced by 12, 68, 48%, respectively. The observed effect might be due to a competition between *B*, *T*, or *X* and

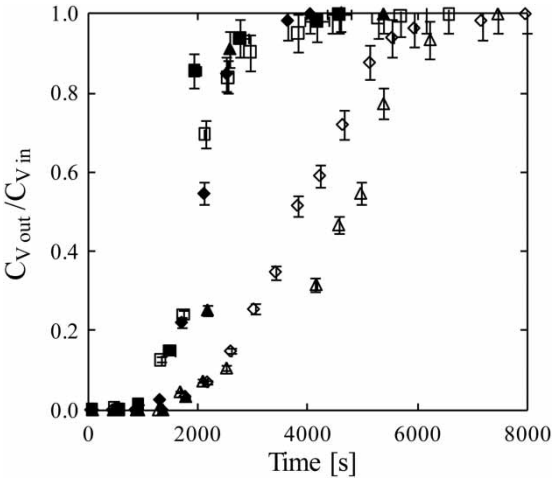

Figure 3 | Influence of humidity on the adsorption of VOCs (*B*, *T* or *X*) over out-gassed natural zeolite at 623 K. Filled markers represent the presence of humidity; open markers mean the absence of humidity. (□/■) Benzene, (Δ/▲) toluene, (◇/◆) xylene. Experimental conditions: 0.15 g of zeolite, 0.05 $dm^3\,min^{-1}$, 101 kPa, 293 K. VOC inlet concentrations ($C_{V\,in}$): benzene (8.8 μmol dm^{-3}), toluene (2.2 μmol dm^{-3}) and xylene (1.2 μmol dm^{-3}).

water for zeolite active sites. Water reduces the number of available Brønsted acid sites (Kulkarni & Muggli 2006), reducing zeolite adsorption capacity toward the selected VOC molecules (*B*, *T*, or *X*).

FTIR study of adsorbed VOC on natural zeolite

Figure 4 shows the Fourier transform infrared spectroscopy (FTIR) spectrum obtained after the subtraction of the collected spectrum for the out-gassed natural zeolite samples at 623 and 823 K, with and without adsorbed VOC. The results show peaks at 1,443; 1,473; and 1,527 cm^{-1} for adsorbed benzene on the out-gassed sample at 623 K and at 1,489 and 1,540 cm^{-1} for adsorbed benzene on the out-gassed sample at 823 K. For adsorbed toluene on the out-gassed sample at 623 K, a peak at 1,473 cm^{-1} is registered; while peaks at 1,473 cm^{-1} and at 1,536 cm^{-1} are registered for the out-gassed sample at 823 K. Malherbe & Wendelbo (2003) associate the region around 1,450–1,540 cm^{-1}, with a maximum at 1,487 cm^{-1}, with benzene adsorbed on zeolites, as well as a band around 1,477 cm^{-1} with toluene adsorption. In xylene spectra, a peak at 1,520 cm^{-1} could be evidence of xylene adsorption on the out-gassed sample at 623 K (Marie *et al.* 2005). This peak is shifted to 1,530 cm^{-1} on the out-gassed sample at 823 K.

CONCLUSIONS

The adsorptive capacity of natural and modified zeolite samples was investigated in this study. Experimental results were analysed by using the Langmuir adsorption model. Results indicated that the adsorptive capacity is enhanced when out-gassed zeolite samples at 623 K were used. Brønsted acid sites are claimed in this study as responsible for benzene, toluene and xylene abatement using natural and modified zeolite samples. The FTIR study showed that benzene, toluene and xylene molecules form bonds with acid sites on natural zeolite surface. The presence of humidity has a negative effect on natural zeolite adsorption capacity toward benzene, toluene and xylene vapours. Chilean natural zeolite chemicals, and thermally pre-treated, could be used as an alternative adsorbent for VOCs abatement in wastewater treatment facilities.

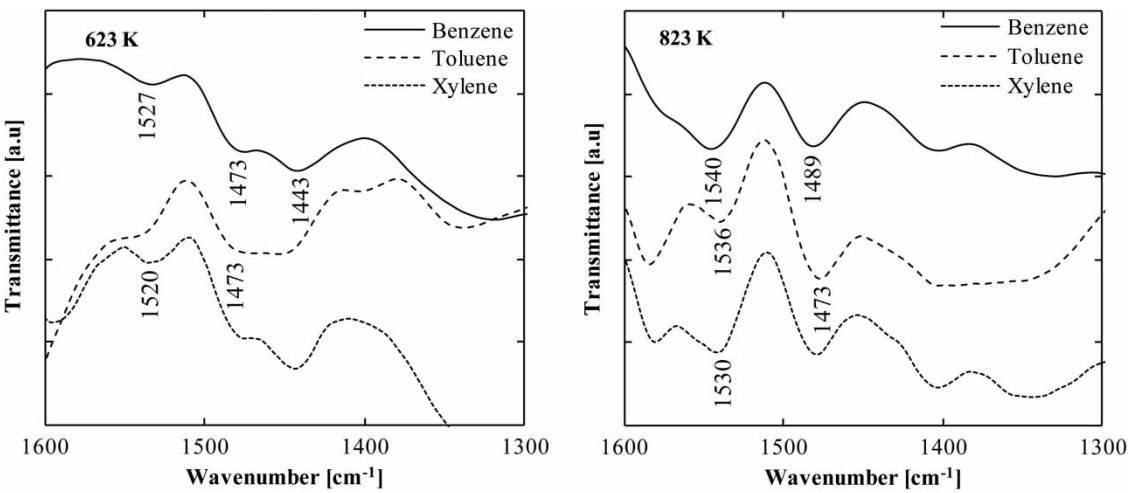

Figure 4 | FTIR spectra of adsorbed VOC over natural zeolites (out-gassed at 623 and 823 K). The spectrum of the out-gassed zeolite sample without adsorbed VOC was subtracted.

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REFERENCES

Alejandro, S., Valdés, H. & Zaror, C. A. 2011 Natural zeolite reactivity towards ozone: the role of acid surface sites. *Journal of Advanced Oxidation Technologies* **14** (22), 182–189.

Allen, S. J., Ivanova, E. & Koumanova, B. 2009 Adsorption of sulfur dioxide on chemically modified natural clinoptilolite. Acid modification. *Chemical Engineering Journal* **152** (2–3), 389–395.

Barrer, R. M. 1964 Molecular sieve sorbents from clinoptilolite. *Canadian Journal of Chemistry* **42** (1), 1480–1487.

Barthomeuf, D. & De Mallmann, A. 1990 Adsorption of aromatics in NaY and AlPO4–5. Correlation with the sorbent properties in separations. *Industrial and Engineering Chemistry Research* **29** (7), 1435–1438.

Brosillon, S., Manero, M. H. & Foussard, J. N. 2001 Mass transfer in VOC adsorption on zeolite: experimental and theoretical breakthrough curves. *Environmental Science and Technology* **35** (17), 3571–3575.

Ghiaci, M., Abbaspur, A., Kia, R. & Seyedeyn-Azad, F. 2004 Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41. *Separation and Purification Technology* **40** (3), 217–229.

Iranpour, R., Cox, H. H. J., Deshusses, M. A. & Schroeder, E. D. 2005 Literature review of air pollution control biofilters and biotrickling filters for odor and volatile organic compound removal. *Environmental Progress* **24** (3), 254–267.

Kuleyin, A. 2007 Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite. *Journal of Hazardous Materials* **144** (1–2), 307–315.

Kulkarni, A. P. & Muggli, D. S. 2006 The effect of water on the acidity of TiO2 and sulfated titania. *Applied Catalysis A: General* **302** (2), 274–282.

Langmuir, I. 1916 The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American Chemical Society* **38** (11), 2221–2295.

Luo, J. & Lindsey, S. 2006 The use of pine bark and natural zeolite as biofilter media to remove animal rendering process odours. *Bioresource Technology* **97** (13), 1461–1469.

Malherbe, R. R. & Wendelbo, R. 2003 Study of Fourier transform infrared-temperature-programmed desorption of benzene, toluene and ethylbenzene from H-ZSM-5 and H-beta zeolites. *Thermochimica Acta* **400** (1–2), 165–173.

Marie, O., Thibault-Starzyk, F. & Massiani, P. 2005 Conversion of xylene over mordenites: an operando infrared spectroscopy study of the effect of Na+. *Journal of Catalysis* **230** (1), 28–37.

McClellan, A. L. & Harnsberger, H. F. 1967 Cross-sectional areas of molecules adsorbed on solid surfaces. *Journal of Colloid and Interface Science* **23** (4), 577–599.

MINSAL DS 594 1999 Decreto supremo n° 594 aprueba reglamento sobre condiciones sanitarias y ambientales básicas en los lugares de trabajo. Ministerio de Salud de Chile. 15 de Septiembre 1999.

Monneyron, P., Manero, M. H. & Foussard, J. N. 2003 Measurement and Modeling of single and multicomponent adsorption equilibria of VOCs on high silica zeolites. *Environment Science and Technology* **30** (11), 2410–2414.

Mudliar, S., Giri, B., Padoley, K., Satpute, D., Dixit, R., Bhatt, P., Pandey, R., Juwarkar, A. & Vaidya, A. 2010 Bioreactors for treatment of VOCs and odours – A review. *Journal of Environmental Management* **91** (5), 1039–1054.

Roque-Malherbe, R. 2000 Complementary approach to the volume filling theory of adsorption in zeolites. *Microporous and Mesoporous Materials* **41** (1–3), 227–240.

Valdés, H., Farfán, V. J., Manoli, J. A. & Zaror, C. A. 2009 Catalytic ozone aqueous decomposition promoted by natural zeolite and volcanic sand. *Journal of Hazardous Materials* **165** (1–3), 915–922.

Valdés, H., Padilla, E. & Zaror, C. A. 2011 Influence of chemical surface characteristics of natural zeolite on catalytic ozone abatement. *Ozone Science and Engineering* **33** (4), 279–284.