



# Highly dealuminated Y zeolite as efficient adsorbent for the hydrophobic fraction from wastewater treatment plants effluents

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## ABSTRACT

In this work we report that highly dealuminated zeolite Y is a hydrophobic material that is able to remove selectively fatty acids and hydrocarbon compounds from the effluent of an urban wastewater treatment plant (UWTP). This adsorbent capability of zeolite Y could lead to an improved quality of UWTP effluents. Typical domestic wastewaters contain detergents, soaps and surfactants that are only partially removed in conventional UWTP. In the present work using an effluent from a UWTP located at Ribarroja del Turia (Valencia, Spain) containing 10 ppm of total organic carbon, we have been able to retain by adsorption on the dealuminated Y zeolite up to 16 and 60% of the organic matter of the effluent at pH values 7.2 and 4, respectively. Characterization of the adsorbed organic matter by Fourier transformed infrared (FT-IR), <sup>1</sup>H NMR and GC-MS after derivatization has shown that the zeolite adsorbs selectively the hydrophobic compounds of the effluent.

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## 1. Introduction

Freshwater is a precious natural resource that is increasingly limiting economic development in many geographical areas [1]. In order to minimize the environmental impact of urban wastewater and at the same time to make possible its reuse for agricultural irrigation, it is mandatory to devise more efficient and safe urban wastewater treatments [2,3]. Up to now most of the urban wastewater treatments are based on primary sedimentation and microbiological decontamination combined sometimes with tertiary processes [4]. The current technologies for urban wastewater processing are still far from being completely satisfactory and the total organic carbon (TOC) of the effluents after wastewater treatment is still much higher than the typical values from fresh natural waters [5,6].

Among the type of chemical compounds widely present in urban wastewater effluents [5,7], those having a long alkyl chains are very common since there are used in soaps and detergents [8–10]. These types of amphiphilic organic compounds can go through the wastewater treatment plant without undergoing a complete elimination and will form part of the organic matter present in the effluents of urban wastewater treatment plant (UWTP) [11–13].

In the present paper we describe that dealuminated large pore Y zeolites can be very efficient adsorbents for removing fatty compounds from the effluents of conventional UWTPs. Zeolites are

microporous aluminosilicates with a large surface area that have been widely used as gas adsorbents and ionic exchangers [14–16]. In contrast although zeolites have been used to adsorb organic molecules in organic solvents [17], the use as adsorbent in aqueous solutions has been comparatively much less employed. Typically the most widely used low cost adsorbents for organics in water are activated carbon, natural clays and organic resins [18]. The aim of the present work is to provide a comparison of the adsorption of fatty acids in dealuminated zeolite with polymeric fractioning resin typically proposed for removal of hydrophobic organic matter from water. It has found that dealuminated zeolites are significantly more efficient for this task than the polymeric resins.

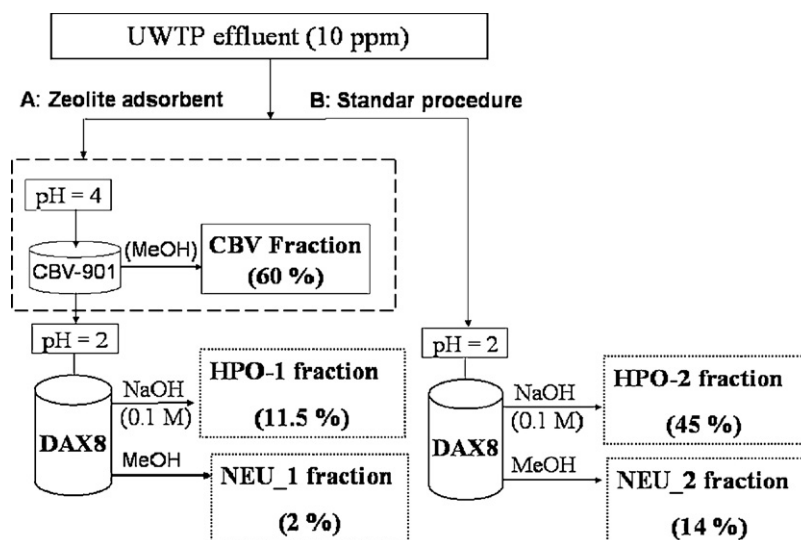
## 2. Experimental

### 2.1. Materials

The adsorbents used in the present study are two commercially available zeolite Y (CBV-901 from Zeolyst International and CBV-100 from PQ Industries) with a framework SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 80 and 5.1 for CBV-901 and CBV-100, respectively. The total surface area of CBV-901 and CBV-100 is 700 and 900 m<sup>2</sup>/g, respectively. The unit cell formula for the CBV-901 and CBV-100 is Na<sub>2.1</sub>[Al<sub>4.78</sub>Si<sub>191</sub>]·H<sub>2</sub>O and Na<sub>55</sub>[Al<sub>55</sub>Si<sub>139</sub>]·H<sub>2</sub>O. Prior to its use the zeolite was calcined at 550 °C for 12 h.

Isothermal vapour adsorptions were carried out after careful dehydration of CBV-901 at 400 °C under 10<sup>−2</sup> Torr for 5 h using a Micromeritics ASAP 2000 apparatus.

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**Scheme 1.** Experimental procedure for fractionating hydrophobic organic compounds and names and origin of the different fractions under study. The numbers in brackets below the fraction code indicates the percentage of the initial dissolved organic matter (DOM) present in the effluent that represents this fraction. The CBV fraction corresponds to the highest percentage of the effluent DOM. The terms HPO and NEU stand for hydrophobic and neutral fractions.

DAX8 resin as beads was supplied by Supelco. DAX8 is an acrylic ester-based polymer with a specific surface area of  $160 \text{ m}^2/\text{g}$  and a pore size of  $225 \text{ \AA}$ . The molecular formula of DAX8 is  $[\text{C}_3\text{H}_4\text{O}_2]_n$ . The resin was exhaustively washed according to the standard method [19], until the resin did not leach detectable organic matter.

All the solvents were of HPLC analytical grade. N,O-bis(trimethylsilyl)trifluoroacetamide with 10% of trimethylchlorosilane (BSTFA + 10% TMCS) was supplied by Sigma–Aldrich.

## 2.2. Sampling

For the present study effluents from a UWTP located at Ribarroja del Turia (Valencia, Spain) have been used. This UWTP serves to the towns of the Comarca del Turia (Eliana, Ribarroja del Turia and Villamarchante) zone with a population of 70,732 inhabitants and the incoming water is almost exclusively domestic wastewater, with minor inlets from industrial or agricultural origin. The main treatment process of the plant is microbiological degradation (prolonged aeration). TOC at the entrance and at the exit of the plant is 100 and 10 ppm, respectively. The total inorganic carbon (TIC) content at the entrance and exit of the UWTP is 94 and 81 ppm, respectively. The free pH of the effluent was 7.2 units. Other quality parameter data are summarized in Table S1 in supplementary material.

## 2.3. Adsorption experiments

First, the water from the UWTP was filtered through a  $0.45 \text{ }\mu\text{m}$  filter in order to remove suspended particles.

Adsorption experiments to determine TOC and TIC reduction by zeolite CBV-901 were carried out stirring magnetically a suspension of the zeolite powder (12 g) in a volume of 2 L of the UWTP effluent. Experiments to determine the maximum TOC removal were carried out using different amounts of zeolite CBV-901 (0.6, 1.2, 1.8 and  $2.6 \text{ g/L}$ ) in 200 mL of the effluent of the UWTP. The series of adsorption experiments to determine the influence of pH on the adsorption capacity of the zeolite was performed at the free pH of the effluent (7.2) and a pH 4 and 5. These acid pH values were achieved using HCl (0.1N). Adsorption kinetics were carried out at  $20 \text{ }^\circ\text{C}$  by analysing periodically aliquots from the suspension. Before measuring TOC and TIC values, the sample at the required time was

filtered through  $0.45 \text{ }\mu\text{m}$  nylon filter in order to remove the zeolite and stop the adsorption.

Fractioning of hydrophobic organic compounds was carried out using zeolite CBV-901 followed by DAX8 resin (procedure A) or DAX8 resin alone (procedure B) as indicated in Scheme 1. Fractioning using zeolite was performed by stirring magnetically at room temperature for 2 h at pH 4 a suspension of zeolite powder ( $12 \text{ g/L}$ ) in 2 L of UWTP effluent. After the adsorption the zeolite was extracted with methanol (MeOH, 200 mL) by stirring magnetically the suspension for 1 h. The MeOH solution was filtered, the solution dried under reduced pressure and the resulting residue analyzed by  $^1\text{H}$  NMR and Fourier transformed infrared (FT-IR) spectroscopy. The supernatant coming from the UWTP effluent after treatment with CBV-901 zeolite was acidified at pH 2 with HCl (0.1 M) and flushed through a column containing DAX8 resin (250 g) at a flow rate of  $1 \text{ mL/min}$ . The adsorbate on DAX8 resin was recovered by flowing through the column a 0.1 M aqueous NaOH solution. Concentration of the basic NaOH eluate under reduced pressure gives a hydrophobic fraction denoted as HPO that was also analyzed by  $^1\text{H}$  NMR and FT-IR spectroscopy. Finally, the DAX8 column was extracted with MeOH (500 mL,  $3 \text{ mL/min}$ ) yielding a fraction denoted as NEU that was also concentrated and analyzed by  $^1\text{H}$  NMR and FT-IR. Scheme 1 summarizes the names and origin of the fractions that have been analyzed in the present study.

## 2.4. Total organic (TOC) and inorganic (TIC) carbon analysis

TOC and TIC were analyzed using a High-TOC Elementar II. The determination was based on the Pt-catalyzed combustion of organic matter in water at  $950 \text{ }^\circ\text{C}$  and IR detection and quantification of  $\text{CO}_2$ . TIC was analyzed by automatic addition of HCl excess to the water and quantification of the total evolved  $\text{CO}_2$  by IR detection.

## 2.5. Spectroscopic techniques

Liquid state  $^1\text{H}$  NMR spectra of the samples were recorded in deuterated methanol on a Varian Gemini 3000, 300 MHz, using  $\text{CH}_3\text{OH}$  as reference.

FT-IR spectra were recorded for ambient equilibrated samples using a Jasco FT-IR-460 PLUS spectrophotometer. Each fraction was

mixed in a mortar with anhydrous KBr powder and the resulting solid mixture pressed to 10 ton for 5 min to obtain a pellet. Prior to record the FT-IR spectra the samples were dried at 50 °C for 24 h.

### 2.6. Derivatization and GC–MS analysis

The three fractions obtained from CBV-901 (CBV) and DAX8 (HPO and NEU) after concentration were silylated as previously reported [20]. Briefly, the fractions were acidified to pH 2 with HCl (0.1 M) and concentrated at 40 °C. Then, the fractions were suspended in BSTFA containing 10% TMCS and the solution stirred at 80 °C for 8 h. The resulting silylated mixture was dissolved in anhydrous acetonitrile, filtered through a 0.45 µm membrane, and injected in a GC–MS (Hewlett Packard HP6890 Chromatograph and quadrupole mass detector Agilent 5973). The capillary column (30 m) contains crosslinked (5%) phenylmethylsilicone (HP-5MS) as stationary phase. He was used as a carrier gas (1.2 mL/min). The injection volume was 1 µL. The injection and detector temperatures were 250 and 280 °C, respectively. The oven temperature program starts at 50 °C for 3 min, then it increases at a rate of 8 °C/min up to 90 °C, maintains this temperature for 2 min, and subsequently rises again at a rate of 15 °C/min up to 280 °C for 10 min.

Product identification was done based on the mass spectra of the silylated derivative present in the reaction mixture by comparing with the library data NIST98. Quantification was made using nitrobenzene as external standard.

## 3. Results and discussion

In the case of the UWTP of Ribarroja the TOC content at the entrance and at the exit of the plant is in average 100 and 10 ppm, respectively. The effluent of this plant goes into the river Turia that has a TOC content of 1.5 ppm. Therefore the organic content of the UWTP is about six times higher than that of the river freshwater. It would be more convenient from the environmental point of view if the organic content of the UWTP effluent is further reduced by implementing an additional polishing treatment. In the context to improve the quality, it is known that effluents from UWTP contain a significant percentage of amphiphilic organic compounds used as domestic detergents and surfactants [21]. These compounds are significantly hydrophobic due to the presence of long alkyl chains [22,23]. The aim of the present work is to show that highly dealuminated zeolites are good adsorbents for this type of organic compounds having fatty chains. To prove the suitability of dealuminated zeolites as adsorbent of these compounds, we have selected a commercially available Y zeolite having a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 80. In the zeolite literature it is well documented that a decrease in the framework aluminium content decreases the hydrophilicity of the internal voids increasing their adsorption capacity towards hydrophobic compounds [24,25]. Due to the similar ionic radius between Si<sup>4+</sup> and Al<sup>3+</sup> the latter metal ion can replace isomorphically silicon in the zeolite lattice [14,15]. However, each time that Al<sup>3+</sup> replaces a Si<sup>4+</sup>, a negative charge is introduced in the framework that requires the presence of a charge balancing cation in the micropores. Therefore, as consequence of the presence of framework aluminium there is an increase of the affinity of the zeolite pores for water. When zeolites are synthesized, particularly zeolite Y, a certain amount of aluminium is required in the synthesis, since otherwise the zeolite does not crystallize. The dealuminated Y zeolite used in the work is obtained by post-synthetic treatment starting from an as-synthesized zeolite Y (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 5.1) that was treated with steam to produce the migration of the aluminium to extraframework positions followed by exhaustive washing. To prove the hydrophobicity of CBV-901 we have performed a series of adsorption isotherms comparing the relative adsorption capacity

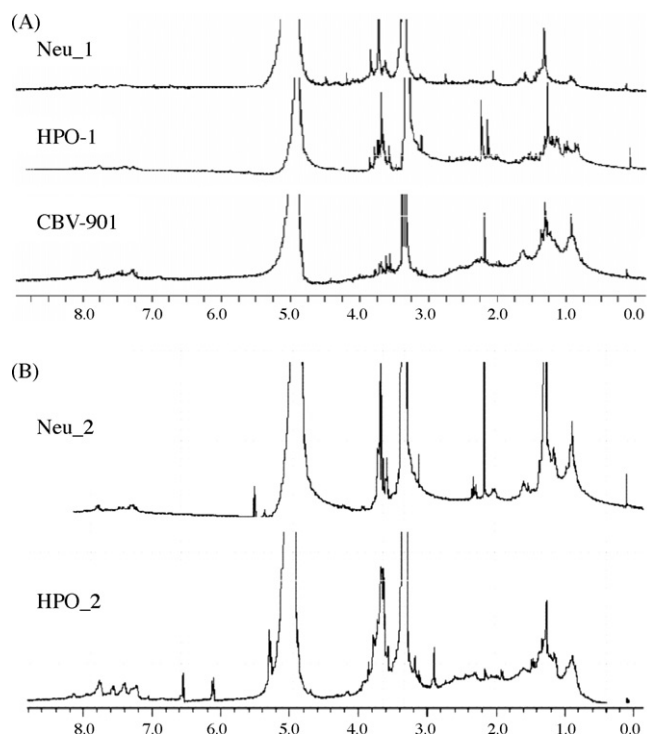
for water and cyclohexane for zeolite CBV-901 to show its preferential adsorption for the apolar cyclohexane with respect to polar water.

The adsorption isotherms for water (see Fig. S1, in supplementary material) show that CBV-901 adsorbs very low amounts of water at  $p/p_0 < 0.5$ . In contrast adsorption of cyclohexane (see also Fig. S1) exhibits a type 1 adsorption isotherm typical for microporous materials. The resulting experimental hydrophobicity index measured as gram of cyclohexane divided by gram of water per zeolite unit mass measured at 7 and 5 Torr vapour pressure for cyclohexane and water, respectively, was 20. This value indicates a strong preference for cyclohexane vs. water and agrees very well with that previously reported in the literature for analogous materials [24,25]. In comparison the hydrophobicity index under the same conditions for a conventional zeolite Y containing a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> framework ratio of 5.1 (CBV-100) is 1, indicating the much higher hydrophilicity of this conventional zeolite Y (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 5.1) as compared to the zeolite CBV-901 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 80) under study.

Having shown the affinity of highly dealuminated CBV-901 for hydrophobic compounds, we proceeded to test the ability of this material for the selective adsorption of fatty acids and hydrophobic compounds from dissolved organic matter (DOM) that are present in the effluent of UWTP (Ribarroja, see Section 2) operating through a conventional prolonged aeration. The procedure followed in this study to determine the type of compounds adsorbed on zeolite CBV-901 is outlined in Scheme 1. These experiments were carried out contacting a large excess of zeolite (12 g) in 2 L of the UWTP effluent. When the effluent is contacted with CBV-901 for 2 h a significant reduction of the TOC was observed. The reduction of TOC depends on the amount of zeolite added and the pH of the adsorption. The maximum adsorption occurs at pH 4 (60%) while at pH 5 and 7.2 the maximum TOC reduction were 37 and 17%, respectively. Besides TOC adsorption, we also observed a remarkable adsorption capacity for HCO<sub>3</sub><sup>-</sup>. After adsorption of TOC from the effluent, the zeolite was recovered by filtration and extracted with MeOH. This procedure allows recovering organic matter from CBV-901 that accounts for more than 95% of the decrease observed in the effluent TOC during CBV-901 adsorption. Thus, all the organic matter adsorbed on CBV-901 from the effluent could be recovered by methanol extraction and submitted to analysis.

In order to determine the type of organic compounds retained in the zeolite as well as those that have not been adsorbed, the effluent after being treated with zeolite was passed through a DAX8 resin that is a recommended adsorbent for the fractioning of hydrophobic compounds in natural waters [19]. The aim is to determine which compounds are not adsorbed on zeolite CBV-901, but adsorbed on DAX8 resin. CBV-901 adsorb preferentially the hydrophobic compounds present in UWTP, but it could be that due to the limit in the pore size and the structure of the organic matter some hydrophobic compounds that are adsorbed in DAX8 are not retained by the zeolite.

The retained DOM in DAX8 resin was extracted first with an aqueous basic solution (NaOH, 0.1 M) to obtain the HPO fraction, and subsequently with MeOH yielding NEU fraction (Scheme 1). For the sake of comparison we performed an analogous fractioning procedure without the step of zeolite adsorption. Actually, the operational procedure followed in the present study is that commonly used to determine hydrophobic compounds except that in one case we include a previous step consisting in zeolite adsorption (Scheme 1). Typically analysis of the individual organic compounds present in the effluents of UWTP is very difficult and it is almost impossible to identify specific compounds. For this reason it is common practise to fraction the organic compounds according to their affinity with polymeric resins [19]. The two most used resins are DAX8 and XAD4 that are acrylic ester-based polymer and styrene–divinylbenzene copolymer, respectively. The fractions



**Fig. 1.**  $^1\text{H}$  NMR spectra of CBV and hydrophobic fractions (A).  $^1\text{H}$  NMR spectra of HPO-2 and NEU-2 fractions (B). Fatty compounds are characterized by signals from 2.5 to 0.5 ppm that are more intense for the CBV fraction. The spectra have been recorded in perdeuterated methanol (strong signals centred at 5.0 and 3.2 ppm).

retained in DAX8 resin are termed as hydrophobic and neutral in contrast to those retained in XAD4 that are termed as transphilic [19]. Thus, our hydrophobic zeolite is more alike to the DAX8 resin since both materials exhibit affinity for hydrophobic compounds dissolved in water.

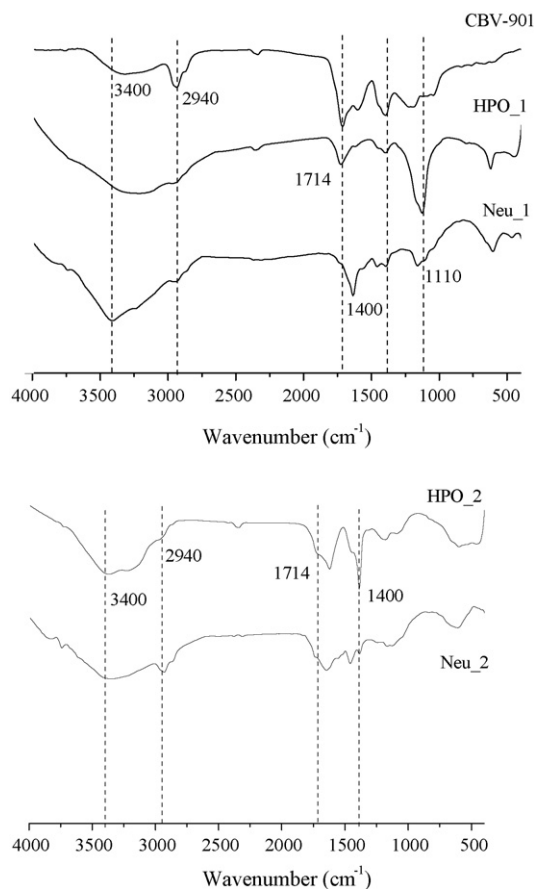
All the fractions indicated in Scheme 1 were studied by  $^1\text{H}$  NMR and FT-IR spectroscopy, as well as GC-MS analysis of the mixtures after derivatization with BSTFA containing 10% TMCS (see Scheme S1 in supplementary material for the protocol of spectroscopic characterization).

Comparison of the spectra clearly reveals that zeolite CBV-901 is remarkably efficient and selective for the adsorption of a large extent of fatty acids and other hydrophobic compounds present in the UWTP effluent. Thus, Fig. 1A shows a comparison of the  $^1\text{H}$  NMR spectra of the CBV, HPO-1 and HPO-2 fractions. As it can be seen there, the  $^1\text{H}$  NMR of the CBV fraction contains a significant proportion of signals in the 2.6–0.8 ppm attributable to aliphatic protons as well as hydrogens in  $\alpha$  position to C=O groups, all these signals typical of fatty acids [26]. Notably the signals between 3 and 4 ppm corresponding to carbohydrates and peptides [27,28] are relatively small in the  $^1\text{H}$  NMR spectrum of CBV fraction (see below the discussion of HPO-2). Also the  $^1\text{H}$  NMR spectra of the CBV fraction shows some aromatic hydrogens appearing between 7 and 8 ppm.

In agreement with the preferential adsorption of fatty compounds in CBV-901, the supernatant from the treatment with CBV-901 zeolite after elution through DAX8 resin and desorption with basic aqueous solution (HPO-1) exhibits a significantly reduced proportion of aliphatic and aromatic protons and a relatively high intensity of the signals between 3 and 4 ppm attributable to carbohydrates and peptides. Similar trend was observed for the  $^1\text{H}$  NMR spectrum of the NEU-1 fraction that barely shows aliphatic hydrogens (see Fig. 1A). Thus from the  $^1\text{H}$  NMR spectroscopy study of the hydrophobic fractions from the effluent of the UWTP it can be concluded that zeolite CBV-901 shows a remarkable affinity for the

fatty acids and hydrophobic compounds. This conclusion is reinforced when the  $^1\text{H}$  NMR spectra recorded for the DAX8 adsorbates from the UWTP effluent without zeolite treatment (Fig. 1B) corresponding to 45 and 14%, respectively, of the total DOM are compared with those previously commented for zeolite CBV-901. Using DAX8 at pH 2 two fractions were obtained from desorption of the organic matter previously adsorbed on the resin when the effluent was eluted through this resin (see Scheme 1 for treatments and nomenclature of the fractions). The  $^1\text{H}$  NMR spectrum of HPO-2 shows signals that correspond to the averaged contribution of the  $^1\text{H}$  NMR spectra of CBV and HPO-1 fractions. Importantly the spectrum of HPO-2 contains simultaneously aliphatic, aromatic, carbohydrate and peptides hydrogens appearing in the whole scale of chemical shifts. Moreover, the  $^1\text{H}$  NMR spectrum of NEU-2, although showing predominant signals for carbohydrates or peptides, contains also aliphatic and aromatic protons in a much higher percentage than the  $^1\text{H}$  NMR spectrum of the NEU-1 analog fraction. This indicates that when no zeolite is used, the DAX8 resin is not able to discriminate fatty acids and hydrophobic compounds from carbohydrates and oligopeptides. This comparison of  $^1\text{H}$  NMR spectra of the different fractions indicates the selective adsorption of the most hydrophobic compounds in zeolite CBV-901 and the much less affinity of this microporous solid to adsorb carbohydrates and peptides.

Similar conclusions can be obtained based on FT-IR spectroscopy [29–31]. Fig. 2 shows the set of FT-IR spectra corresponding to the five fractions to illustrate the influence of zeolite treatments prior to adsorption on DAX8 resin. As can be seen in Fig. 2 the FT-IR spectrum



**Fig. 2.** FT-IR spectra of the different fractions. The vertical lines and their corresponding wavenumbers indicate to the most important bands in the IR due to O-H ( $3400\text{ cm}^{-1}$ ), C-H ( $2940$  and  $1430\text{ cm}^{-1}$ ), C=O ( $1714\text{ cm}^{-1}$ ) and C-O ( $1110\text{ cm}^{-1}$ ) vibrations.

of the CBV fraction shows relatively weak O–H vibration band and relatively strong peaks at 2940, 1714 and 1608  $\text{cm}^{-1}$  attributable to aliphatic alkyl chains, aliphatic carboxylic compounds and aromatic rings, respectively. In comparison the FT-IR spectrum of HPO-1 fraction shows stronger O–H and C–O vibrations appearing between 3200 and 1110  $\text{cm}^{-1}$ , respectively. The aliphatic C–H stretching bands and the aromatic vibrations appearing at 2940 and 1608  $\text{cm}^{-1}$  are considerably reduced for HPO-1 in comparison to CBV. In the same way, the FT-IR spectrum of NEU-1 does not show the peak 2940 and 1714  $\text{cm}^{-1}$  characteristic of the fraction CBV. Therefore, the series of FT-IR spectra of the fractions obtained with the zeolite treatment illustrates in a visual form the remarkable selectivity of zeolite CBV-901 for fatty acids and hydrophobic compounds.

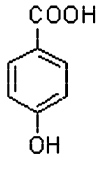
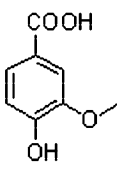
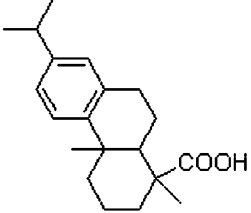
Fig. 2 also contains the FT-IR spectra of the HPO-2 and NEU-2 fractions obtained using exclusively the DAX8 resin. These two spectra do not show the preferential fatty compound adsorption observed for CBV and that is reflected in the ratio of the peaks at 2940  $\text{cm}^{-1}$  vs. 3400  $\text{cm}^{-1}$  corresponding to C–H vs. O–H vibrations.

To gain a deeper understanding of the type of compounds selectively adsorbed on the hydrophobic zeolite and determine the chemical structure of the individual compounds present in the hydrophobic fractions of UWTP effluent, we proceeded to derivatization of the CBV, HPO-1 and NEU-1 fractions using BSTFA containing 10%TMCS (see Scheme S2 in supplementary material for the derivatization procedure). This reagent under standard conditions (see Section 2) is able to effect the exhaustive trimethylsilylation of acidic and neutral hydroxyl groups rendering trimethylsilyl derivatives that can be analyzed by GC–MS.

When the CBV and HPO-1 were treated with BSTFA + 10% TMCS and analyzed by GC–MS a series of compounds were identified. The structure of the individual compounds characterized and their estimated concentrations are given in Tables 1 and 2. As it can be seen in these tables the main compounds present in fraction CBV are fatty acids from 8 to 18 carbons together with aromatic carboxylic acids. Actually, only four fatty acids, namely estearic, cetyl, palmitic and lauric acids, account for the 14% of this fraction, what is very remarkable considering the complexity of the chemical mixture forming the UWTP effluent. In comparison to this CBV fraction, HPO-1 contains very residual amounts of fatty acids, being predominant the silyl derivatives of more polar polyhydroxylic compounds and monosaccharides. Previous studies have shown that oligosaccharides can undergo hydrolysis to the corresponding monosaccharides under the harsh acid conditions (pH < 2, 80 °C for 8 h) employed in the derivatization [32] and, therefore, it could be that monosaccharides are really formed in the silylation treatment. Analogous derivatization treatment for NEU-1 did not lead to any volatile compound, suggesting a more complex mixture of high molecular mass compounds. Altogether the data of compound analysis of Tables 1 and 2 show that saccharides are not retained in the zeolite CBV-901 that is very selective for fatty acids and aromatic carboxylic acids. This selectivity can be very nicely proved by presenting selective ion monitoring (SIM) chromatograms of the fractions following those ions that are specific for silylated monosaccharides. As presented in Fig. 3A, mass spectrometry fragmentation of trimethylsilyl derivatives of monosaccharides gives rise to an intense  $m/z$  204 Da peak corresponding to the ion of an ethylenediol fragment having two trimethylsilyl units.

**Table 1**

Compounds detected by GC–MS after silylation of the CBV fraction. The number below the structure represents the estimated quantity ( $\mu\text{g}/\text{mg}$  sample) in the mixture and the number in brackets the match-quality of the proposed structure (database NIST98).

$\text{H}_3\text{C}-(\text{CH}_2)_6-\text{COOH}$ 16.1 (80)	$\text{H}_3\text{C}-(\text{CH}_2)_7-\text{COOH}$ 8.6 (87)	$\text{H}_3\text{C}-(\text{CH}_2)_{10}-\text{COOH}$ 25 (91)
$\text{H}_3\text{C}-(\text{CH}_2)_{12}-\text{COOH}$ 25.1 (98)	$\text{H}_3\text{C}-(\text{CH}_2)_{13}-\text{COOH}$ 4.2 (93)	$\text{H}_3\text{C}-(\text{CH}_2)_{14}-\text{COOH}$ 32 (97)
$\text{H}_3\text{C}-(\text{CH}_2)_{15}-\text{COOH}$ 1.2 (90)	$\text{H}_3\text{C}-(\text{CH}_2)_{16}-\text{COOH}$ 55.1 (99)	$\text{HOOC}-(\text{CH}_2)_7-\text{COOH}$ 16.4 (80)
$-(\text{H}_2\text{C})_7-\text{HC}=\text{C}(\text{H})-(\text{CH}_2)_7-\text{COOH}$ 8.9 (97)		
 6.1 (93)	 21 (82)	 10.0 (95)
Total identified: 229.7 $\mu\text{g}/\text{mg}$		

**Table 2**

Compounds detected by GC–MS after silylation of the HPO-1 fraction. The number below the structure represents the estimated quantity ( $\mu\text{g}/\text{mg}$  sample) in the mixture and the number in brackets the match-quality of the proposed structure (database NIST98).

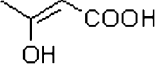
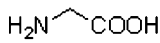
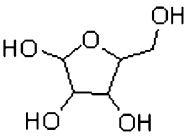
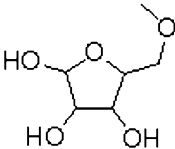
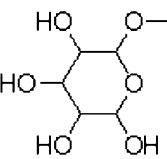
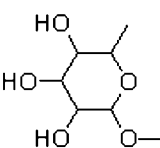
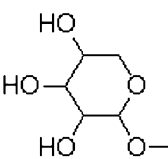
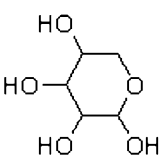
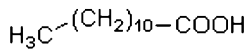
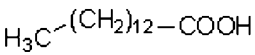
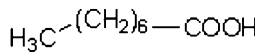
			
7.3 (80)	1.1 (95)	4.7 (80)	6.7 (87)
			
4.1 (82)	13.5 (90)	16.3 (79)	11.2 (90)
			
1.4	0.7	0.36	
Total identified: 69.36 $\mu\text{g}/\text{mg}$			

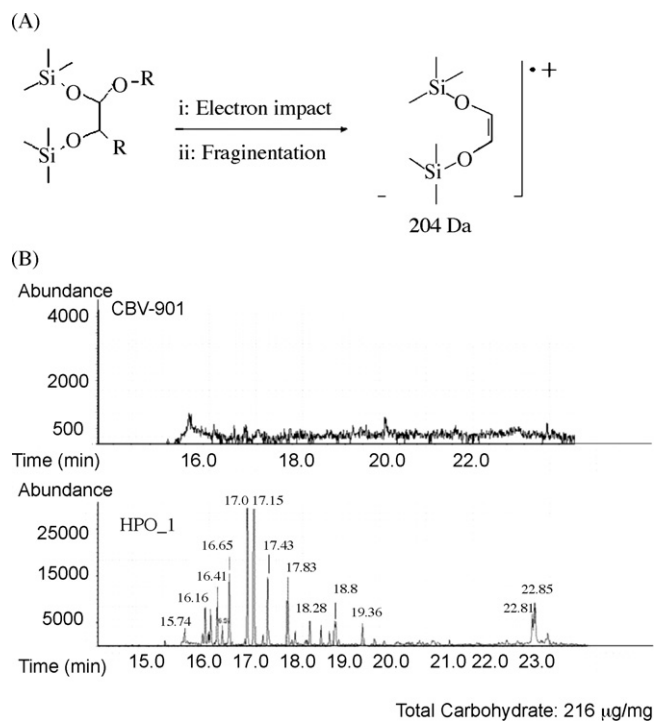
Fig. 3B shows the SIM chromatograms monitoring the 204 Da peak for the CBV and HPO-1 fraction. As it can be seen in this figure, this fragment characteristic of saccharides is present in many peaks in the HPO-1 fraction but is almost absent in the CBV fraction. A

complete collection of the mass spectra for each of the peaks in Fig. 3B are shown in Table S2 of the supplementary material.

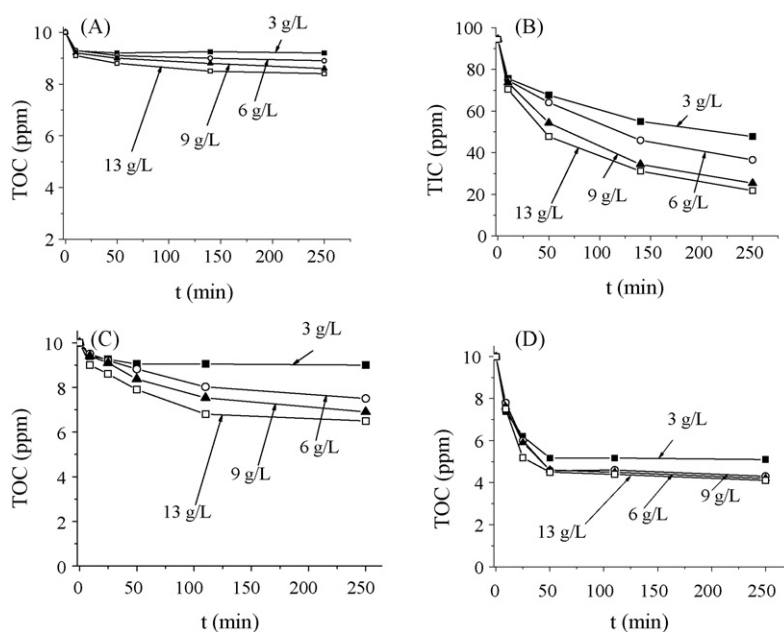
After having determined the type of organic compounds that are adsorbed on zeolite CBV-901, and in order to show the possible practicality of the use of zeolites as a polishing treatment in UWTP effluents, we performed a study of the minimum zeolite amount for optimum TOC removal as well as the influence of pH on the adsorption capacity. The temporal profile of TOC removal vs. time upon addition of increasing zeolite amounts are shown in Fig. 4. The amount of organic compounds removed at the longest time is assumed to be the equilibrium point of the adsorption.

The pH range of the study was selected considering that most aliphatic carboxylic acids (as those fatty acids being adsorbed on zeolite CBV-901, see Table 1) have a  $\text{p}K_a$  about 4.5 and in water they are predominantly dissociated as carboxylate at pH above 5 and as carboxylic acid at pH 4. Actually, as it can be seen in Fig. 4, the pH of the adsorption plays an important role in the adsorption. Adsorption at pH of 4, in which the carboxylic acid should predominate, is extremely favourable and up to 60% of the TOC of the UWTP effluent can be retained by the zeolite. Even more, the adsorption isotherms are coincident for zeolite amounts above 6 g/L, indicating that all the hydrophobic compounds present in the water can be adsorbed using this zeolite amount. In contrast, the percentage of TOC reduction at pHs 5 and 7.2 depends on the amount of zeolite and is significantly lower than at pH 4. Nevertheless, it has to be remarked that at pH 7.2 (the value of the free pH of UWTP effluent) a TOC reduction of 9% can be obtained just with 3 g/L and can be increased up to 17% with 13 g/L. Therefore the data obtained indicates that there is not an amount of zeolite for maximum adsorption optimum.

To help to rationalize the difference in the adsorption behaviour of the zeolite CBV-901 between pH values of 5 and 7.2, an interesting observation was the zeolite adsorption capacity for inorganic carbon. The TIC of the UWTP effluent is much higher than the amount



**Fig. 3.** Structure and origin of the peak at 204 Da specific of silylated carbohydrates (A). Comparison of carbohydrate content as determined by monitoring at 204  $m/z$  in SIM MS spectra for the CBV and HPO-1 fractions after derivatization by trimethylsilylation (B).



**Fig. 4.** Decrease of total organic (A) and inorganic (B) carbon using different amounts of CBV-901 at pH 7.2. Decrease of total organic and inorganic carbon using different amounts of CBV-901 at pH 5 (C) and 4 (D).

of organic hydrophobic compounds (TIC 94 ppm vs. TOC 10 ppm). At pH 7.2, this inorganic carbon consists mainly in bicarbonate and the adsorption capacity of zeolite CBV-901 for bicarbonate at pH 7.2 is very high (up to 52% TIC reduction for 3 g/L). In this regard, it has to be noted that bicarbonate decomposes at pH 5 giving  $\text{CO}_2$  and it is present at pH 5 and, for this reason, the adsorption capacity of zeolite CBV-901 for hydrophobic organic compounds at pH 5 is significantly higher than at pH 7.2. Thus,  $\text{HCO}_3^-$  present in the UWTP effluent in larger amounts than fatty acids competes for adsorption at pH 7.2, but not at pH 5. Finally, it should be commented that the conditions shown in Scheme 1, in where our analytical study and compound characterization was performed, correspond to the optimum conditions for the maximum adsorption of organic compounds in the zeolite (pH 4, large amount of zeolite). Under these conditions (13 g/L, pH 4) we compare the adsorption capacity of dealuminated CBV 901 as presented in Fig. 4D with that of the conventional NaY zeolite with high aluminium content. The results show that at the equilibrium the TOC reduction using NaY was only 6%. As expected this value clearly illustrates the advantages of using CBV 901 with high Si/Al ratio.

#### 4. Conclusions

The effluent of UWTP based on conventional biological treatments has typically a high TOC value, due in a large extent to hazardous hydrophobic compounds used as domestic detergents. In the present work we have shown that dealuminated CBV-901 zeolite adsorbs selectively fatty acids and aromatic carboxylic acids present in the UWTP effluents. Conventional DAX8 resin recommended as adsorbent for hydrophobic compounds in water is remarkably less selective and retains saccharides and peptides in addition to fatty acids and aromatic carboxylic acids than CBV-901. We have also observed that the effluent pH value strongly influences the adsorption capability of the zeolite, being adsorption largely favoured at  $\text{pH} \leq 4$ . This influence is due to the decomposition of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  and the transformation of carboxylates into carboxylic acids.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.11.057.

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