

ADSORPTION AND DESORPTION OF FUEL-BASED COMPOUNDS FROM WATER THROUGH SYNTHETIC ZEOLITE ZSM-5

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This research is devoted to study the adsorption/desorption of Volatile Organic Compounds (VOCs) from aqueous solutions by means of a zeolite ZSM-5. In recent years, the drawback of the strong and rapid development of the chemical and agrochemical industries has caused a release of large number of pollutants in the environment. The aquatic ecosystem is resulted one of the major recipient of these toxic compounds. Specifically, water reserves represented by groundwater are seriously compromised in many industrial areas, in particular in districts hosting petrochemical activities and oil industry. Hence, the removal of fuel-based compounds from natural water is a compelling task due to their harmful effects both on the environment and human health, even at very low concentration. Hydrophobic zeolites are environmentally compatible materials, which have been employed as adsorbents for the removal of contaminants from water bodies. Due to their chemical-physical and structural features, zeolites represent fundamental adsorbents for the recovery of groundwater polluted by organic contaminants, such as chlorinated compounds and hydrocarbons. On the basis of the above statements, the combination of chromatographic, diffractometric and thermogravimetric techniques was employed to investigate the adsorptive-desorptive properties of hydrophobic synthetic zeolite as well as the temperature dependence of the desorption processes. Specifically, *in situ* HT synchrotron XRPD (time-resolved) was used as a tool to understand the features of organophilic ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 280$) when 1,2-DCE, TOL, and MTBE (both as single component as well as binary mixtures) are adsorbed and desorbed. The structural modifications of ZSM-5 zeolite were monitored through thermal treatment from room temperature to 600 °C. Moreover, the understanding of the competitive behaviour of adsorbed pollutants in binary mixture and/or in presence of humic acids and the adsorption capacity of the regenerated zeolites have been also tested. Finally, some regenerated samples have been tested in order to verify their adsorption capacity.

INTRODUCTION

Water contamination is increasing from the end of 20th century due to a very fast development of industries and of agricultural practices, as well as a badly conceived urbanization. Being frequently a recipient for these contaminants, the aquatic ecosystem and the water quality are seriously deteriorated and sometime hopelessly compromised. Today, less than 3% of water is truly usable for the human practices (Perego *et al.*, 2013). Often, recycled water and treated wastewater effluents deriving by malfunctioned wastewater treatment plants is discharged into the environment. This determines not only the contamination of surface water (lakes and rivers), but also of groundwater aquifers. For this reason, surface and groundwater pollution is considered a global emergency and the removal of hazardous organic compounds from the water bodies becomes a common objective. In particular, the presence of these chemicals at ultra-trace levels might cause the development of sub-lethal toxic effects in aquatic organisms (*i.e.*, reproductive and immune dysfunctions, neurological disorders) and in human health. The USGS defines these compounds as Emerging Organic Contaminants (EOCs), including any substance (natural or synthetic) which is present in the environment beyond ultra-trace levels and that could cause adverse ecological and human health effects. Kept in many things of everyday usage and resistant to natural degradation processes, these pollutants are continuously released into the environment where they can accumulate and persist over time provoking negative effects (Raghav *et al.*, 2013; Gavaskar *et al.*, 1995).

Emerging contaminants are normally divided into categories that describe their main features; among them, great attention has been paid on the removal of VOCs mostly derived from oil and gas exploration and production. The traditional wastewater treatments (vaporization, dilution, decomposition, and reactions to

sunlight action) designed to degrade or remove organic compounds or reduce the levels of their concentrations are not completely effective. In the recent years, new technologies which employ different types of materials were developed to support the traditional methods. In particular, adsorption technologies (based on the physical-adsorption process) and adsorbent materials have been shown to be an effective and eco-friendly alternative to remove chemicals from water.

MATERIALS AND METHODS

The materials used in this work are the following. On regard to organic molecules, toluene (TOL, purity 99.9%), methyl-tert-butyl-ether (MTBE, purity 99.8%), 1,2-dichloroethane (1,2-DCE, purity 99.8%), chlorobenzene (CB, purity 99.9%) caffeic acid (CA, purity 99.8%) and p-hydroxybenzaldehyde (p-HBA, purity 99.8%) were obtained from Sigma-Aldrich (Steinheim, Germany). The zeolite sample used in this study is a hydrophobic ZSM-5 (CBV28014, Zeolyst International) characterized by $\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 280$, Na_2O content $< 0.05\%$ w/w, NH_4^+ content $< 0.1\%$ w/w, and specific surface area of $400 \text{ m}^2\text{g}^{-1}$.

The concentration of contaminants in the aqueous solution was determined by Headspace Gas Chromatography coupled to Mass Spectrometry (HS-GC-MS). Adsorption isotherms were determined using the batch method. *In situ* high-temperature X-ray diffraction experiments were carried out at the high-resolution powder diffraction beamline ID22 at the European Synchrotron Radiation Facility, ESRF (Grenoble, France) from room temperature to $600 \text{ }^\circ\text{C}$. Measurements of XRPD patterns by conventional radiation at room temperature of both unloaded and loaded/reloaded samples were performed on a Bruker AXS D8 Advance diffractometer equipped with Si(Li) solid state detector (Sol-X). The experimental conditions were the following: Cu $K\alpha_{1,2}$ radiation ($\lambda = 1.54178 \text{ \AA}$), 2θ range $3\text{-}110^\circ$, step size 0.02° , time/step 12 s, scattering, divergence, and receiving slits 0.6, 0.6 and 0.1 mm, respectively. The changes of the crystal structure accompanying the mixture adsorption were investigated by performing Rietveld refinements using the EXPGUI interface (Toby, 2001), for General Structure Analysis System (GSAS; Larson & von Dreele, 2000). Besides, TG and DTA measurements of both the calcined and reloaded ZSM-5 samples were performed in air at up to $900 \text{ }^\circ\text{C}$ using a Netzsch STA 409 PC LUXX[®] - simultaneous TG/DTA thermogravimetric analyser operating at $5 \text{ }^\circ\text{C}/\text{min}$ heating rate under $50 \text{ ml}\cdot\text{min}$.

RESULTS AND DISCUSSION

In this work, an exhaustive picture on the adsorption and desorption both of single component as well as of binary mixture of VOCs within the ZSM-5 crystal lattice (*i.e.*, a microporous MFI material) was provided. By using the information gained from structural refinements as input of the isotherm modelling step it was possible to provide a physical description of the model. Four representative water contaminants, *i.e.*, 1,2-DCE, TOL, MTBE, and CB, were selected among VOCs molecules as samples to be tested.

Firstly, the adsorption from aqueous solutions of systems based on a single component as well as on binary mixtures was investigated by means of the batch adsorption method. Adsorption kinetics and adsorption isotherms provide an overview on the effectiveness of the VOCs adsorption within the ZSM-5 structure as well as an exhaustive picture on the VOCs dynamic adsorption.

Secondly, XRPD on the previously analysed powders was performed using both conventional and non-conventional X-ray radiations. These data, refined by means of the Rietveld method, corroborate those from adsorption techniques, and clearly reveal the incorporation of the investigated contaminants. In particular, structural refinements highlighted that, in all the examined cases, organic molecules were adsorbed into two independent crystallographic sites. These sites are located at the intersection (*i.e.*, of straight and sinusoidal channels) and within the sinusoidal channel, namely site 1 and site 2, respectively (Fig. 1, Pasti *et al.*, 2016). Besides, co-adsorbed water molecules were also detected. A small fraction of adsorbed water plays an important role in stabilizing the guest organic molecules within the zeolite host framework. The refined distances revealed

strong interactions between organic compound-water molecule complexes (clusters or short chains) and the framework oxygen atoms (Fig. 2, Martucci *et al.*, 2015). This evidence was also confirmed by the deformation of 10-ring tetrahedral channels opening after organics compound adsorption and explains the variation of lattice parameters.

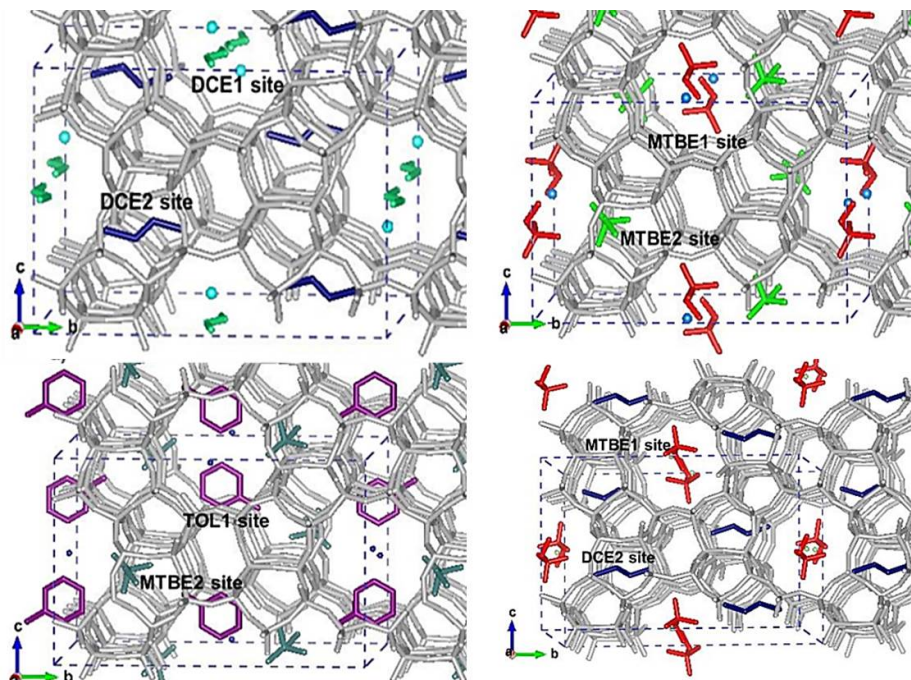


Fig. 1 - Modelled atoms of ZSM-5 loaded with VOCs. Adsorption sites are located at intersection and sinusoidal channel.

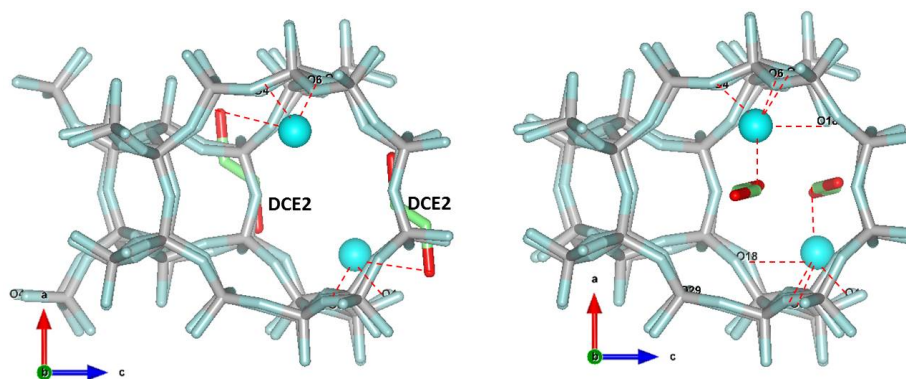


Fig. 2 - Location of 1,2-DCE and water molecules in ZSM-5 along [100] and [010] directions, respectively.

All these findings indicated that ZSM-5 is a flexible material able to efficiently adsorb fuel-based compounds in its internal channels system. This adsorption can be conceived as an irreversible adsorption at ambient conditions. However, it is possible to induce the desorption of the adsorbed species, and completely regenerate the exhausted (*i.e.*, loaded with organic contaminants) ZSM-5, by heating. To achieve a complete understanding of the regeneration process, the desorption dynamics that occur during the thermal treatment were also investigated.

The *in situ* HT XRPD, performed at the beamline ID22 (ESRF, Grenoble), was used in order to continuously monitor the pollutants desorption process as well as the structural modifications which the ZSM-5

undergoes upon thermal treatment. The evolution of a series of diffraction patterns as function of temperature shows the occurrence of a phase transition in each loaded samples (Fig. 3, Rodeghero *et al.*, 2017). In particular, it was observed that the phase transition temperature is function of the involved contaminant species. In all the examined samples, Rietveld refinements indicate that the ZSM-5 phase transition occurs within the 75-100 °C temperature range involving a symmetry change from monoclinic (space group $P2_1/n$) to orthorhombic ($Pnma$ or $P2_12_12_1$ space group).

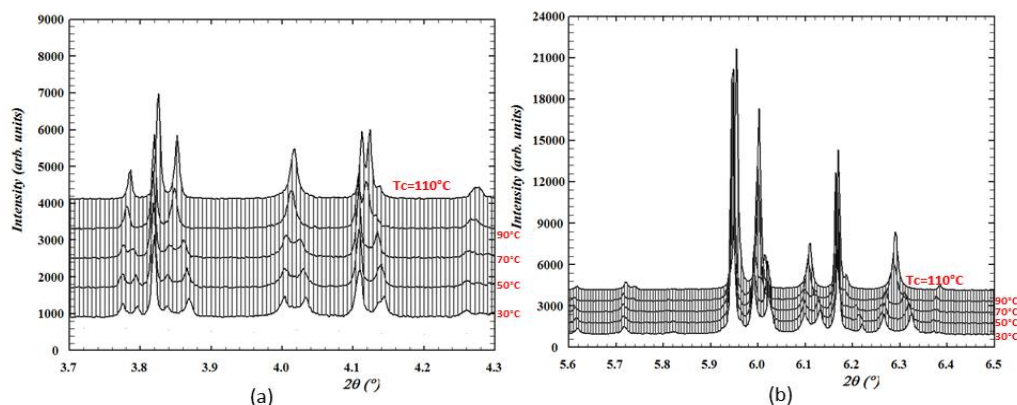


Fig. 3 - Evolution of ZSM-5-MTBE XRPD patterns close to the phase transition temperature.

After the adsorption of a single compound or binary mixtures, a careful inspection on the unit-cell parameters variation revealed that, up to 100 °C, the unit-cell volume slightly increased. At the same time, no changes were observed in the extra-framework site occupancies indicating that this transient framework expansion was related to the release of the oligomers-framework oxygens interactions. It is well known that, during the initial heating stages, a weakening of hydrogen bonding network occurs in the zeolite frameworks, and it can be explained as a “pore-mouth-breathing” motion. This motion is accompanied by a transient opening and regularization of the zeolite channels, and afterward by a contraction. For temperatures higher than 100 °C, and after each phase transition, the unit-cell volume decreases and the hosted organic molecules start to desorb. The expulsion process is accompanied by a diffusion of the host molecules through the zeolite channels system. As a general trend, it was observed that the site 1 (intersection site) was empty in the 250-300 °C temperature range. Differently, the molecules confined at site 2 (sinusoidal channel) showed a more scattered desorption process. Anyway, the maximum desorption temperature observed for site 2 was about 350 °C. In the case of a site 2 desorption temperature higher than that of site 1, a blocking effect can be invoked. Specifically, the species hosted at the sinusoidal channel (site 2) move more slowly than those adsorbed at the intersection (site 1). When a multi-component system (binary mixtures) is involved, the desorption temperature of organic molecules for both sites 1 and 2 can be inferred from that of a zeolite which hosts a single component.

Once regenerated (thermally treated), some of the investigated zeolite samples (*i.e.*, those with 1,2-DCE and TOL as single components) were tested again in order to verify whether these reactivated materials might be reused to remove emerging organic contaminants from wastewater. With this purpose, the regenerated samples of ZSM-5 were subjected to new VOCs adsorption cycles. The regenerated ZSM-5 reloaded with 1,2-DCE did not show any significant difference in the saturation capacity. Besides, the regenerated zeolite did not exhibited any crystallinity loss or deformations in the channel apertures, and possessed unit-cell parameters that can be almost overlapped with those of the fresh material. The refined occupancies obtained by the Rietveld method indicated that both location and content of 1,2-DCE molecules remained substantially unchanged. Hence, it is confirmed that, after regeneration, ZSM-5 is able to re-adsorb an amount of 1,2-DCE comparable to that previously adsorbed by the fresh material. The same behaviour was also observed when the regenerated ZSM-5

was reloaded with TOL (Fig. 4, Rodeghero *et al.*, 2016). These results highlight that ZSM-5 zeolite is a very promising adsorbent material with unchanged adsorption performances even after several adsorption/desorption cycles. The achieved deeper understanding of the adsorption/desorption behaviour of ZSM-5 is of great help in the optimization of water remediation technologies like PRBs using zeolites as “molecular sieve” adsorbing materials to remove fuels-based pollutants from water.

Additionally, the competitive aspect has been also evaluated. For example, the adsorption isotherms of CB and TOL as a single component in ZSM-5 show very similar trends.

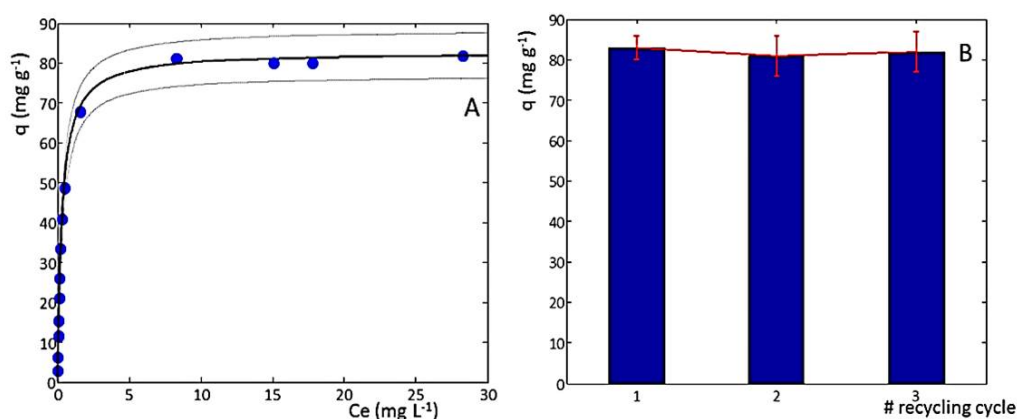


Fig. 4 - A) Isotherm for TOL adsorption onto ZSM-5; B) Pseudo second order kinetics constant vs. TOL saturation capacity on ZSM-5 after thermal regeneration.

The evaluation of their competitive behaviour when adsorbed as binary mixture (CB/TOL) revealed a very similar competitive Langmuir isotherm, meaning that both TOL and CB had similar saturation capacity and affinity for the ZSM-5 zeolite. On the contrary, a different behaviour emerged whether the adsorption isotherms of single components differ one from each other. In the specific case of binary mixtures formed by MTBE/1,2-DCE and MTBE/TOL, it was highlighted that, albeit both components were adsorbed, the loading of a second organic molecule tended to expel the first one adsorbed (Fig. 5, Pasti *et al.*, 2016).

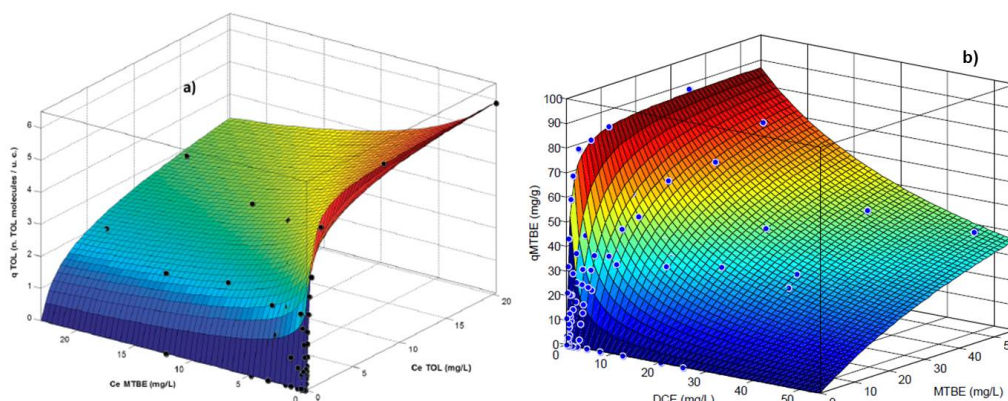


Fig. 5 - Surface fitting a) number of TOL adsorbed molecules per ZSM-5 unit cell vs. the equilibrium concentrations of TOL and MTBE in aqueous solution; b) number of MTBE adsorbed molecules per ZSM-5 unit cell vs. the equilibrium concentrations of TOL and MTBE in aqueous solution. The points represent the experimental data.

Since the Rietveld structural investigation provided information on the relative position of molecules inside the ZSM-5 structure, the adsorption data of equimolar binary mixtures were fitted to a Langmuir model based on the results obtained from these refinements. The short refined intermolecular distances among adsorption sites clearly prevents the simultaneous occupancy of one site by more than one component, when these compounds are adsorbed from binary mixtures. The complementary approach above described, *i.e.*, the integration of structural information with thermodynamic equilibrium data, allowed to obtain an excellent model to realistically describe the adsorption process and it was helpful in interpreting the adsorption mechanisms.

Finally, adsorption studies of VOCs were also performed to provide insights on the zeolite selectivity during removal processes. A competitive behaviour was observed when the mixture involves VOCs and humic monomers, *e.g.*, CA and p-HBA. Rietveld refinements indicated that humic monomers and VOCs occupied a similar position. Consequently, the VOCs adsorption capacities and/or adsorption kinetics could be reduced in the presence of these monomers. However, as demonstrated by adsorption isotherms, ZSM-5 zeolite adsorbs preferentially and selectively VOCs. For this reason, it can be assumed that ZSM-5 zeolite is suitable for the treatment of groundwater and wastewater also in presence of humic monomers.

CONCLUSION

In conclusion, in this work the combination of *in situ* HT synchrotron XRPD and chromatographic techniques was employed to explore the adsorption features of a ZSM-5 zeolite. In particular, it was observed that this material is characterized by very favourable adsorption kinetics as well as by a strong shape selectivity towards organic molecules. Moreover, this material can be efficiently regenerated at about 350 °C without any significant difference in the saturation capacity and without any significant crystallinity loss. Furthermore, the absence of humic substances interference has been demonstrated.

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