



Adsorptive removal of α -endosulfan from water by hydrophobic zeolites. An isothermal study

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ABSTRACT

This paper deals with the removal of α -endosulfan from water over HY and steamed HBEA zeolites. Experiments were performed to understand the adsorption mechanisms of α -endosulfan on zeolites and to determine the most efficient adsorbent for the purification of water contaminated by this pesticide. The experiments exhibit that α -endosulfan was adsorbed in the micropores. In the case of HY zeolites an adsorption of α -endosulfan molecules on Brønsted sites was pointed out, due to a preferential water adsorption in mesopores. Moreover a physisorption of α -endosulfan occurred in micropores. For steamed HBEA zeolites physisorption in micropores was pointed out as the adsorption mode. For both types of zeolites a decrease of the adsorption capacities was noticed when the acidity of zeolites increased. There was also a linear relation between the adsorption capacities of α -endosulfan and the hydrophobicity (HI) of the samples and by determining the values of HI for a type of zeolite it was possible to deduce the uptake of α -endosulfan. The HY(40) sample was the most efficient for the removal of α -endosulfan from water because of preferential adsorption of water molecules in mesopores and lower acidity. For this sample the adsorption capacity for α -endosulfan was about 833.33 mg/g where for the most effective HBEA sample (St700(3)) the adsorption capacity was about 793.65 mg/g.

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1. Introduction

In many countries pesticides are widely used to increase the yield of crops. Despite its recent prohibition in 2006 in West Africa [1] α -endosulfan remains one of the most widespread pesticides in African farms. Recently this pesticide was also banned from many other countries such as New Zealand, Paraguay, EU, etc. It is mainly used in cotton farms, but also for the production of vegetables in the southern Europe for example [2–4]. The toxicity of α -endosulfan was clearly documented for humans and animals [5–7]. Both toxicological and epidemiological studies [8–10] were realized, and many diseases such as cancers and neurological affections were identified as potential effects of the exposure to this pesticide [11,12]. Due to its high life-time α -endosulfan occurs in surface waters and groundwaters in West Africa farming regions [13] at levels exceeding the norms adopted by WHO for drinking water (0.10 μ g/L). Unfortunately in African rural regions water is directly consumed by peoples without any treatment, inducing many consequences on the health of these poor and rural peoples.

In the literature there are a few papers dealing with low cost methods for the removal of α -endosulfan from water. The biological treatments were documented [14,15] but their application for drinking water is difficult. Many physico-chemical methods can be applied such as oxidative methods [16,17] or adsorption methods [18] for the potabilization of water contaminated by organochlorinated pesticides but these methods are not generally cost effective for the rural people.

Due to their low cost and their regeneration ability zeolitic adsorbents are good candidates for the treatment of water contaminated by organochlorinated pesticides. The aim of the present paper is to study the removal performances of α -endosulfan in water over synthetic HBEA and HY zeolites. An isothermal study was performed to understand the adsorption mechanisms of the pesticide by the different solids. The effect of the structure of the zeolites and their hydrophobicity will be particularly discussed.

2. Experimental

Adsorption experiments were performed in batch reactor at room temperature by using synthetic faujasite type zeolites (HY) and protonic beta type zeolites (HBEA) according to the protocol described by Khalid et al. [19] for the adsorption of phenol in water. To determine the adsorption isotherms, 200 mg of each

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Table 1
Physicochemicals characteristics of zeolites.

Samples	Treatments	Framework Si/Al ratio	Acidity Brønsted ^a ($\mu\text{mol g}^{-1}$)	Porosity			BET surface (m^2/g)	HI
				V_{micro}^b ($\text{cm}^3 \text{g}^{-1}$)	V_{meso}^b ($\text{cm}^3 \text{g}^{-1}$)	V_{total}^b ($\text{cm}^3 \text{g}^{-1}$)		
Cal	Calcination of NH ₄ BEA (Zeolyst)	33	315	0.203	0.382	0.585	480	4.03
St500(3)	Steaming, 93.3 kPa water, 773 K, 3 h	36	293	0.168	0.288	0.501	546	6.03
St600(3)	Steaming, 93.3 kPa water, 873 K, 3 h	63	200	0.179	0.383	0.613	594	8.04
St700(3)	Steaming, 93.3 kPa water, 973 K, 3 h	110	179	0.171	0.234	0.439	528	8.42
HY(16)	No	21.57	327	0.313	0.107	0.429	789	3.72
HY(20)	No	25.6	213	0.315	0.136	0.468	830	4.22
HY(40)	No	33.93	133	0.325	0.118	0.449	825	4.55

^a Determined by pyridine adsorption at 423 K followed by FTIR.

^b Determined by the *t*-plot diagram.

zeolitic adsorbent was added to 10 mL of a known concentration of α -endosulfan in water. The solutions were stirred and a few amount of supernatant liquid was regularly analyzed by high performance liquid chromatography (HPLC) until the concentration of α -endosulfan in water was constant. Usually the thermodynamic equilibrium was achieved after 10 min but the stirring was maintained during 1 h to ensure that the equilibrium remains constant. Indeed by analyzing the supernatant liquid it was noticed a decrease of the concentration of α -endosulfan from 0 to 10 min and a stabilization of the concentration after 10 min. Adsorption experiments were performed with water samples with different concentrations of α -endosulfan; these concentrations varied from 10 to 30 mg/L. The amount of α -endosulfan in water was analyzed by using a high performance liquid chromatography system (HPLC, VARIAN Prostar). The HPLC was equipped with a reverse phase column (ChromSpher Pesticides) and an ultraviolet (UV) detector (254 nm, Model 340). The experiments were realized with methanol (1 mL/min) as mobile phase.

The HBEA zeolites were dealuminated by steaming of a parent CP 814E sample provided by Zeolyst International. This sample was designed by "Cal" in the text. The steaming method was fully described in a previous paper [20]. Indeed, the BEA zeolites were dealuminated by water steam at different temperatures and during different times in order to remove the framework aluminum atoms with the removing of Al-OH groups. Thus the protonic acidity of the zeolites (Brønsted acidity) associated to Al-OH groups could be reduced. The parent sample (Cal) was treated under a flow of water and air ($P_{\text{water}} = 93.3 \text{ kPa}$) for 3 h at 500 °C, 600 °C or 700 °C. The samples were denoted as St500(3), St600(3) and St700(3), depending on the steaming temperature. Steaming time was the same – 3 h. Faujasite zeolite samples (HY) were provided by Zeolyst International. These samples were directly used as adsorbents without further post-treatment. Faujasite samples were denoted as HY(16), HY(20) and HY(40) where the numbers 16, 20 and 40 indicate the global Si/Al ratios of faujasite zeolites determined by elemental analysis.

The physicochemical characteristics of the samples were obtained by several techniques. The Brønsted acidity was determined by pyridine adsorption followed by a Nicolet Magna FTIR 550 spectrometer (resolution 2 cm^{-1}) at 423 K; the acidity was calculated from the integrated area of the PyH bands, using the values of the molar extinction coefficients of these bands ($1.13 \text{ cm}^{-1} \text{ mol}^{-1}$) as established by Wang et al. [21]. The nitrogen adsorption performed at 77 K by a Tristar Micrometrics instrument allowed the assessment of BET areas and both microporosity and mesoporosity. The hydrophobicity of solids was determined using the method described by Weitkamp [22,23]. Basically, competitive water and toluene adsorption experiments were carried out at 35 °C with a fixed bed reactor coupled to a Varian Star 3900 gas chromatograph

(GC) equipped with a TCD detector. 100 mg of zeolite were activated at 350 °C under a dried nitrogen flow for 12 h. After cooling, the zeolite was thermostated at 35 °C; then, a constant helium flow (10 mL/min) saturated at 35 °C with water and toluene vapor was released over the sample (downstream). Water and toluene partial pressures were respectively $5.6 \times 10^3 \text{ Pa}$ and $6.2 \times 10^3 \text{ Pa}$. The relative pressure was $P/P_0 = 1$. The gas mixture from the adsorber was periodically analyzed (intervals of 1 min) by GC, and the water and toluene adsorption capacities were obtained by integrating the obtained breakthrough curves for water and toluene. The hydrophobicity index (HI) was thus determined by the relation below (1).

$$\text{HI} = \frac{X_{\text{toluene}}}{X_{\text{water}}} \quad (1)$$

where X_{toluene} , toluene adsorption capacity (g/g); X_{water} , water adsorption capacity (g/g).

3. Results and discussion

3.1. Physicochemical characteristics

The physicochemical characteristics are reported in Table 1.

The dealumination of BEA samples by steaming exhibited as expected an increase of the framework Si/Al ratio with the severity of the dealumination. This increase of Si/Al ratio induced a decrease of Brønsted acidity as shown by Marques et al. [24]. Due to the removal of Brønsted acidic sites we had also an increase of the Weitkamp hydrophobicity indexes. Indeed Brønsted acidic sites are water preferential adsorption sites in the case of steamed HBEA samples and the removal of these sites improves the hydrophobic character of the zeolites [20]. HY samples were chosen with different framework Si/Al ratios, and consequently different hydrophobicity levels. The most hydrophobic samples were those with the lowest Si/Al ratios.

The specific surfaces were relatively important for all the samples and HY samples had higher BET areas than HBEA samples. The microporous and mesoporous volumes of HY samples were also greater than those for HBEA samples. The lower values of hydrophobicity indexes noticed for HY samples were due to a preferential and more important water condensation in the mesopores instead of adsorption on Brønsted sites [25]. Thus by comparison with HBEA samples where the Brønsted sites were removed by steaming inducing a decrease of water uptake and an increase of HI values the HY samples were characterized by lower HI values [25].

The kinetic diameter of α -endosulfan was determined by Monte Carlo simulations with Cerius² software and was about 7.2 Å. By comparison with the pores aperture for HBEA and HY zeolites

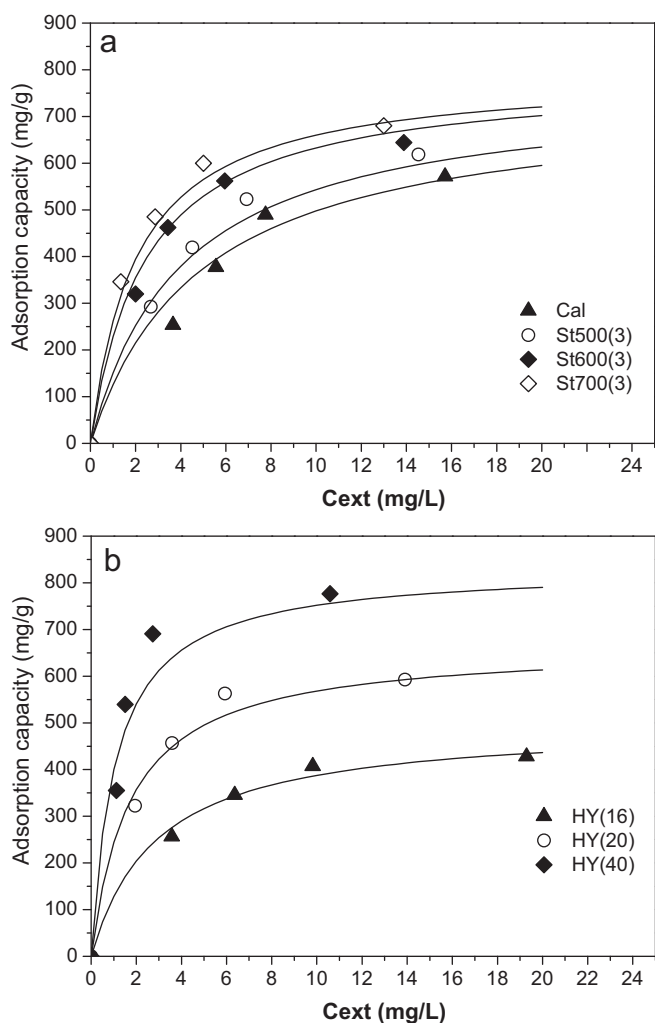


Fig. 1. (a) Langmuir modelization of α -endosulfan adsorption isotherms over steamed HBEA samples. (b) Langmuir modelization of α -endosulfan adsorption isotherms over HY samples.

($6.4 \times 7.6 \text{ \AA}$ and 7.4 \AA respectively for the large pores of HBEA and HY zeolites) the molecule of α -endosulfan can be easily adsorbed by the zeolites if we just consider the steric hindrance of the sorbate.

3.2. Adsorption experiments

The adsorption isotherms for steamed HBEA and HY zeolites are presented on Fig. 1. The isotherms are type I isotherms suggesting that the molecules of α -endosulfan are exclusively adsorbed in micropores; no molecules are adsorbed by capillary condensation in mesopores [25]. On the contrary, according to previous studies [26–28] it is well documented that water molecules are adsorbed under the form of water clusters occupying both microporous and mesoporous volumes. For both types of zeolites the isotherms show an increase of α -endosulfan adsorption capacities when the Brønsted acidity decreases. This shows that the Brønsted acidic sites are not the preferential adsorption sites for α -endosulfan molecules. Moreover when the Brønsted sites are removed we can notice an increase of hydrophobicity due to the decrease of water adsorption. This suggests that for acidic samples water molecules are preferentially adsorbed on Brønsted acidic sites instead of α -endosulfan molecules. More the samples are hydrophobic more the adsorption of α -endosulfan molecules is promoted. This can be explained by a lower adsorption of water clusters in micropores

Table 2
Langmuir parameters for the adsorption of α -endosulfan over steamed HBEA and HY zeolites.

Samples	Adsorption capacity (mg/g)	K (L/g)
Cal	740.74	0.205
St500(3)	763.36	0.247
St600(3)	787.40	0.410
St700(3)	793.65	0.490
HY(16)	500	0.345
HY(20)	666.67	0.577
HY(40)	833.33	0.923

allowing a better adsorption of α -endosulfan molecules in these micropores.

The different isotherms presented in this study are well fitted by the model of Langmuir. This suggests a monolayer adsorption of α -endosulfan molecules in the solids. The different parameters resulting from the Langmuir modelization are reported in Table 2. It is noticed for both types of solids that the interactions between α -endosulfan molecules and zeolites increase when the acidity of the zeolites decrease. For HBEA samples for example, the values of K (L/g) for Cal and St700(3) increase from 0.205 to 0.490 when the acidity decrease from 315 to $179 \mu\text{mol g}^{-1}$. It appears thus that Brønsted acidic sites are not the adsorption sites for α -endosulfan molecules. Moreover the presence of these sites goes against the adsorption of α -endosulfan. The adsorption capacities for monolayer vary with the Brønsted acidity for the two types of zeolites (Fig. 2). By considering the slopes of the curves (adsorption capacity versus acidity) it is noticed that the variation of α -endosulfan uptake with acidity is less important for HBEA samples than for HY samples. Indeed for HY samples the adsorption capacity is low for the most acidic sample (HY(16)) and increases quickly when acidity decreases. This can be seen from Table 2 where adsorption capacities increase significantly from 500 mg/g for HY(16) to 833.3 mg/g for HY(40). On the other hand in the case of steamed HBEA samples, if for the most acidic sample (Cal) the adsorption capacity is higher than that for the most acidic HY sample (740.74 mg/g for Cal and 793.65 mg/g for St500(3)). The moderated increase of α -endosulfan uptake in the case of HBEA samples can be explained by the effect of the microporous volume of these solids. Indeed the microporous volumes are lower for HBEA samples and

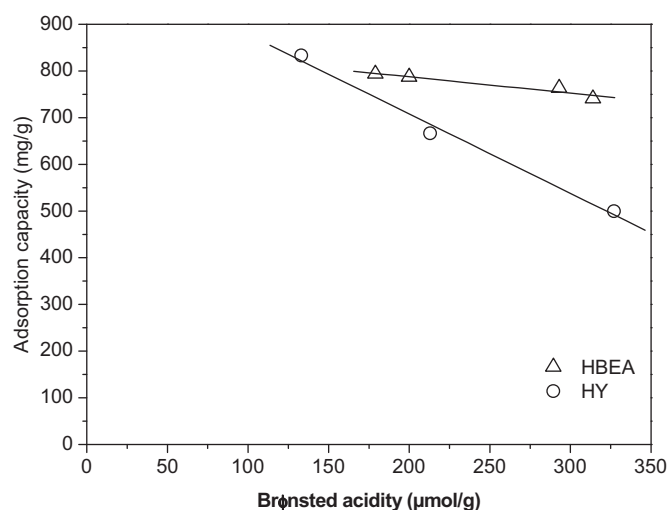


Fig. 2. Evolution of α -endosulfan uptake with the Brønsted acidity for HY and steamed HBEA samples.

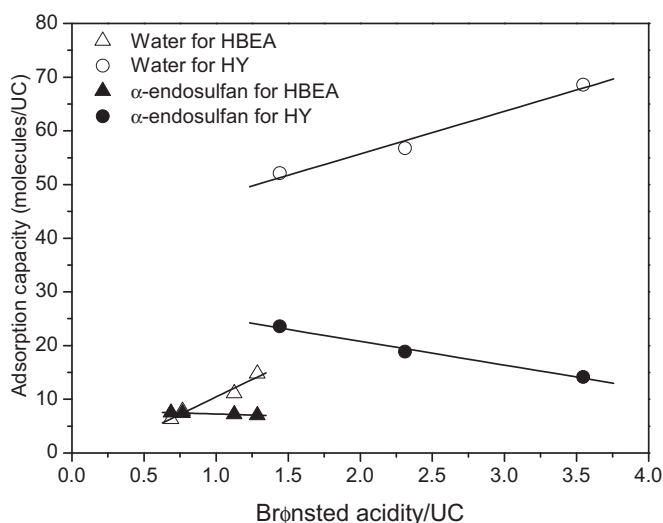


Fig. 3. Water and α -endosulfan adsorption capacities per unit cell versus Brønsted acidity per unit cell for HY and steamed HBEA samples.

higher for HY samples (Table 1). When microporous volumes are low the adsorption capacity of α -endosulfan is restricted in spite of a noticeable decrease of Brønsted acidity. Indeed, normally the decrease of Brønsted acidity should favor the adsorption of α -endosulfan because the water clusters become smaller [26], and the competition between water clusters and α -endosulfan molecules for the access to the micropores is minored. But as the microporous volumes are low it is difficult for α -endosulfan molecules to take advantage of the reduction of water competition to enhance their access to the micropores. The size of α -endosulfan molecule (7.2 Å) is very close to the aperture of the pores in the case of HBEA samples (about 6.7 Å) so α -endosulfan molecules are not easily adsorbed in the micropores even when the competition with water molecules is reduced. On the contrary when the microporous volumes are high in the case of HY zeolites (the pores aperture are about 7.4 Å), the adsorption of α -endosulfan is significantly favored when the samples are dealuminated (reduction of Brønsted acidic sites): indeed, first there is an easier access of α -endosulfan molecules to the micropores and secondly there is a reduction of the competition between α -endosulfan and water clusters for the access to the micropores because of the reduction of the size of water clusters [26]. To conclude on this point, we can say that for both zeolite types the α -endosulfan uptake is related to the Brønsted acidity of the solids. But in the case of HY samples the uptake of α -endosulfan is more affected by the acidity of the sample. Indeed, the Brønsted acidic sites are water adsorption sites and the presence of these sites promotes the adsorption of water inducing a greater competition between water and α -endosulfan molecules for the access to the pores of the zeolites. So the most acidic samples are the less effective for the adsorption of α -endosulfan in water. This phenomenon is minored in the case of HBEA samples because of the closer values for the diameter of endosulfan molecules and the micropore apertures.

Fig. 3 exhibits the competition between water molecules and α -endosulfan molecules for the adsorption on Brønsted sites. The adsorption capacities (in molecules per unit cell) are represented versus the concentration of Brønsted acidic sites per unit cell. The unit cell represents the smallest form of the zeolite. The water adsorption was performed by microgravimetry according to the protocol detailed formerly [20]. When Brønsted acidity increases we have a linear increase of water uptake and a linear decrease of α -endosulfan uptake. The same trend is observed for both HBEA and HY zeolites. The amount of sorbate adsorbed per Brønsted sites

and for the other kind of sites (porous volume) are determined respectively by the slopes and intercepts of the curves presented on Fig. 3. The molecules of α -endosulfan are better adsorbed by Brønsted sites for HY samples than for HBEA samples (respectively 4 molecules per Brønsted site and 0.79 molecules per site). This confirms the preferential adsorption of water clusters [25] on Brønsted sites in the case of HBEA samples and we have respectively 13 and 8 molecules per acidic site for HBEA and HY samples. In the case of HBEA samples the molecules of α -endosulfan are not adsorbed by Brønsted sites but are physisorbed in the available microporous volume; when the samples are very acid water molecules are adsorbed on the Brønsted acidic sites under the form of bigger clusters, which occupy a part of the microporous volume and reduce thus the remaining space for the adsorption of α -endosulfan molecules. In the case of HY samples we still have water clusters on Brønsted sites but water molecules are preferentially physisorbed in the mesoporous volume. Due to their nucleophilic character some molecules of α -endosulfan can be thus adsorbed on Brønsted sites under the form of clusters in the microporous volume. Indeed the chlorine and sulfur atoms present in the α -endosulfan molecules may have specific interactions with Brønsted acidic sites, inducing chemisorption of α -endosulfan. The same phenomenon was shown for the adsorption of chlorobenzene on hydrophobic zeolites in presence of water [29].

3.3. Effect of hydrophobicity

The effect of the hydrophobicity of steamed HBEA and HY samples on the removal of α -endosulfan in water was studied. The hydrophobicity indexes (HI) determined according to the method of Weitkamp [22] were used for the quantification of hydrophobicity. The variations of α -endosulfan uptake with HI are represented on Fig. 4. We can notice a linear increase of α -endosulfan uptake with the increase of HI. By referring to the slopes of the two curves we can consider that the variation of the α -endosulfan uptake depends closely on the structure of the zeolite. For HY samples, a significant increase of α -endosulfan uptake with HI was observed, while the increase was moderated for steamed HBEA samples. It was also seen that for a given zeolite structure (HY, HBEA, etc.) the removal performances of α -endosulfan can be easily predicted for each sample by knowing its hydrophobicity index (HI). When the HI values are close the HY samples have higher performances than steamed HBEA samples for the elimination of α -endosulfan from water. Indeed the most hydrophobic HY sample has a HI

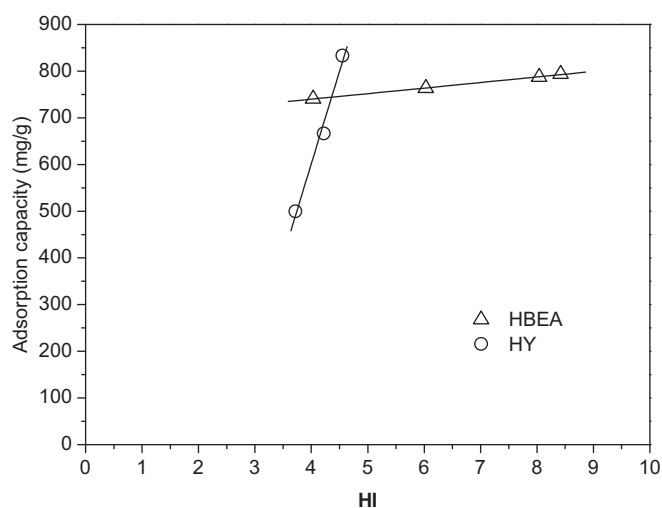


Fig. 4. Evolution of α -endosulfan uptake with hydrophobicity indexes (HI) for HY and steamed HBEA samples.

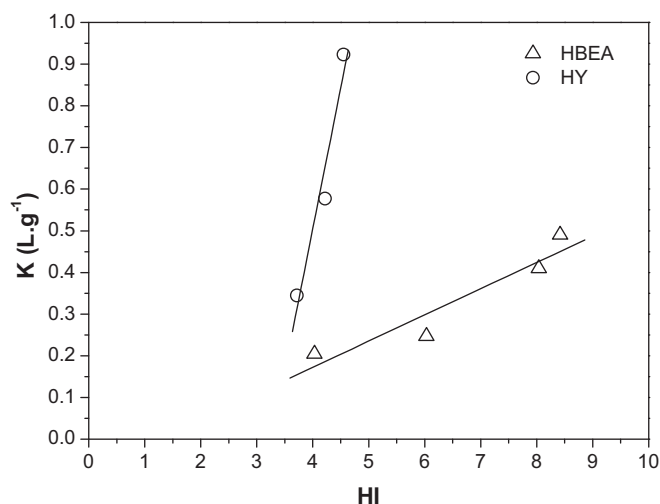


Fig. 5. Evolution of Langmuir K parameter with hydrophobicity indexes (HI) for HY and steamed HBEA samples.

value of 4.55 and an adsorption capacity of 833.33 mg/g while the less hydrophobic steamed HBEA sample has a HI value of 4.03 and an adsorption capacity of 740.74 mg/g. Moreover the adsorption capacity of the most hydrophobic HBEA sample (HI = 8.42) remains lower than that of the most hydrophobic HY sample (Table 2). From the obtained results, it can be concluded that hydrophobic HY samples are the best designed for the removal of α -endosulfan from water by comparison with steamed HBEA samples. From Fig. 5 it can be seen that the interactions between α -endosulfan molecules and zeolites are stronger for HY samples and weaker for steamed HBEA samples. Thus we can say that HY samples have better affinity for α -endosulfan molecules. For HY faujasite samples α -endosulfan molecules are both chemisorbed on Brønsted acidic sites and physisorbed by capillary condensation in the micropores (supercages) while for beta HBEA samples we just notice physisorption of α -endosulfan molecules by capillary condensation in the zeolites micropores.

4. Conclusions

The adsorption of α -endosulfan was studied over HY and steamed HBEA zeolites. The obtained isotherms were type I isotherms inducing an adsorption of α -endosulfan in micropores. The isotherms were well fitted by the model of Langmuir and the adsorption capacities increased when the Brønsted acidity of the samples decreased. The variation of α -endosulfan uptake with the acidity was more significant for HY samples than for HBEA samples because of a preferential water adsorption in mesopores instead of adsorption on Brønsted acidic sites, in the case of HY samples. For both HY and HBEA samples α -endosulfan was absorbed by capillary condensation in the microporous volume. Moreover for HY samples we pointed out an adsorption of α -endosulfan molecules on Brønsted acidic sites because of the water preferential adsorption in mesopores. This chemisorption of α -endosulfan on Brønsted acidic sites is probably due to specific interactions between sulfur and chlorine atoms of α -endosulfan molecule and H protons of Brønsted sites. On the contrary for HBEA samples the adsorption of α -endosulfan on Brønsted sites was restricted by the preferential adsorption of big water clusters on Brønsted sites which occupy the micropores.

The adsorption capacities of the samples were closely related to their hydrophobicity indexes (HI). Indeed the hydrophobic character of the samples reduced the adsorption of water molecules on Brønsted sites allowing thus a better uptake of α -endosulfan

in the micropores. In the case of HY samples this phenomenon was minored by the preferential adsorption of water by capillary condensation in mesopores. Consequently for lower values of HI we had higher α -endosulfan adsorption capacities due to a more important water adsorption in mesopores.

By considering a zeolite structure it was possible to predict the removal performances of samples for α -endosulfan in water by determining their hydrophobicity indexes (HI). In the present study the HY(40) sample was the most efficient for the removal of α -endosulfan from water.

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