

"REVISION 3"

HIGHLIGHTING THE CAPABILITY OF ZEOLITES FOR AGRO-CHEMICALS CONTAMINANTS REMOVAL FROM AQUEOUS MATRIX:

EVIDENCES OF 2-ETHYL-6-METHYLANILINE ADSORPTION ON ZSM-12

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ABSTRACT

Chloroacetanilides and their degradation products are frequently detected in surface and subsurface water due to their relatively high water solubility and their high potential to leach and migrate through the soil and contaminate ground water.

In this study we explored for the first time the capability of ZSM-12 zeolite for 2-ethyl-6-methylaniline ($C_2H_5C_6H_3(CH_3)NH_2$, labelled EMA) removal from water by combining chromatographic, thermogravimetric and synchrotron X-ray powder diffractometric techniques.

Rietveld refinement revealed the incorporation of about 4 EMA molecules per unit cell, in very good agreement with the weight loss given by TG analyses and with the saturation capacity determined by the adsorption isotherms.

The formation of supramolecular complexes mediated by coadsorbed water and their strong interaction to framework oxygens confers stability to the pollutants in the zeolite cages. This prevents adsorbed molecules from desorbing as well as the entering of other competitive molecules. The rapid kinetics combined with the good adsorption capacity makes ZSM-12 a promising material to control and minimize water pollution from acetanilide compounds as well as other agro-chemicals contaminants.

KEYWORDS

2-ethyl-6-methylaniline adsorption, water pollution, ZSM-12, chromatography, thermogravimetry, synchrotron X-ray powder diffraction.

INTRODUCTION

The degradation of water resources is an increasing problem world-wide, and many efforts have been made to control point source pollution from homes and industry. However, water pollution from agriculture is becoming a major concern due to the widespread use of agro-chemicals in modern agriculture. Indeed, many of these substances have (Otero et al. 2012) harmful effects on aquatic organisms, insects and mammals and they persist in the aquatic systems for many years after their application (Shukla et al. 2006). In Europe, pesticides are considered hazardous substances as specified in current directives regarding water (Levitan 2000). The World Health Organization reported that ~3,000,000 cases of pesticide poisoning and 220,000 deaths occur in developing countries (World Health Organization 2010).

Drinking water quality standard should not exceed 1×10^6 ug/l for an individual pesticide concentration and 5×10^6 ug/l for the total pesticide concentration (EC, Directive 98/83/EC 1998). Due to the diffuse nature of contamination from agro-chemicals and the mobility of these compounds in the environment, their presence is difficult to control.

The pesticides are transferred from soil to water through various pathways (e.g. surface runoff, subsurface and groundwater flows) either in solution or adsorbed onto particles. (Boithias et al. 2011). Among the agro-chemicals mentioned above, Metolachlor ($C_{15}H_{22}ClNO_2$, 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide, labelled MTC) and its metabolites are frequently detected in surface and subsurface water (from 1×10^6 ug/l to more than 1×10^9 ug/l. (Traub-Eberhard et al. 1995; Gaynor et al. 1995) due to its relatively high water solubility (530 mg/l) which facilitates leaching, migrating through soil and contaminating ground water (Nennemann et al. 2001). Moreover, chloroacetanilide degradation products such as 2-ethyl-6-methylaniline ($C_2H_5C_6H_3(CH_3)NH_2$, labelled EMA) are more or equally toxic compared to their parent pesticide compound (Fava et al. 2000; Fava et al. 2001; Kimmel et al. 1986; Osano et al. 2002a; Osano et al. 2002b) and are promutagens in the Ames test (Kimmel et al. 1986). The rate and the extent of chloroacetanilide degradation strongly depend on environmental conditions such as temperature (Osano et al. 2003), moisture content (Gerstl et al. 1998), concentration of hydroxyl radicals (OH) (Webster et al. 1998) and microbial activity (Bollag et al. 1986; Liu et al. 1995; Stamper and Tuovinen 1998). Therefore, it is mandatory to develop mitigation measures able to prevent diffusion of pollutants into environment in order to reduce their impact (Zhang, and Zhang 2011). Many treatment strategies have been proposed for the removal of these pollutants, including biological, chemical and/or physical methods (Kovaivos et al. 2011, Bezbaruah et al. 2009; Zadaka et al. 2009; Liu et al. 2010; Coffinet et al. 2012; Elsayed et al. 2014).

Despite the availability of various clean up methods, adsorption by organic or inorganic sorbent media is still preferred due the high removal efficiency and reduced operational cost. Activated

charcoal, mesoporous phenolic resin and mesoporous carbon are characterized by high surface area and narrow mesopore distribution thus exhibiting good properties as adsorbents depending on their particle size, porosity, degree of carbonization and method of activation. (Jiang et al. 2006; Lopez-Ramon et al. 2007; Bakouri et al. 2009). Organoclays and organo/ layered double hydroxides have also been proven to be suitable in reducing and even preventing the environmental impact caused by some pesticides, particularly metolachlor (Reichle 1986; ; Rives 2001; Wang et al. 2005; Otero et al. 2012; Chaara et al. 2011; Si et al. 2009; Nennemann et al. 2001; Mastrocicco et al. 2009).

As an alternative, zeolites have been investigated for the removal of pesticides from water (De Smedt et al. 2015). These microporous materials represent a promising candidate for the environmentally friendly removal of agro-chemicals from water. The main advantages of zeolites are related to the structural and chemical features of their framework, which can be modulated by varying the pore opening and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (SAR). Typically, these materials have a large surface area, high specific capacity, and are characterized by high mechanical, biological and chemical stability and strong adsorption selectivity. In particular, it has been demonstrated that High Silica Zeolites (HSZs) show strong selectivity (Martucci et al. 2012a; Martucci et al. 2012b; Pasti et al. 2012; Arletti et al. 2012; Blasioli et al. 2014; Martucci et al. 2013; Kyzas et al. 2013; Vilaça et al. 2011; Rakić et al. 2013; Datt et al. 2012) and very fast kinetics in the adsorption of organic species. Moreover, their high stability in water and their resistance to aggressive chemical solutions make these materials a promising and efficient alternative to other reactive adsorbent media (Amorim et al. 2012; Datt et al. 2013; Gençand and Dogan 2015; Rossner et al. 2009; Damjanović et al. 2010; Pasti et al. 2013; Martucci et al. 2015; Martucci et al. 2014; Martucci et al. 2015; Martucci et al. 2013; Pasti et al. 2016; Rodeghero et al. 2017a; Rodeghero et al. 2017b; Leardini et al. 2014; Braschi et al. 2012; Sacchetto et al. 2013). Exhausted zeolites can be easily regenerated and reused thus preventing the disposal of contaminated materials. The most common regeneration techniques include thermal (Wang et al., 2006; Rodeghero et al. 2017a, 2017b; Leardini et al., 2014), chemical and extraction (Braschi et al., 2016; Wang et al., 2006; Jung et al.,

2004), electric/electrochemical (Zhang et al., 2013), photochemical (Litter and Quici, 2010; Braschi et al., 2016) treatments, as well as microwave (Polaert et al., 2010; Zendejdel et al., 2014) and ultrasound methods (Wang and Yang, 2007). Recently, the adsorption capacity of thermally regenerated zeolites was demonstrated to be very close to the initial loading capacity. This shows that the heating process does not affect the adsorption properties of regenerated samples (Leardini et al., 2014; Martucci et al., 2015b; Braschi et al., 2016). In the present work we explore for the first time the capability of ZSM-12 to remove contaminant metabolites from an aqueous matrix. For this purpose, EMA was chosen as target metabolite. ZSM-12 zeolite (MTW topology) was chosen as its channel system could be an attractive host to incorporate EMA. The structure of the ZSM-12 host is reported in Figure 1. The framework has a one-dimensional pore system delimited by 12 membered-rings (12MRs) (Baerlocher et al. 2007) $\{[010] 5.6 \times 6.0\text{\AA}\}$, which is slightly larger than that of MFI zeolites $\{[100] 5.1 \times 5.5 \leftrightarrow [010] 5.3 \times 5.6\}$. The regular one-dimensional nanochannel system imposes severe space restrictions and geometrical constraints on the guest species thus preventing inserted molecules from escaping and other competitive molecules from entering (Corma 1997; Rosinski et al. 1974; Trewella et al. 1985; Fyfe et al. 1988).

To date, this zeolite is used as an efficient catalyst for the shape selective conversion of long hydrocarbon molecules such as the isomerization and alkylation of aromatic hydrocarbons (Perego et al. 1996; Millini et al. 1998; Yoo et al. 2003; Pazzucconi et al. 2000; Bortolini et al. 2013). It has not yet been used as sorbent.

To assess the capability of ZSM-12 for removal of EMA from aqueous matrix, chromatographic, thermogravimetric and synchrotron X-ray powder diffractometric techniques were applied. In particular, to evaluate the structural basis for the EMA sorption, characterization by X-ray powder diffraction was carried out on the as-synthesized, the calcined and the EMA loaded – ZSM-12, respectively. The complexity of this host-guest system highlights the importance of understanding and controlling not only the interactions of guests with the host but also the interactions between guests and the influence of coadsorbed molecules. The results described here

provide the basis for understanding the fate and transport mechanisms of EMA in the environment and in particular in zeolite soil and water applications.

EXPERIMENTAL SECTION

2. Materials and Methods

Synthesis.

The hydrothermal ZSM-12 synthesis (SAR=38) was carried out following the protocol proposed by Millini et al. (2004) using NaOH, aluminium source $[\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}]$ and 6-azonia-spiro-[5,5]-undecane as structure directing agent (SDA). The bromide salt of SDA was dissolved in demineralized water and then exchanged into the hydroxide form by electro dialysis. The resulting solution was heated at 353 K and tetraethylortosilicate (TEOS, Aerosil 200) was gradually dropped into the solution under stirring. After aging at room temperature for 4 h, the mixture was filtered and washed with deionized water and dried overnight at 423 K. The solid product was then calcined by raising the temperature from room temperature to 600°C in 1 hour, then holding at 600°C for 4 hours. Finally, adsorbents were kept at room temperature for 3 hours. Air circulation was maintained during heating. The samples were kept in a desiccator and used within 2 days after thermal treatment.

Batch Adsorption.

The adsorption isotherm was determined using the batch method. Batch experiments were carried out in duplicate in 20 ml crimp top reaction glass flasks sealed with PTFE septa (Supelco, Bellefonte, PA, USA). The flasks were filled in order to have the minimum headspace and a solid/solution ratio of 1:2 ($\text{mg}:\text{ml}^{-1}$) was employed. After equilibration, for 24 hours at a temperature of 25.3 ± 0.5 °C under stirring, the solids were separated from the aqueous solution using centrifugation (14000 rpm for 30 min).

Chromatographic determinations of EMA before and after the contact with ZSM-12 were made on a Waters HPLC system (Waters Associates, Milford, Mass) equipped with a binary pump and a DAD UV–VIS detector. The column was a Kromasil Eternity 0.46 x 15 cm C18-packed, particle diameter 5 μm , (Eka Nobel). An injector (7725i, Rheodyne, Cotati, CA, USA) with a 20 μL loop was employed. The mobile phase was a mixture of water and ACN, 50:50% v/v. Solvents were filtered before use (Nylon 66 membranes, 0.45 μm , Supelco, Bellefonte, PA, USA). The concentration of EMA was determined by measuring UV absorbance and by interpolating values against previously constructed calibration curves.

Thermal analyses.

Thermal analyses (TG and DTA) of both calcined (ZSM-12-C) and EMA loaded – ZSM-12 (ZSM-12-EMA) were performed on a STA 409 PC LUXX® - Netzch. The measurements were carried out in air flow with a heating rate using a 10°C/min heating rate up to 900 °C.

2.4. X-ray Powder Diffraction Data Collection and Refinement Strategy

The XRD patterns of calcined ZSM-12 before and after EMA loading were collected at the MCX beamline of Elettra - Sincrotrone Trieste, (Italy) using a fixed wavelength of 0.827Å (Rebuffi et al. 2014) (Figure 2).

The powders were loaded and packed in a 0.5 mm boron capillary, mounted on a standard goniometric head, and spun during data collection. The diffraction patterns were recorded through a scintillation detector in the 3–50 2θ range. Structural refinements were performed by full profile Rietveld analysis using the GSAS package (Larson and Von Dreele 2004) with the EXPGUI interface (Toby 2001). The refinements of both ZSM-12-C and ZSM-12-EMA samples were performed in the $C2/c$ space group using the starting framework model reported in Fyfe et al. (1990). The background profiles were firstly edited manually and further empirically fitted using a Chebyshev polynomial with 26 variable coefficients. The Bragg peak profile was modeled using a

pseudo-Voigt function with 0.01% cut-off peak intensity. The scale factor, 2 θ -zero shift, and unit-cell parameters were accurately refined. Table 1 reports the refinement parameters for all samples investigated. The extra-framework sites were located by difference Fourier maps and H-atoms were not considered within the structure refinement due to their low scattering factors. The thermal displacement parameters were constrained in the following way: the same value for all the tetrahedral atoms, a second value for all the framework oxygen atoms, a third one for the extraframework atoms. Soft restraints were applied on the tetrahedral cations and coordinated framework oxygen atom distances during the first stages of refinement, and left free in the last cycles.. Selected bond angles are listed in Table 2. The detailed structural refinements of both calcined and EMA loaded ZSM-12 are described separately in the following section.

RESULTS AND DISCUSSION

Adsorption from aqueous solutions

The data obtained from batch experiments at room temperature were fitted to the Langmuir isotherm model (Foo and Hameed 2010). Figure 3 shows the adsorption isotherm of EMA on zeolite ZSM-12: it can be observed that the adsorption isotherm is concave, and it is characterized by a steep initial zone and a saturation zone (plateau adsorbed concentration). The concave shape of the adsorption isotherm indicates a favourable adsorption and therefore a practical applicability of ZSM-12 in adsorption based technologies. The Langmuir model describes an adsorption process on a homogenous surface, and it does not take into account adsorbate-adsorbate interactions, and adsorbate-solvent interactions. Furthermore, the model represents an adsorbent characterized by energetically equivalent sites. This hypothesis can, at least in first approximation, be satisfied by considering that the interaction energies of different sites are close enough to each other to be equivalent to a single site characterized by an adsorption energy and adsorption constant

corresponding to the average values of those of all adsorption sites on the adsorbent material (Ruthven 1984). This model has been applied to describe the adsorption on different zeolites of many organic compounds both from gas and liquid phases (Rodeghero et al. 2017a, 2017b; Rodeghero et al. 2016; Perego et al. 2013; Leardini et al. 2014).

Table 3 summarizes the adsorption values obtained from the adsorption of EMA on ZSM-12. The high determination coefficient confirms that the Langmuir model represents the data well, and therefore, that EMA molecules adsorb on sites of zeolite having similar energy values. This finding, however, is not sufficient to assess which sites of the framework are participating in the adsorption process. The estimated saturation capacity of ZSM-12 is lower than that found for S-Metolachlor on organosilicas, (Kumar et al. 2013, Otero et al. 2014, Lopez et al. 2015). However, the adsorption onto ZSM-12 seems to be more favourable than that on organosilica in the low concentration range, which is more similar to environmental conditions. (Otero et al. 2013). Additionally, the saturation capacity (see Table 3) of EMA on ZSM-12 is higher than that reported for Metolachlor onto activated carbons (Kumar et al. 2013). Therefore, ZSM-12 seems to be a promising adsorbent material for the removal of pesticide metabolites from an aqueous matrix. To gain more information on the ZSM-12 sites involved in the adsorption process, a structural analysis was performed.

Thermal and structural analyses

To better understand the ZSM-12 finding, the structure of the sample after calcination (ZSM-12-C) was refined starting from the structural model reported by Fyfe et al. (1990) taken from the International Zeolite Association (IZA) website (calcined ZSM-12, MTW framework). A monoclinic unit cell with space group $C 2/c$ was used with the initial unit cell dimensions of $a = 24.8633(3) \text{ \AA}$, $b = 5.01238(7) \text{ \AA}$, $c = 24.3275(7) \text{ \AA}$, $\beta = 107.7215(6)^\circ$, cell formula units $Z=1$ (Figure 4a). Our refinement is in good agreement with others (Brouwer 2008; Fyfe and Brouwer 2006; Kasunič et al. 2009). Figure 4b shows TG/DTG/DTA curves of the title compound. The first weight

loss (as well as endothermic peak in DTA) from room temperature to about 105°C can be related to the desorption of physically adsorbed water from the surface (~1.8% dry wet/wet). The residual one (~3.0% dry wet/wet) comprises the desorption of carbonaceous residue from SDA calcination escaping from the micropores.

In both calcined ZSM-12 and EMA loaded ZSM-12, the absence of additional diffraction peaks as well as of C-centering forbidden peaks indicates that the space group does not change after adsorption. The *C2/c* space group was maintained in ZSM-12-EMA structure refinement, which was performed starting from the framework atomic coordinates obtained for ZSM12-C. Notwithstanding this, the position of diffraction peaks (and consequently, the unit cell parameters) in the two patterns are not remarkably modified ($a = 24.9984(11)$ $b = 5.03362(14)$ $c = 24.3844(8)$ $\beta = 107.9428(26)$ Cell volume = 2919.12(19) in ZSM-12-C; $a = 24.993(7)$ $b = 5.0341(9)$ $c = 24.377(5)$ $\beta = 107.879(18)$ Cell volume = 2918.9(12) in ZSM-12-EMA, respectively). The difference electron density map revealed an electron cloud in the ZSM-12 channels whose molecular geometry is very close to the EMA ideal one. It reveals the presence of seven partially occupied extra-framework sites (C1, C2, C3, C4, C5, C6 and N, respectively), localized inside the 12MR (Figure 5a) fitting the 12-ring aperture very well (Figure 5a). Reasonable values for C-C-C, N-C-C angles were obtained without using the rigid model approach (Table 2).

The refined distances of EMA from the framework oxygen atoms suggest that the organic molecules interact with the framework (i.e. N-O9 3.01(1) Å, N-O11 3.16(1) Å, C4-O6 2.87(1) Å, C6-O6 3.15(1) and 2.51(1) Å respectively) and this interactions are mediated by another extraframework site detected in the Difference Fourier map which was assigned to co-adsorbed water (W-O9 2.53(1) Å, W-O11(1) 2.67 Å, W-O6 2.99(1) Å, W-N 2.82(1) Å). Furthermore, the occupancy of EMA and water atoms refined to 4.0 (14% in dry weight) and 4.5 molecules (2% in dry weight) per unit cell, which correlates well with the weight loss observed by thermogravimetric

analysis. Figure 5b shows the TG/DTG/DTA curves of the loaded sample. Also in this case the first weight loss (as well as endothermic peak in DTA) from room temperature to about 105°C can be related to the desorption of physically adsorbed water/EMA from the surface (~3.0% dry wet/wet). The residual one (~17.0.0% dry wet/wet) comprises the desorption of extraframework species (EMA and water molecules) from within the channels.

Water molecules interact with both the NH₂- and methyl groups of EMA thus forming oligomers bonded to framework oxygens (Figure 7). The occurrence of such molecular complexes was also detected in hydrophobic zeolites loaded with non-polar species (Pasti et al. 2012; Martucci et al. 2012; Arletti et al. 2012; Leardini et al. 2014; Martucci et al. 2015; Rodeghero et al. 2017; 2017b). They “immobilize” the pollutants in the cages thus preventing inserted molecules from desorbing as well as the entering of other competitive molecules.

After EMA adsorption, the analysis of rings was useful to calculate pore diameter variations in ZSM-12. As reported by Bermúdez and Sastre (2017) “*Pores differ from rings in that pores are those rings which define channels; thus, ‘pores’ are a subgroup of ‘rings’.*” In this work the ring diameters have been calculated considering the distance between two opposite oxygen atoms and then subtracting twice the IZA recommended value of the oxygen radius (1.35 Å). This information is crucial for a deep knowledge of both transport properties as well as zeolite–adsorbate and adsorbate–adsorbate interactions (Bermúdez and Sastre 2017; Foster et al. 2006; Curtis and Deem 2003; Haldoupis et al. 2011; Krishna and van Baten 2012).

The ZSM-12-EMA diameters of 12-rings become larger and circular with respect to the ZSM-12-C ones and the Crystallographic Free Areas (C.F.A.) of the rings undergo a marked increase to best fit the organic molecule in the 12-ring aperture (Figure 6).

IMPLICATIONS

The increased awareness of soils, water and ground water contamination by chloroacetanilide herbicides has pushed research towards economically feasible and environmentally friendly remediation technologies. Adsorption is a simple and economic procedure involved in the water treatment which is able to control the mobility, fate, bioavailability and reactivity of emerging organic pollutants in the environment. Zeolites show high surface area, high specific capacity, mechanical, biological/chemical stability and high adsorption selectivity thus representing economically feasible and environmentally friendly adsorbent media capable of removing these pollutants from water.

In this work the efficiency of ZSM-12 zeolite for agro-chemicals contaminant (2-ethyl-6-methylaniline, EMA) removal from aqueous matrix was highlighted by chromatographic, thermogravimetric and synchrotron X-ray powder diffractometric techniques.

We have herein demonstrated that synthetic ZSM-12 is a good candidate for pesticide metabolite EMA removal. Indeed, its adsorption isotherm follows a Langmuir model, and shows a favourable adsorption. In addition, the saturation capacity of ZSM-12 is higher than that of other widely employed adsorbent materials such as activated carbon and mesoporous organosilica. Indeed, the saturation capacity of granular activated was found to be equal to 3.3 mg g^{-1} (Kumar et al. 2013). On the other hand, in mesoporous organosilicas, which show very high saturation capacity (500 mg g^{-1}) the adsorption quantities on these materials do not exceed 50 mg g^{-1} with solution concentration lower than 30 mg L^{-1} . Thus indicates a lower adsorption efficiency in concentration ranges similar to natural conditions (Otero et al. 2013). The organic molecules are effectively embedded in the zeolite framework as demonstrated from structural analysis. EMA interacts with water molecules to form oligomers which, in turn, interact with framework atoms. The formation of these supramolecular complexes stabilizes the pollutants in the zeolite cages thus preventing adsorbed molecules from desorbing as well as the entering of other competitive molecules. All these findings

contribute to assess that ZSM-12 could be a promising materials to control and minimize water pollution from EMA as well as other agro-chemicals contaminants.

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FIGURE CAPTURES

Figure 1. ZSM-12 (MTW topology) one-dimensional pore system view along [010].

Figure 2. Representative Rietveld refined pattern for ZSM-12-c (a) and ZSM-12-EMA (b) respectively. Observed (crosses), calculated (green line), Bragg diffraction peaks (vertical bars) and the difference profile (violet line) obtained by GSAS evaluation program Figure 3. Adsorption isotherms of EMA on ZSM-12 at 298.5 K.

Figure 4. ZSM-12-C (a) and ZSM-12-EMA (b) TG/DTG/DTA curves.

Figure 5. ZSM-12-EMA structure view along [010].

Figure 6. Experimental diameters of 12-rings in four ZSM-12-C and ZSM-12-EMA, respectively.

Figure 7. Interactions of water molecules-EMA oligomers with framework oxygens.

FIGURE 1

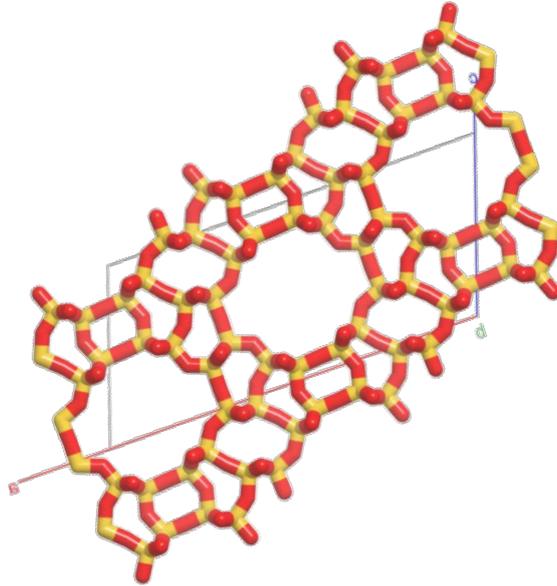


FIGURE 2

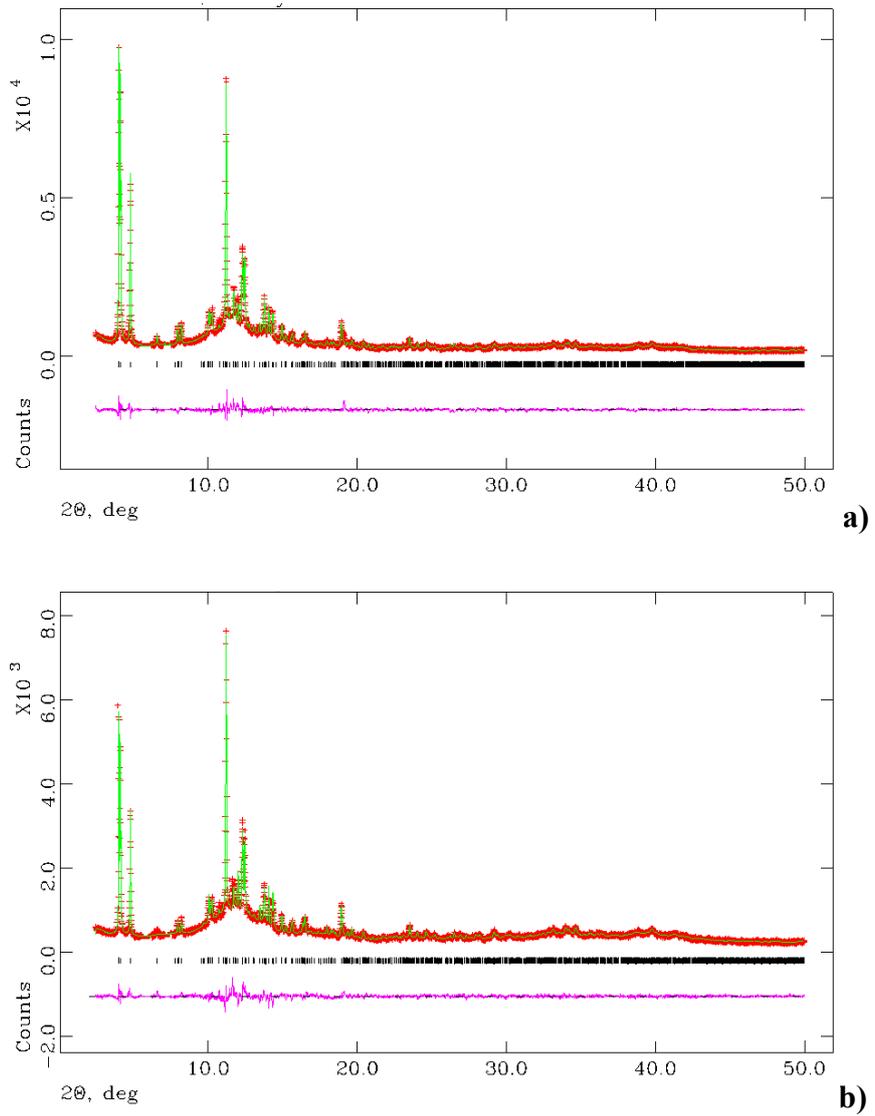


FIGURE 3

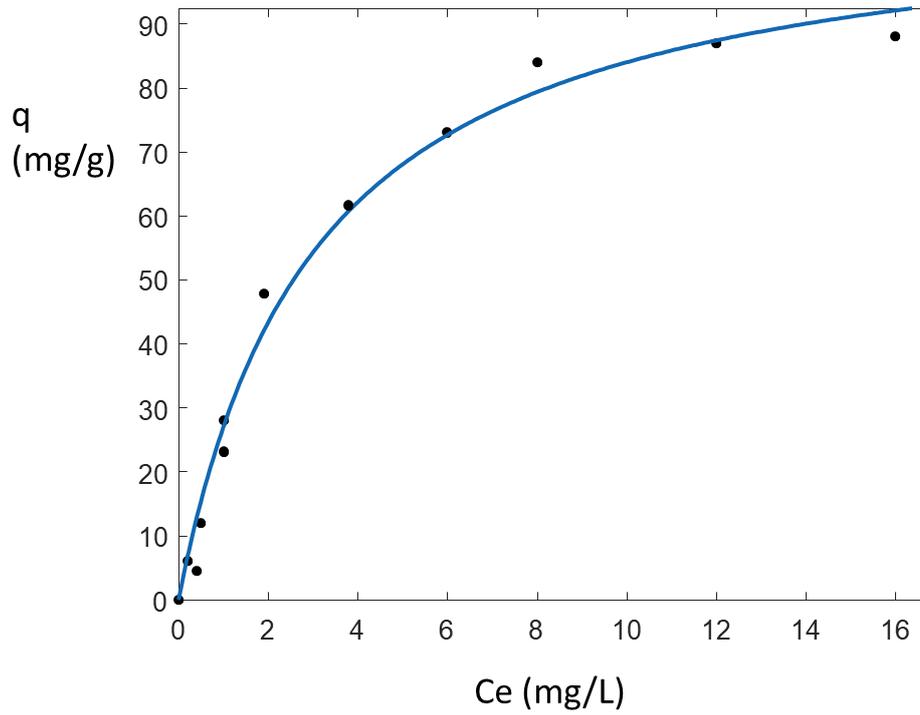


FIGURE 4

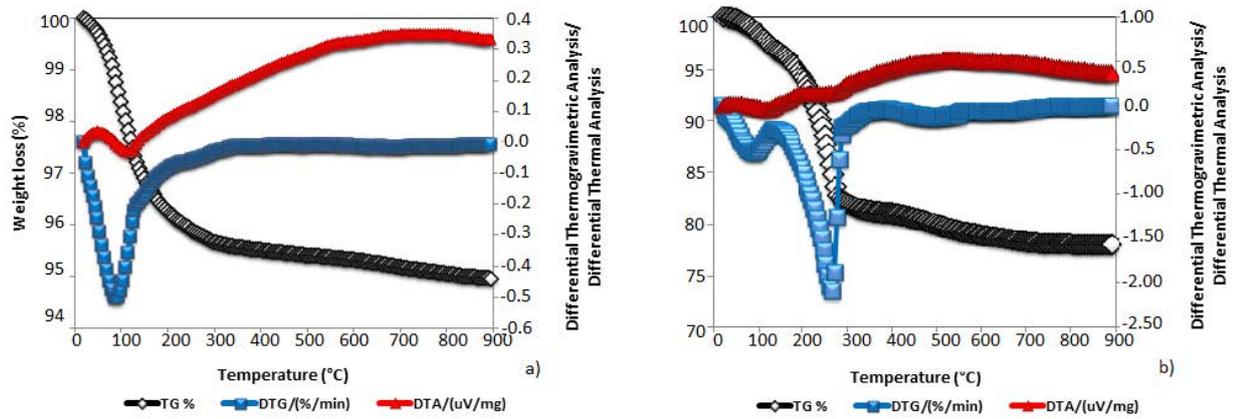


FIGURE 5

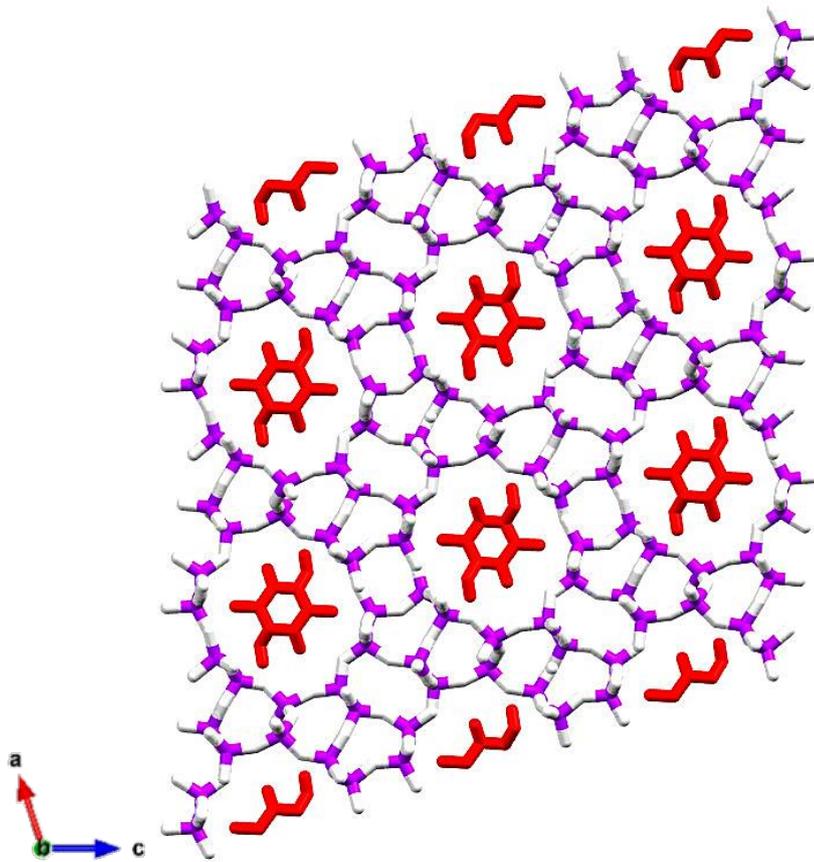
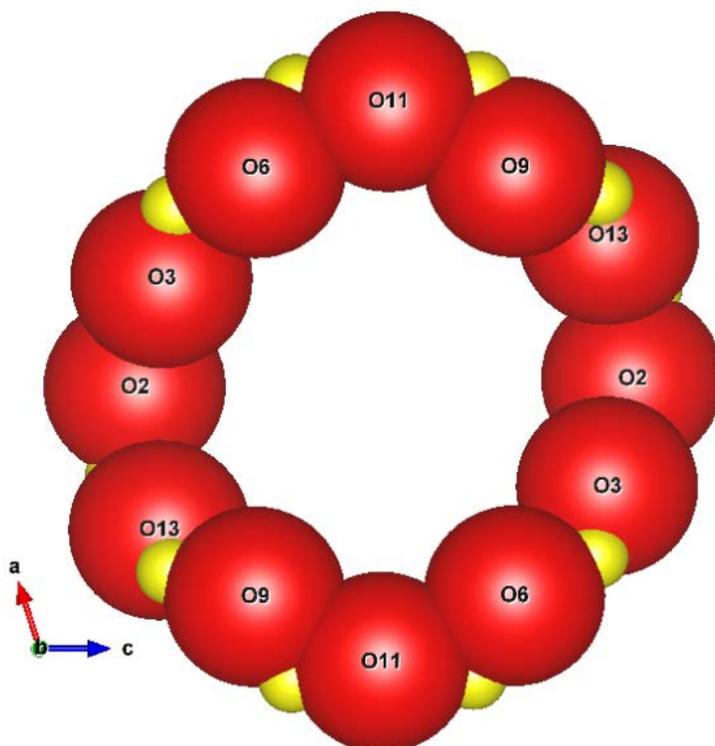


FIGURE 6



ZSM-12-C	Distance (Å)	Free Diameter (Å)
O11-O11	9.297	6.597
O6-O6	8.022	5.322
O3-O3	8.534	5.834
O2-O2	8.134	5.434
O9-O9	8.863	5.737
CFA (Å ²)= πr^2	r=mean radius=2.892	26.269
ELLIPTICITY (ϵ)	$\epsilon=(O11-O11)/(O2-O2)$	1.159
ZSM-12-EMA	Distance (Å)	Free Diameter (Å)
O11-O11	9.915	7.215
O6-O6	8.822	6.122
O3-O3	8.645	5.945
O2-O2	8.733	6.033
O9-O9	8.863	6.163
CFA (Å ²)= πr^2	r=mean radius=3.147	31.113
ELLIPTICITY (ϵ)	$\epsilon=(O11-O11)/(O3-O3)$	1.147

FIGURE 7

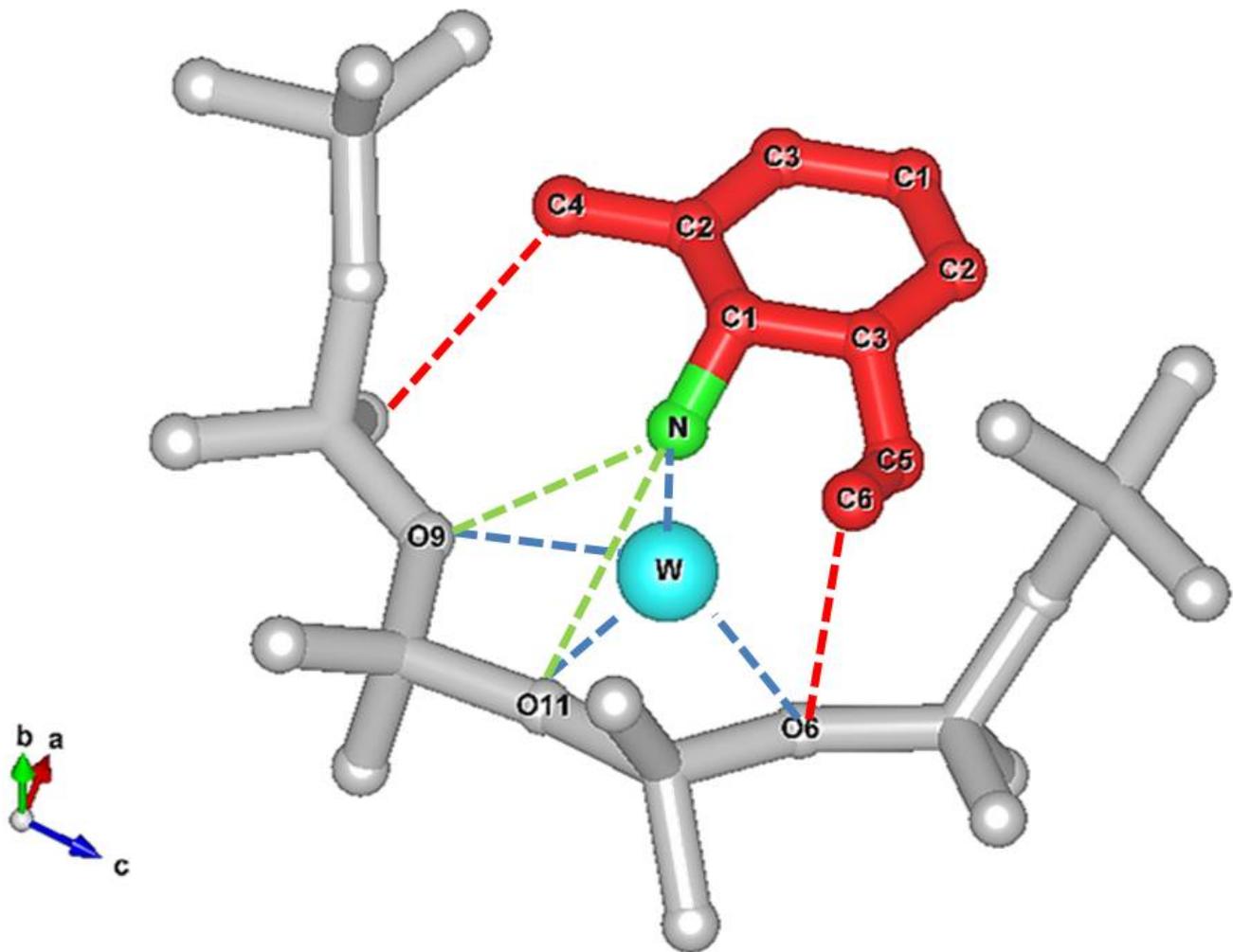


Table 1. Crystal data and refinement parameters for ZSM-12-C and ZSM-12-EMA, respectively.

	ZSM-12-C	ZSM-12-EMA
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	24.9984(11)	29.993(7)
<i>b</i> (Å)	5.0336(1)	5.0341(9)
<i>c</i> (Å)	24.3844(8)	24.377(5)
β	107.9(1)	107.9(2)
<i>V</i> (Å ³)	2919.1(2)	2918.9(2)
Incident radiation wavelength (Å)	0.82700	0.82700
Refined pattern 2θ range (°)	3.00-50.00	3.00-50.00
<i>R</i> _{wp} (%)	7.40	7.71
<i>R</i> _p (%)	6.00	6.05
<i>R</i> ² (%)	9.10	11.30
N. of contributing reflections	1889	1797
<i>N</i> _{obs}	9312	9357
<i>N</i> _{var}	101	152

Table 2 Selected angles (°) of 2-ethyl-6-methylaniline in ZSM-12-EMA.

ZSM-12-EMA	Angle(°)
C2-C1-C3	121.2(1)
C2-C1-N	119.7(1)
C3-C1-N	108.2(1)
C1-C2-C3	119.5(1)
C1-C2-C4	122.3(1)
C3-C2-C4	118.2(1)
C1-C3-C2	119.3(1)
C1-C3-C5	111.6(1)
C2-C3-C5	117.2(1)
C3-C5-C6	114.7(1)

Table 3: Estimated parameter for Langmuir model ($q = \frac{q_s b c}{1 + b c}$); in parenthesis are reported the confidence bonds at 95% of probability.

q_s (mg/g)	b (g/L)	R²
109.7 (97.65, 121.8)	0.326 (0.2179, 0.4341)	0.9869