

UPTAKE OF ANILINE AND NITROBENZENE FROM AQUEOUS SOLUTION BY ORGANO-ZEOLITE

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ABSTRACT

Adsorption mechanisms of toxic non-ionic organic contaminants (NOCs), aniline and nitrobenzene, with natural-zeolite and organo-zeolite (OZ) were investigated in both batch and continuous systems. In batch tests, the adsorption capacity of aniline and nitrobenzene onto natural zeolite surface is very low or almost nil but becomes significant upon modifying the zeolite surface by hexadecyltrimethylammonium (HDTMA). A partitioning mechanism is proposed to be responsible for the adsorption of NOCs onto OZ. The effectiveness of the partitioning mechanism is directly connected with hydrophobic properties of the NOCs. The column tests were carried out as an indicator for continuous system. The breakthrough curves were constructed for OZ/NOC system and the adsorption capacity of NOCs onto OZ under the present conditions were determined as 2.36 and 3.25 mg per gram of OZ, for aniline and nitrobenzene, respectively. A schematic model is proposed to account for the adsorption of NOCs onto OZ.

Keywords: Organo-zeolite, organic contaminant, partitioning mechanism, sorption, clinoptilolite

INTRODUCTION

A natural zeolite mineral, clinoptilolite has three basic properties; ion exchange, adsorption and molecular sieve. These properties are exploited in a wide spectrum such as abatement of air, water and soil pollution, purification of natural gases, agriculture and animal husbandry [1-13]. Organo-zeolite (OZ) or modified the zeolite is defined as the modified form of natural zeolite (NZ) in which zeolite particle surface is covered by cationic surfactants like HDTMA, TMA (Tetramethylammonium), BTEA (Benzyltriethylammonium). OZ is also used for adsorbing non-ionic organic contaminants (NOCs) in water i.e., naphthalene, benzene, toluene, phenol, xylene, perchloroethylene [14-17], inorganic anionic contaminants i.e., chromate, selenate [18-20], various anionic dye molecules [21] and resin acid from paper process streams [22]. In addition to modified zeolite minerals, a number of modified clay and modified earth minerals are also used in the adsorption of NOCs [23-28]. The literature results indicate that adsorption capacity of natural zeolite, clay and earth minerals for NOCs is nil or very low, but becomes remarkable upon modifying them by typical quaternary amines.

Aniline and nitrobenzene, which are aromatic NOCs, are usually generated from petrochemical plants, coal conversion plants and leaks from underground storage tanks [25]. They have harmful effects on human health and other

lives. The maximum threshold values for aniline and nitrobenzene in wastewater are 2 and 1 mg l⁻¹, respectively [29,30]. Although there are numerous studies on the adsorption mechanism(s) of aniline and nitrobenzene on different organo-clays [31-33], there is only one study on aniline adsorption on OZ [15] and none on the uptake of nitrobenzene onto OZ. More importantly, there appears to be no data about the adsorption of these NOCs on OZ in a column. In the present study, the adsorption mechanism of aniline and nitrobenzene onto HDTMA-treated clinoptilolite (OZ) is investigated in both batch and continuous (column) systems with the aim of identifying the mode and extent of their uptake.

MATERIALS AND METHODS

A natural adsorbent zeolitic tuff from the Gördes region of Turkey (hereafter will be referred to as zeolite) assaying about 92 % clinoptilolite, 4.5 % smectite, 2.5 % cristobalite and 1 % mica was used. The Si/Al ratio in the zeolite sample is 5.31, its external surface area obtained by BET method is 16.73 m²g⁻¹, its total cation exchange capacity (CEC) and external CEC determined by modified Ming and Dixon method [18] are 172 and 8.5 cmol kg⁻¹, respectively. For the modification of zeolite surface, HDTMABr [CH₃(CH₂)₁₅N(CH₃)₃ Br 99% purity, Sigma] was used. The properties of NOCs aniline

[C₆H₅NH₂, 99% purity, Panreac] and nitrobenzene [C₆H₅NO₂, 99% purity, Merck] were used. Some properties of NOCs are given in Table 1.

Preparation of Organo-Zeolite For Batch Tests

The zeolite sample was ground in a ball mill for 1.5 hours and passed through a 100 µm sieve and then used in the preparation of organo-zeolite (OZ) for batch adsorption tests. A sample of 50 g zeolite was placed in a 2 litre beaker and 1 litre of HDTMABr solution of 2x10⁻² M was added into the beaker. The pulp was conditioned on a magnetic stirrer for 2 h at 400 rpm at room temperature. The solid material was rinsed off twice with distilled water after solid-liquid separation by centrifugation (Hettich Universal 16A Centrifuge). The sample was centrifuged again, and dried in an oven at 100 °C for 2 h. The dry sample was ground in an agate mortar for one minute to produce an organo-zeolite sample of minus 100 µm in size. The organic carbon contents of this sample (OZ) and the natural zeolite (NZ) are 4.96 and 0.31 % by weight, respectively (Carbon-Sulfur Determinator, Multilab-CS).

Adsorption Tests in Batch System

First, stock solutions of 1500 mg l⁻¹ of aniline and nitrobenzene were prepared with distilled water of less than 3 µmhos cm⁻¹ in conductivity. Aniline and nitrobenzene solutions of 10 ml at different concentrations in the range of 100-1500 mg l⁻¹ were removed from their stock solutions and transferred into 50 ml centrifuge tubes containing 0.5 g of OZ or natural zeolite. They were conditioned on a shaking-table for 2 h at 400 rpm in order to reach equilibrium, followed by centrifugation at 5500 rpm. The supernatants were analysed by UV-Spectrophotometer (UV-1208 Shimadzu) of a wave length (λ) of 259 nm (for nitrobenzene) and 280 nm (for aniline). The adsorbed amount was calculated as

$$\Gamma = (C_i - C_e) \cdot a / m \quad (i)$$

where Γ is the amount adsorbed (mg g⁻¹), a is the supernatant volume (l), C_i and C_e , respectively, are the initial and equilibrium concentrations of NOC (mg l⁻¹) and m is the amount of sorbent (g).

Column Tests

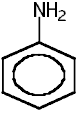
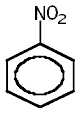
In the column tests, zeolite crushed to 1-2 mm particle size was washed with tap water and dried at 100 °C for 4 h. A sample of 300 g dry zeolite was taken and placed into a Fibreglas column of 3 cm in diameter and 100 cm in length. The HDTMABr solution of 70 mg l⁻¹ prepared in distilled water was fed into the column from the top by a peristaltic pump at an average flow rate of 64 ml min⁻¹ at its natural pH of 7.5-8.5 at room temperature. Effluent samples were collected at the bottom of the column at every 0.5 h in the first 2 hours and then at one hour intervals through 25 hours. The samples were analysed for HDTMA using the two phase titration method [34]. The HDTMA-treated zeolite (OZ) was then used for the capture of NOCs.

Aniline or nitrobenzene solution of 30 mg l⁻¹ NOC was placed into the feed tank and fed from the top of the column containing the OZ at an average flow rate of 64 ml min⁻¹ at its natural pH at room temperature. Samples taken from the effluent were analysed by UV-spectrophotometer. The breakthrough curves for NOCs/OZ system were constructed by plotting the number of bed volumes (BV) passing through the column versus C/C₀. Bed Volume is defined as;

$$BV = f \cdot t / V \quad (ii)$$

where f is the flowrate of feed solution (ml min⁻¹ or m³ min⁻¹), t is the appearance time (min), V is the fixed bed volume including the voids (m³) and C_0 and C are the column influent and column effluent concentrations of the substance (mg l⁻¹).

Table 1. Some properties of nonionic organic contaminants.

Non-ionic organic contaminants	Solubility in water at 25 °C (g l ⁻¹)	Partitioning coefficient in octanol-water (K _{ow}) [26,33]	Permitted maximum threshold values in wastewaters (mg l ⁻¹)	Molecular structure
Aniline	3.6	7.9	2	
Nitrobenzene	1.9	70.8	1	

Batch Adsorption

Figure 1 shows the adsorption curves of aniline and nitrobenzene for both natural zeolite (NZ) and organo-zeolite. The adsorption capacity of NZ with aniline remains nil at all equilibrium concentrations, while that of OZ increases almost linearly with increasing nitrobenzene concentration. At 500 mg l⁻¹ of equilibrium aniline concentration, the adsorption density reaches 4.5 mg per gram of OZ and at 1000 mg l⁻¹ it reaches 8 mg per gram of OZ. For nitrobenzene, the adsorption capacity of natural zeolite at 100 mg l⁻¹ is 1 mg g⁻¹ and reaches 2.5 mg g⁻¹ at 300 mg l⁻¹ above which it remains constant at this capacity. However, the adsorption capacity of nitrobenzene on OZ rises sharply with increasing the equilibrium concentration of nitrobenzene. It is interesting to note that the adsorption curves of OZ exhibits a linear character indicative of partitioning (non-competitive) adsorption mechanism of NOCs, as will be explained later. It is also evident that the uptake of nitrobenzene on OZ is higher than that of aniline. As illustrated in Figure 2, the adsorption of NOCs on NZ is marginal; it is assumed that, this results from the hydrophilic character of NZ surface due to the release of such cations as Ca²⁺, K⁺, Na⁺, Mg²⁺ and their subsequent adsorption on the surface or in the crystal structure. Because, these cations have high hydration energy [35,36] their hydrated form adsorb onto natural zeolite surface and thus prevent the adsorption of hydrophobic NOCs. But

nitrobenzene molecules which have more hydrophobic character than aniline (Solubility in water: 1.9 g l⁻¹ for nitrobenzene, 3.6 g l⁻¹ for aniline, Table 1) can interact with hydrophobic siloxane (Si-O-Si) groups on the zeolite surface and thus lead to little adsorption of zeolite. It is known from the literature that aromatic NOCs of hydrophobic structure can adsorb onto natural clay minerals by means of their siloxane groups [37,38].

The linear character of aniline and nitrobenzene adsorption on OZ (see Fig. 1) is in line with the literature reports on aniline adsorption onto HDTMA-treated zeolite [15] and HDTMA-treated bentonite [16], and this indicates that the adsorption of NOCs occurs through partitioning mechanism. It is reported that the partitioning mechanism operates on the basis of interaction of various NOCs with clay minerals and zeolites [17,23,24,26,28,33,39]. As shown in Figure 2 a, hydrophilic zeolite surface can be modified by adsorbed HDTMA layer(s) forming an organic pseudophase (or hydrophobic phase) at the zeolite surface which behaves as a powerful partition medium in the uptake of NOCs from water. Accordingly, the hydrophobic interactions between the NOC and HDTMA molecules of long hydrocarbon chain are controlled mostly by van der Waals forces, and consequently the NOCs are captured by OZ. The adsorption mechanism of NOCs onto organo-clays with organic cations of long hydrocarbon chain is characterized by partitioning mechanism, while that with organic cations of short hydrocarbon chain (or small aromatic organic cations) is driven by competitive sorption mechanism [23,24].

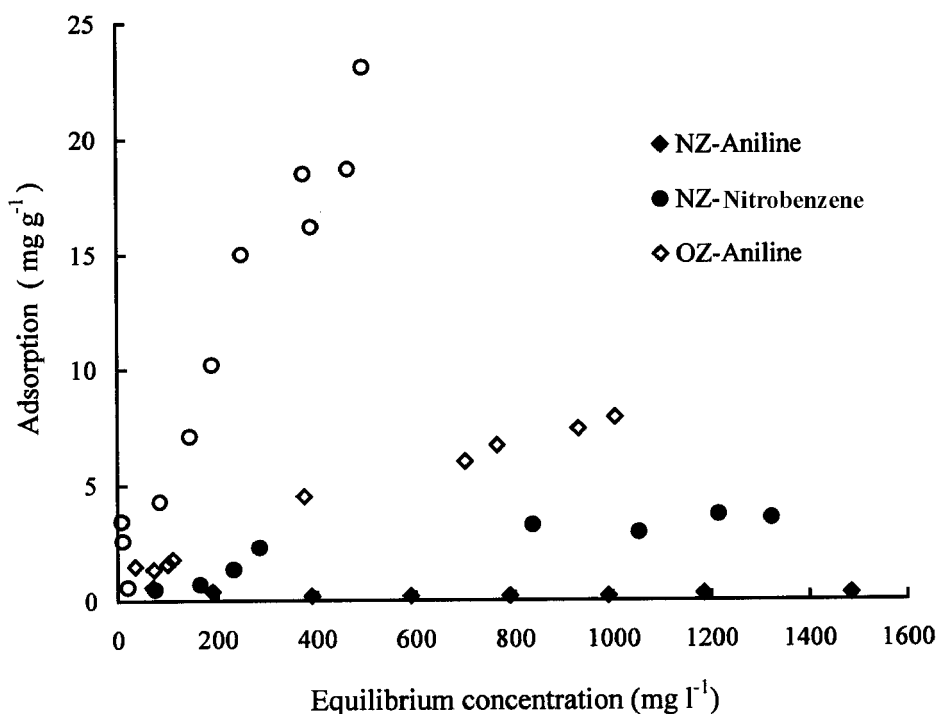


Figure 1. Adsorption of NOCs, aniline and nitrobenzene, by natural- and organo-zeolite.

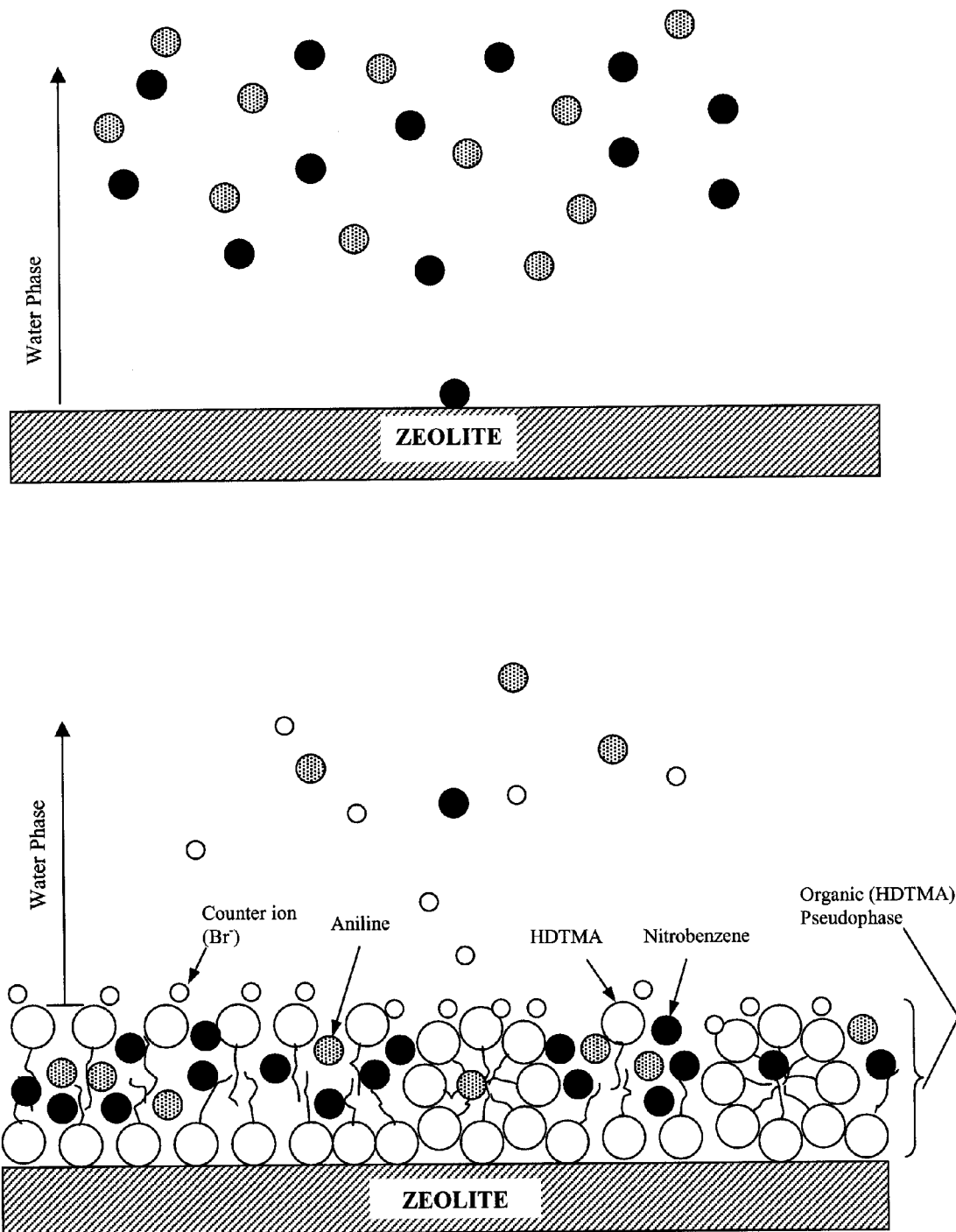


Figure 2. Schematic illustration of adsorption of NOCs on to organo-zeolite.

On the other hand, the organic carbon content of natural sorbent (i.e. soil, clay) has been repeatedly correlated to the sorption of NOCs from water [24]. Consequently, OZ adsorbs easily the NOCs from water due to their high organic carbon content (4.96 %). However, the literature [40] shows that surfactant-modified zeolite prepared at the bilayer HDTMA sorption on zeolite is stable in aqueous and

nonaqueous medium. Accordingly, in the present study OZ was prepared in 2×10^{-4} mol HDTMA per g of zeolite indicative of bilayer and micel sorption of HDTMA on the zeolite surface [41], as seen in Figure 2. Another study reported that aniline adsorption onto HDTMA modified zeolite [15] at bilayer coverage yields an aniline uptake of ~ 2.7 mg g⁻¹; this is lower than our results which occurred at bilayer

and micellar modification (5 mg g⁻¹). This difference is attributed to the experimental conditions of particle size and zeolite purity. While these are respectively 0.4-1 mm and 74 % in the work of Li et al. (15), they are -0.1 mm and 92 % in the present study.

As seen in Figure 1, there is a steady increase rather than a sharp increase in the uptake of NOCs onto OZ; this is a typical indicator of partitioning (non competitive) sorption mechanism. However, the sorption of nitrobenzene is larger than that of aniline due to the differences in their solubility and partitioning coefficient values given in Table 1. Partitioning mechanism is defined as the tendency or preference of a surfactant (or compound) between two different phases (i.e., water and organic) and this preference can be characterised by a term “partition coefficient or distribution coefficient” [42,43]. That is, the weight of fraction of solute in the organic phase (C_{org}) divided by the weight of fraction of solute in the water phase at equilibrium. The partition coefficient (K) is dependent on pH, salinity, and ionic strength in the water phase [42]. The octanol-water partitioning coefficient (K_{ow}) of nitrobenzene is 70.8 while that of aniline is 7.9 [26, 33]. Also the solubility of nitrobenzene is lower than that of aniline in water at 25 °C (Table 1) . Both the solubility and partitioning coefficient values indicate that aniline is more conducive to remain in the water phase instead of organic (HDTMA) phase than nitrobenzene. Therefore, aniline adsorption onto OZ is lower than nitrobenzene adsorption as seen in Figure 2. Also, similar results with aniline and nitrobenzene adsorption onto organobentonite have been obtained [26].

In general, a large body of experimental results originating from van der Waals adsorption or physical adsorption can be expressed by means of the Freundlich equation [44]. The adsorption isotherms in Figure 1 can be characterized by the linear form of Freundlich equation as

$$\ln \Gamma = \ln \kappa + 1/n \ln C_e \quad (iii)$$

where κ and n are the empirical parameters depending on the nature of solid and adsorbate, and determined from the intercept and the slope of the line, respectively (Table 2).

Table 2. Freundlich parameters (κ , n) in the adsorption of aniline and nitrobenzene onto NZ and OZ.

Solute (NOC) / Adsorbent	κ	n
Nitrobenzene/ Organo-Zeolite	1.2535	2.4160
Aniline /Organo-Zeolite	0.1306	1.6998
Nitrobenzene/ Zeolite	0.0288	1.4573

The large κ parameter describing nitrobenzene adsorption by OZ, from which the adsorption free energy is calculated, shows that the ability of nitrobenzene adsorption onto OZ is better than that of aniline.

Column Tests

In order to see the ability of NOCs to adsorb onto HDTMA-treated zeolite in a continuous (dynamic) system, column tests were performed. It must be noted that the HDTMA-treated zeolite (or organo zeolite) was prepared by means of passing the HDTMA solution through a fixed bed of natural zeolite column for 27 h. That is, the 1-2 mm OZ used in the column tests is not the same as the one (-0.1 mm in size) used in the batch tests.

As shown in Figure 3, the breakthrough curves in the column tests have been constructed for HDTMA adsorption onto natural zeolite and for NOCs/HDTMA-treated zeolite.

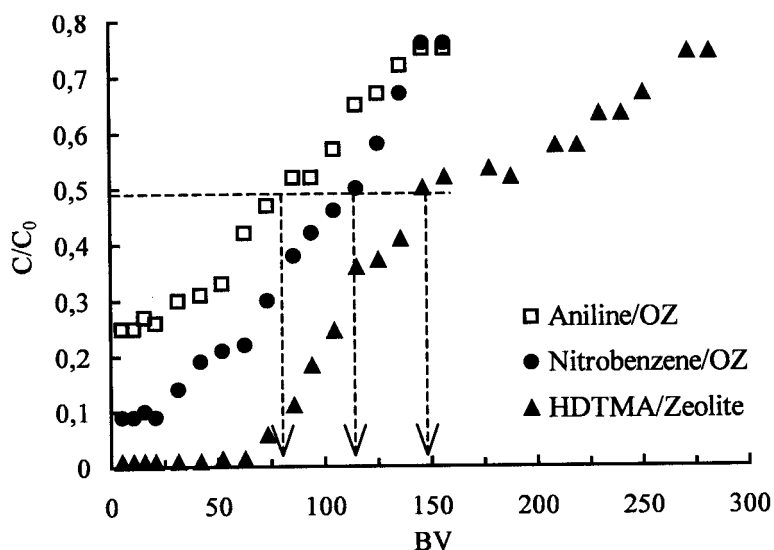


Figure 3. Breakthrough curves for HDTMA/zeolite, nitrobenzene/OZ and aniline/OZ systems.

Unlike batch systems there is not a static equilibrium of sorption process and the position of equilibrium is always changing [45,46]. The shape of the breakthrough curve, also the mass transfer of a substance, depends on factors such as flow rate, particle diameter of solid phase, feed concentration of the substance in solution, solution pH and temperature [1,46]. Figure 3 clearly shows that, up to 62.68 BV (or 6 h) the HDTMA⁺ ions (C_0 , is 70 mg l⁻¹) in solution fed into the column are adsorbed by the zeolite bed, that is, the HDTMA concentration of effluent solution (C) is 0.65 mg l⁻¹. The breakpoint occurs at 62.68 BV, above which the HDTMA concentration (C) in the effluent solution increases. At the end of the 27 hours of operation (282 BV) the C/C₀ reaches 0.75 and remains constant beyond it. The total HDTMA adsorption capacity of the zeolite bed was calculated approximately as 12.54 mg HDTMA per gram of zeolite using equation (iv) suggested by Ames [1]:

$$\Gamma = V_b \times C_0 / W_b \quad (\text{iv})$$

in which V_b is the volume of effluent solution to the BV value corresponding to the "C/C₀ = 0.5" point (I), W_b is the weight of the zeolite bed (g) in the column and C_0 is the influent concentration of substance (mg l⁻¹). For instance, for HDTMA adsorption V_b is 53.76 l at C/C₀ = 0.5, W_b is 300 g and C_0 is 70 mg l⁻¹.

The adsorption capacity of 12.54 mg HDTMA/g-zeolite obtained from the column test is very low in comparison to that of 56.9 mg HDTMA per g-zeolite (or 2×10^{-4} mol HDTMA per g-zeolite) obtained from the batch tests [41]. This may partially result from the large particle size of zeolite used in the column and also of the method applied to obtain OZ. Because HDTMA⁺ ions can exchange only with the external cations of zeolite, the larger particle size may result in the lower external cation exchange capacity. Apart from the cation exchange, the other adsorption mechanism for HDTMA/zeolite system is hydrophobic (chain-chain) interaction [41,47]. Accordingly, it is assumed that the HDTMA adsorption onto zeolite can change with particle size as pointed out by Ames [1] for Cs⁺/Clinoptilolite system. However, dynamic equilibrium conditions in the column system and static equilibrium conditions in the batch system can affect differently the adsorption of HDTMA on natural zeolite.

Although there are a number of column studies in the literature relevant to the removal of ionic contaminants such as heavy metals, ammonium, radioactive metals from water by zeolite [1,8,47,48], only one has been found on the NOCs adsorption on sorbents modified by surfactants or organic compounds; this is polyoxyethylated nonylphenols adsorption on HDTMA-treated soil materials [27]. They demonstrated that polyoxyethylated nonylphenols can be effectively removed from water by a HDTMA-treated soil in column. It is clear that the results obtained about the NOC

adsorption on OZ is not as good as expected because the breakpoints for both aniline and nitrobenzene occur very fast. For both aniline and nitrobenzene, the C/C₀ values of 20.9 BV are 0.25 and 0.1, respectively. After the 15 h (156 BV) of operation the effluent concentrations of aniline and nitrobenzene reached 22.13 and 22.87 mg l⁻¹, respectively. Aniline and nitrobenzene adsorption capacity of OZ were approximately calculated using equation (iv). But it must be noted that for influent concentrations (C_0) of aniline and nitrobenzene respectively, 22.5 (this value was determined by subtraction of 0.25 C_0 from C_0 , C_0 is 30 mg l⁻¹) and 27 mg l⁻¹ (this value was determined by subtraction of 0.10 C_0 from C_0 , C_0 is 30 mg l⁻¹) were used instead of the original feed concentration of NOCs, 30 mg l⁻¹. Subsequently, the approximate adsorption capacity of OZ bed for aniline and nitrobenzene were determined as 2.36 and 3.25 mg per gram of OZ, respectively. As seen, the effective amount of nitrobenzene adsorption onto OZ is higher than the aniline according to the differences in their partitioning mechanism explained above.

It is clear that the differences between the results obtained from column tests and those from batch experiments are significant. That is, under the experimental conditions the adsorption of NOCs per gram of OZ in a continuous system is much lower than that in the batch system. This is attributed to the improper modification of zeolite surface by HDTMA in the column. In other words, the required amount of HDTMA to adsorb NOCs in the organic phase at the zeolite surface is not sufficient. In addition, HDTMA sorption on zeolite in dynamic equilibrium conditions in the column system and static equilibrium conditions in the batch system can affect the adsorption of NOCs onto OZ differently.

CONCLUSIONS

The results demonstrate that HDTMA-treated zeolite (or organo-zeolite) is an effective sorbent for NOCs (aniline and nitrobenzene) while the natural zeolite can not be used for the uptake of NOCs from water.

Partitioning mechanism is responsible for NOC adsorption onto organo-zeolite and the effectiveness of this mechanism significantly depends on the hydrophobic properties of NOC molecules (i.e., its solubility in water, partitioning coefficient in octanol-water phases) and sorbent's organic carbon contents. The test methods of sorption (batch or continuous test methods) and the physical parameters i.e., particle size of the sorbent used are also important for this mechanism.

The column studies reveal that the adsorption of aniline and nitrobenzene onto OZ under the present study is respectively determined as 2.36 and 3.25 mg per gram of OZ. The lower adsorption probably results from the improper HDTMA modification of the zeolite surface in the column.

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