

Sorption of Nonionic Organic Contaminants by Organo-Zeolite

B.Ersoy & E.Sabah

Afyon Koçţlepe University, Engineering Faculty, Afyon, Turkey

U.Mart & M.S.Çelik.

Istanbul Technical University, Mining Faculty, Istanbul, Turkey

ABSTRACT: Adsorption mechanisms of non ionic organic contaminants (NOCs), aniline and nitrobenzene, which are present in wastewater or underground water were investigated with natural-zeolite and organo-zeolite (OZ) in both batch and continuous systems. Adsorption capacities of aniline and nitrobenzene onto natural zeolite surface is very low or almost zero for the case of aniline but when the zeolite surface was modified by hexadecyltrimethylammonium (HDTMA) its adsorption capacity increased significantly. Partitioning mechanism is responsible for the adsorption of NOCs onto OZ. The effectiveness of partitioning mechanism is directly associated with hydrophobic properties of the NOCs. The adsorption of nitrobenzene on OZ is found to be higher than that of aniline.

1 GENERAL INSTRUCTIONS

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 (Ames, 1960; Breck, 1974; Mumpton, 1978; Blanchard, 1984; Hlavay et al., 1983; Sirkecioglu et al., 1995). Organo-zeolite (OZ) or modified zeolite is the modified form of natural zeolite in which zeolite surface is covered with cationic surfactants like HDTMA. OZ is also used for adsorbing non ionic organic contaminants (NOCs) in water e.a., benzene, naphthalene, toluene, (Neel, 1992; Li and Bowman, 1998; Li et al., 2000; Huttenlocher et al., 2001), inorganic anionic contaminants such as Chromate, selenate (Haggerty and Bowman, 1994; Sullivan et al., 1998), various anionic dye molecules (Özdemir et al., 2002). In addition to modified zeolite minerals, a number of modified clay and modified earth minerals have been also used in the adsorption of NOCs (Lee et al., 1989; Smith et al., 1990; Gitipour et al., 1997). The literature results indicate that adsorption capacity of natural zeolite, clay and earth minerals for NOCs is nil or very low, but become 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 (Gitipour et al., 1997). They have harmful effects on the health of human and other lives. The maximum threshold values for aniline

and nitrobenzene in water are 2 and 1 ppm, respectively (Budavari, 1989; Lewis and Nowstand, 1991). In the present paper, 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.

2 MATERIALS AND METHODS

The natural adsorbent zeolitic tuff from the Gördes region of Turkey (hereafter will be referred to as zeolite) assaying about 92 percent clinoptilolite was used. The detailed properties of clinoptilolite are given elsewhere (Ersoy and Çelik, 2003). For the modification of zeolite surface, HDTMABr [$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$, 99% purity, Sigma] was used. Aniline [$\text{C}_6\text{H}_5\text{NH}_2$, 99% purity, Panreac] and nitrobenzene [$\text{C}_6\text{H}_5\text{NO}_2$, 99% purity, Merck] were used as NOCs with some properties given in Table 1.

2.1 Preparation of organo-zeolite for batch tests

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 L beaker and 1 L of HDTMABr solution of 2×10^{-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 (Hetiich 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.

Table I Some properties of nonionic organic contaminants

Nonionic organic contaminants	Solubility in water at 25 °C (g /L)	Partitioning coefficient in octanol-water (K_{ow})	Molecular Structure
Anilin 	3.6	7.9	
Nitrobenzene 	1.9	70.8	

2.2 Adsorption tests in hatch system

First, stock solutions of 1500 mg/L of aniline and nitrobenzene were prepared with distilled water. Aniline and nitrobenzene solutions of 10 mL at different concentrations in the range of 100-1500 mg/L 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 an equilibrium, followed by centrifugation at 5500 rpm. The supernatants were analysed by UV-Spectrophotometer (UV-1208 Shimadzu). The adsorbed amount was calculated from the difference between initial and equilibrium concentrations of NOCs in solution.

2.3 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 70 mg/L of HDTMABr solution 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 at its natural pH of 7.5-8.5 at room temperature. Samples

were collected from the effluent at the bottom of the column at every 0.5 h in the first 2 hours and then in one hour intervals through 25 hours. The samples were analysed for HDTMA using the two phase titration method (Ersoy and Çelik, 2003). The HDTMA-treated zeolite (OZ) was then used for the capture of NOCs.

Aniline or nitrobenzene solution of 30 mg/L NOC was placed into the feeding tank and fed from the top of the column containing the OZ at an average flow rate of 64 mL/min 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/C_0 .

$$V = f \cdot t / V \quad (1)$$

Where f is the flowrate of feed solution (mL/min or m³/min), t is the appearance time (min), V is the fixed bed volume including the voids (m³) and C and C_0 are the column influent and column effluent concentrations of the substance (mg/L).

3 RESULTS AND DISCUSSION

3.1 Adsorption

Figure 1 shows the adsorption curves of aniline and nitrobenzene, with 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 nitrobenzene concentration. At 500 mg/L of equilib-

rium aniline concentration the adsorption density reaches 4.5 mg per gram of OZ and at 1000 mg/L it reaches 8 mg per gram of OZ. For nitrobenzene, the adsorption capacity of natural zeolite at 100 mg/L is 1 mg/g and reaches 2.5 mg/g at 300 mg/L above which it remains constant at this capacity. However, the adsorption capacity of nitrobenzene on OZ rises sharply to high levels of adsorption density with

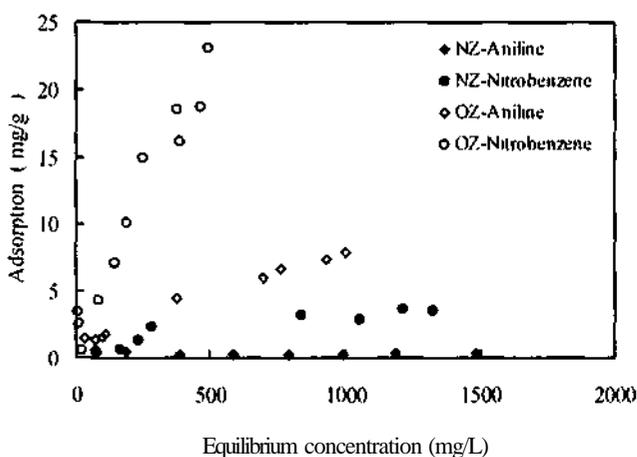


Figure 1 Adsorption of NOCs, aniline and nitrobenzene, by natural- and organo-zeolite.

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. Also, it is also evident that the uptake of nitrobenzene on OZ is higher than that of aniline. It is assumed that, this results from the hydrophilic character of NZ surface due to the release of such cations as Ca^{2+} , K^+ , Na^+ , Mg^{2+} and their subsequent adsorption on its surface or in its crystal structure. Because, these cations have high hydration energy (Atkins, 1994; Sheng and Boyd, 1998) they adsorb water molecules in aqueous solution. These water molecules bonded to natural zeolite surface prevent the adsorption of hydrophobic NOCs onto the zeolite surface. 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 (Jaynes and Boyd, 1991; Stevens et al., 1996).

The linear character of aniline and nitrobenzene adsorption on OZ (see Fig. 1) is in line with the lit-

erature reports on aniline adsorption onto HDTMA-treated zeolite (Li et al., 2000) and this indicates that the adsorption of NOCs occurs through partitioning mechanism. It is reported in the literature that partitioning mechanism operates on the basis of interaction of various NOCs with clay minerals (Li and Bowman, 1998; Hultenloch et al., 2001; Lee et al., 1989; Smith et al., 1990; Zhu et al., 1997; 2000; Jaynes and Vance, 1999; Bowman et al., 2000). The hydrophobic interactions between the NOC and HDTMA molecules of long hydrocarbon chain are controlled mostly by Van der Waals forces. The adsorption mechanism of NOCs onto organo-clays with organic cations of large HC chain is characterized by partitioning mechanism, while that with organic cations of small HC chain (or small aromatic organic cations) is driven by competitive sorption mechanism (Lee et al., 1989; Smith et al., 1990).

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 "partitioning coefficient or distribution coefficient" (Perry and Green, 1984; Standal et al., 1999). 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 is called the partitioning coefficient (K) which is dependent

on pH, salinity, and ionic strength in the water phase (Standal et al., 1999). As seen in Figure I, 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. The octanol-water partitioning coefficient (K_{ow}) of nitrobenzene is 70.8 while that of aniline is 7.9 (Zhu et al., 1997; 2000). Also the solubility of nitrobenzene is 1.9 g/L and that of aniline is 3.6 g/L in water at 25 °C. Both the solubility

and partitioning coefficient values indicate that the 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.

3.2 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

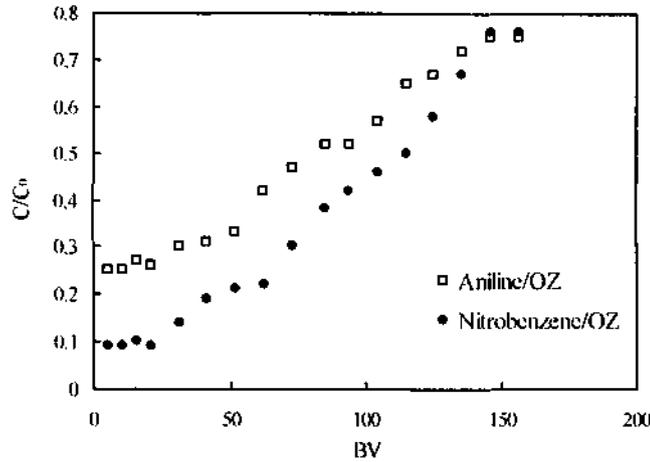


Figure 2 Breakthrough curves for nitrobenzene/OZ and aniline/OZ systems

prepared by means of passing the HDTMA solution through a fixed bed of natural zeolite column for 27 hours. That is, the OZ (1-2 mm in size) 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 2, the breakthrough curves in the column tests have been constructed for NOCs/HDTMA-treated zeolite. Unlike batch systems there is no static equilibrium of sorption process and the position of equilibrium always changes (Harland, 1994). 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 (Ames, 1960; Harland, 1994).

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 (Ames, 1960; Hlavay et al., 1983; Zhao et al., 1998; Mier et al., 2001), only one has been found on the NOCs adsorption onto sorbents modified by surfactants (or organic compounds). This is polyoxyethylated nonylphenols adsorption on HDTMA-treated soil

materials (Hayworth and Burris, 1997) who demonstrated that a NOC surfactant can be removed from water by a surfactant-enhanced sorbent zone. It is clear that the results obtained about the NOC adsorption on OZ is not as good as expected because the break points for both aniline and nitrobenzene occur rather sharp (Figure 2). For both aniline and nitrobenzene, the C/C_0 values at 20.9 BV are 0.25 and 0.1, respectively. After the 15 hours (156 BV) of operation the effluent concentrations of aniline and nitrobenzene reach 22.13 and 22.87 mg/L, respectively. Aniline and nitrobenzene adsorption capacity of OZ were calculated approximately using equation (2) as suggested by Ames (1960).

$$r = V_b \times C_0 / W_b \quad (2)$$

In which V_b is the volume of effluent solution corresponding to the BV value at " $C/C_0 = 0.5$ " point (L), W_b is the weight of the zeolite bed (g) in the column and C_0 is the influent concentration of substance (mg/L).

But it must be noted that for influent concentration (C_0) of aniline and nitrobenzene respectively, 22.35 (this value was determined by subtraction of 0.25 C_0 from C_0 , C_0 is 30 mg/L) and 27.17 mg/L

(this value was determined by subtraction of 0.10 C_o, from e_o, Co is 30 mg/L) were used instead of the original feed concentration of NOCs, 30 mg/L . Subsequently, the approximate adsorption capacity of OZ bed for aniline and nitrobenzene were determined as 2.15 and 3.83 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 the effectiveness of their partitioning mechanism explained above.

It is clear that the differences between the results obtained from the column tests and those from batch experiments are very 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. It is assumed that the main reason for this is that the modification of zeolite surface by HDTMA in column is not made properly. In other words, the required amount of HDTMA to adsorb NOCs in the organic phase at the zeolite surface is not sufficient. In addition, dynamic equilibrium conditions in the column system and static equilibrium conditions in the batch system can affect the adsorption of NOCs onto OZ.

4 CONCLUSIONS

Adsorption capacity of natural zeolite is nil for aniline and 2.5 mg/g for nitrobenzene. When zeolite surface was modified by organic cation (HDTMA), its adsorption capacity for aniline and nitrobenzene reached 4.5 and 23 mg/g at 500 mg/L of NOC equilibrium concentration, respectively

The column studies reveal that the adsorption of aniline and nitrobenzene onto OZ under the present study was determined as 2.15 and 3.87 mg per gram of OZ.

Partitioning mechanism is responsible for NOC adsorption onto organo-zeolitic but the effectiveness of this mechanism largely depends on the hydrophobic properties of NOC molecules (i.e., its solubility in water, partitioning coefficient in octanol-water phases) and also the manner in which sorption tests (batch or continuous test methods) are conducted.

REFERENCES

- Ames t. L. 1960. The cation sieve properties of clinoptilolite. *Am.Min.* 45. 689-700
- Ames L.L. 1962 Effect of base cation on the cesium kinetics of clinoptilolite. *Am. Min.Al.* 1310-1316.
- Atkins A. 1994. *Physical Chemistry* (fifth edition). Oxford University Press. pp.55-90
- Blanchard G. 1984. Maunaye M. and Martin G.. Removal of heavy metals from waters by means of natural zeolites. *Wat. Res.* 18.110.12. 1501-1507.
- Bowman R.S., Sullivan E.J. and Li 7., 2000. Uptake of cations, anions, and nonpolar organic molecules by surfactant-modified clinoptilolite-rich tuff. In: *Natural Zeolites For Third Millennium*. Colella C. and Mumpton F.A. (eds.) De Frede Editore. Napoli, pp 287-297.
- Breck D. W. 1974. *Zeolite Molecular Sieves*. John Wiley. New York. pp. 1-19.
- Budavan S. (editor) 1989 *The Merck Index*, Merck co. Inc., USA
- Ersoy. B. and Çelik. M.S. 2003. effect of hydrocarbon chain length on adsorption of cationic surfactants onto clinoptilolite. *Clays and Clay Min.* 51.2. 173-181.
- Gitipour S., Bowers M.T. Bodocsi A. 1997. The use of modified bentonite for removal of aromatic organics from contaminated soil. *J. Colloid and Interface Sci.* 196. 191-198.
- Haggerty G.M. and Bowman R.S. 1994. Sorption of eliminate and other inorganic anions by organo-zeolite. *Environ. Sci. Technol.* 28.452-458.
- Harland C.F.. 1994. *Ion Exchange Theory and Practice* (second edition). The Royal Society of Chemistry. Cambridge, pp. 1-18.
- Hayworth J.S and Burns D.R. 1997. Nonionic surfactant-enhanced solubilization and recovery of organic contaminants from within cationic surfactant-enhanced sorbent zones. 1. experiments. *Environ. Sci. Technol.* 31. 1277-1283.
- Hlavay J., Vigh G., Olusu V. and Inczedy, J. 1983. Ammonia and iron removal from drinking water with clinoptilolite tuff. *Zehntes. T.* 188-190(1).
- Huttenlocher P., Roehl K. A. and Czurda K. 2001. Sorption of nonpolar aromatic contaminants by chlorosilane surface modified natural materials. *Environ. Sci. Technol.* 35. 4260-4264.
- Jaynes W.F. and Boyd S.A. 1991. Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays and Clay Minerals*. 39, 428-436
- Jaynes W.F. and Vance G.F. 1999. Sorption of benzene, toluene, ethylbenzene, and xylene (BTEX) compounds by hectorite clays exchanged with aromatic organic cations. *Clays and Clay Minerals*. 47. 358-365.
- Lee J.F., Cram J.R. and Boyd S.A. 1989. Enhanced retention of organic contaminants by soil exchanged with organic cations. *Environ. Sci. Technol.* 23.1365-1372.
- Lewis R., I. and Nowstand R. (ed.s) 1991. *Hazwibom Remedial Desk Reference*, New York.
- Li Z., Burt T. and Bowman R.S. 2000. Sorption of ionizable organic solutes by surfactant-modified zeolite. *Environ. Sci. Technol.*, 34. 3756-3760.
- Li Z. and Bowman R.S. 1998. Sorption of perchloroethylene by surfactant-modified zeolite as controlled by surfactant loading. *Environ. Sci. Technol.* 32.2278-2282.
- Mier M.C., Callejas R.L., Gehr R., Cisneros B.E.J., and Alvarez P.I. 2001. Heavy metal removal with Mexican clinoptilolite multi-component ionic exchange. *Wat Res.* 35. 373-378.
- Mumpton F.A. 1995. Natural zeolites: a new industrial mineral commodity. In: *Natural Zeolites: Occurrence, Properties and Use*. Sand L.B. and Mumpton F.A. (eds). pp. 1-27.

- Pergamon Press.Oxford (1978) Sirkecioğlu A. Altav Y. and Erdem-Şenatalar A. Adsorption of H₂S and SO₂ on Bigadiç Clinoptilolite. *Sel. and Tech.M*: 2447-2762.
- Neel D. 1992. Quantification of BTX sorption to surface-altered zeolites. Hydrology Open File Report No:H92-2. New Mexico Institute Of Mining and Technology.
- Özdemir O. Bentli I, Ersoy B. and Sabah fi. 2002 Utilization of porous minerals in the abatement of dyes in textile wastewaters. In: *11th International Conference Environmental Problems Of The Mediterranean Region*. Gokcekus H.(ed.).12-15 April. Neu Nicosia- Northern Cyprus.
- Perry R.H and Green D.W. (eds.) 1984. Perry's Chemical Engineers' Handbook. McGraw-Hill Inc. NewYork.
- Sheng G and Boyd S.A 1998. Relation of water and neutral organic compounds in the outer layers of mixed Ca/trimethylphenylammonium-smectites. *Clays and Clay Mineral*. Ab.* 10-17.
- Smith J.A. Jaffe P.R. and Chiou C.T. 1990. Effect of ten quaternary ammonium cations on tetrachloromethane sorption to clay from water. *Environ. Sei. Technol.* 24. 1167-1172.
- Stevens J.J., Anderson S.I. and Boyd S.A 1996. FTIR study of competitive water-arene sorption on tetramethylammonium- and trimethylammonium-montmorillonites. *Clays and Clay Minerals*. 44. 88-95.
- Standai S.H., Blokhus A.M., Haavik J., Skauge A. and Barth T. 1999. Partition coefficients and interfacial activity for polar components in oil/water model systems. *J.Colloid and Interface Sci.* 212. 13-41.
- Sullivan K.J., Hunter D.B. and Bowman R.S. 1998. Fourier transform infrared spectroscopy of sorbed HDTMA and the mechanism of Chromate sorption to surfactant-modified clinoptilolite. *Environ. Sei. Technol.* 32 :1948-1955.
- Zhao D., Cleare K., Oliver C., Ingram C., Cook D., Szostak R. and Kevan L. 1998. Characteristics of the synthetic heulandite-clinoptilolite family of zeolites. *Microporous and Mesoporous Materials*. 21. 371-379.
- Zhu L., Li Y. and Zhang J.. 1997. Sorption of organobentonites to some organic pollutants in water. *Environ. Sei. Technol.* 31.1407-1410.
- Zhu L., Chen B. and Slien X. 2000. Sorption of phenol, p-nitrophenol, and ammonia to dual-cation organobentonites from water. *Environ. Sei. Technol.* 34. 468-475.