Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption of Nitrobenzene from Water onto High Silica Zeolites and Regeneration by Ozone

J. Reungoat[a]; J. S. Pic[a]; M. H. Manéro[b]; H. Debellefontaine[a]
[a] Département GPE, Laboratoire d'Ingénierie des Procédés de l'Environnement, Institut National des Sciences Appliquées de Toulouse, Toulouse Cedex, France [b] Laboratoire de Génie Chimique, IUT Paul Sabatier GCGP, Toulouse Cedex, France

To cite this Article Reungoat, J. , Pic, J. S. , Manéro, M. H. and Debellefontaine, H.(2007) 'Adsorption of Nitrobenzene from Water onto High Silica Zeolites and Regeneration by Ozone', Separation Science and Technology, 42: 7, 1447 — 1463
To link to this Article: DOI: 10.1080/01496390701289948
URL: http://dx.doi.org/10.1080/01496390701289948

Separation Science and Technology, 42: 1447–1463, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701289948

Adsorption of Nitrobenzene from Water onto High Silica Zeolites and Regeneration by Ozone

J. Reungoat and J. S. Pic
Institut National des Sciences Appliquées de Toulouse, Département GPE, Laboratoire d'Ingénierie des Procédés de l'Environnement, Toulouse Cedex, France

M. H. Manéro
IUT Paul Sabatier GCGP, Laboratoire de Génie Chimique, Toulouse Cedex, France

H. Debellefontaine
Institut National des Sciences Appliquées de Toulouse, Département GPE, Laboratoire d'Ingénierie des Procédés de l'Environnement, Toulouse Cedex, France

Abstract: This work investigates the removal of nitrobenzene (NB), a model pollutant from water, by combining adsorption onto zeolites and regeneration with ozone. The adsorption equilibrium isotherms of NB onto zeolites enabled the best adsorbent to be selected and zeolites with a high Si/Al ratio were the most efficient. The adsorption capacity depended on the Si/Al ratio and on the pore size. In a sequential process coupling adsorption and oxidation by ozone, NB was completely removed from water and the initial adsorption capacity of the zeolite was totally restored. Although

Received 10 October 2006, Accepted 15 January 2007
Address correspondence to H. Debellefontaine, Institut National des Sciences Appliquées de Toulouse, Département GPE, Laboratoire d'Ingénierie des Procédés de l'Environnement, 135 avenue de Rangueil, 31077 Toulouse Cedex, 4, France. E-mail: Hubert.debellefontaine@insa-toulouse.fr

no catalytic effect was noticed, the adsorption produced locally high concentrations, thus enhancing the oxidation rate for NB.

Keywords: Adsorption, high silica zeolite, nitrobenzene, organic pollutants, ozonation, refractory compounds, wastewater

INTRODUCTION

Biological processes are often used in wastewater treatment because they can economically degrade a wide range of compounds. However, toxic organic compounds, like nitrobenzene (NB), cannot be reliably eliminated by this method. Nitrobenzene and its derivatives have a high number of target organs of toxicity (1) and the evidence of carcinogenicity of NB in experimental animals is established by the IARC (1). Cattley (2) recommended that the occupational exposure limit to NB should be only 0.2 ppm. Nitrobenzene is soluble in water ($1.9\ g \cdot L^{-1}$) and most studies (3) report that biodegradation is completed only after 7 to 10 days, a value incompatible with most of the wastewater treatment plants. Finally, the European Union Directive 2001/59/EC states that NB is "toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment." So, other treatments, such as adsorption or chemical oxidation, must be used to remove NB or similar molecules reliably.

Activated carbon is widely used in adsorption processes because of its great adsorption capacity and its affinity towards a large range of organic molecules. When activated carbon is saturated, it has to be regenerated or renewed, which is rather an expensive operation. The adsorbed molecules are then released and still have to be destroyed by an additional treatment. Moreover, this thermal treatment also degrades the activated carbon adsorption properties in the long term.

Another way to remove non-biodegradable molecules is to destroy them via in situ chemical oxidation. The most commonly used oxidant is ozone because it has a high oxidation potential and it does not remain in water. Moreover this process can be used continuously. Ozone decomposition proceeds either by a molecular mechanism or by a radical one. With regard to the molecular mechanism, ozone is a rather selective oxidant as some molecules do not react at all or do react slowly to the attack of ozone. It is the case of NB. Indeed, Hoigné and Bader (4) reported the value $0.09 \pm 0.02\ M^{-1} \cdot s^{-1}$ for the second order rate constant for direct reaction of NB with ozone O_3. On the other hand, ozone can decompose into non-selective hydroxyl radicals $OH^{\bullet}$, known as some of the most powerful oxidizing agents. Beltrán (5) obtained a value of $2.9.10^9\ M^{-1} \cdot s^{-1}$ for the indirect reaction rate constant of NB with hydroxyl radicals. In favorable cases, oxidation processes lead to the complete mineralization of the organic matter but, in practice, hydroxyl radicals are produced at very low concentration levels—in the order of 10^{-14} to 10^{-13} M—and mineralization often remains incomplete and by-products, which can be even more

dangerous for health or the environment than the original compound, are sometimes obtained.

Ozone decomposition into hydroxyl radicals is naturally favored (6) by hydroxydes anions OH^- resulting from a high pH. In order to increase the rate of decomposition and thus to enhance the efficiency of ozonation processes, various advanced oxidation processes (AOPs) have been developed. These processes aim at initiating or catalyzing ozone decomposition and a great number of studies have demonstrated their efficiency. In particular, heterogeneous catalysis is a promising method and zeolites can potentially be a catalytic agent.

Zeolites are porous crystalline aluminosilicates with various frameworks formed by SiO_4 and AlO_4 tetrahedrons connected by oxygen atoms. This crystalline structure gives the zeolites a uniform pore size, making zeolites different from other microporous adsorbents. Pore sizes are in the range of a few Å, allowing small molecules to enter the solid frame and excluding large molecules, thus making zeolites selective adsorbents. Moreover the mineral composition of zeolites makes them highly resistant to chemical agents such as acids and bases or to oxidants such as ozone. Zeolites are basically hydrophilic, but they turn hydrophobic (7) when the Si/Al ratio reaches eight or ten. Zeolites with high Si/Al ratios are called high silica zeolites and are known to have good adsorption properties for organic molecules (8, 9).

Previous studies have shown that organics could be oxidized by ozonated water faster when adsorbed onto zeolites than when not adsorbed, because of the micropore concentration effect (10, 11). For example, Sagehashi (11) reported that 2-methylisoborneol (MIB) was adsorbed onto USY high silica zeolite and determined that the concentration within the pores was about 10^7 greater than in the bulk liquid. In the gas phase, Monneyron (12) showed that high silica zeolites could catalyze ozone decomposition into radical species and that adsorption properties were not significantly modified after exposure to ozone. Hence, it is expected that zeolites could be used for two purposes: to adsorb nitrobenzene and, possibly, to catalyze the decomposition of ozone into active $OH^\bullet$ radicals. Zeolites should undergo regeneration by ozone without degradation of their structure or decrease in their adsorption capacity. Hence, this study investigates the coupling of ozone and zeolites of various types for nitrobenzene (NB) removal in water, and particularly the adsorption properties and the regeneration of the adsorbent.

MATERIALS AND METHODS

Nitrobenzene Solutions

This model pollutant was chosen because of its toxicity, its low biodegradability, and because it is highly refractory to ozone oxidation. 99.5% (Rectapur) nitrobenzene (NB) was purchased from VWR International and aqueous NB

solutions were prepared diluting a known amount of pure NB either in demineralized water or in a pH = 2.2 buffer solution. It was prepared by diluting 1.2 g NaH_2PO_4 per liter dematerialized water and pH was then adjusted to 2.2 by adding 85% H_3PO_4. This acidic buffer solution aims at preventing the self-decomposition of ozone that could hide the catalytic effect which is anticipated.

Adsorbents

The zeolites used in this study are commercially available (from Zeochem, Tosoh, and Tricat) in a powder form, with particle diameter below 10 μm. Two commercial (from Pica) activated carbons were also tested during this work. Both were available in a granular form (particle size in the range 1.5 to 2.0 mm) and they were mechanically crushed to 80 μm particles for the experimental requirements. Finally, a MCM-type material was also studied. This amorphous silica was synthesized on a lab-scale and characterized by a specialized laboratory: ENSCMu (Ecole Nationale Supérieure de Chimie—Mulhouse (France)). All adsorbents were dried overnight in an oven at 105°C before use and no other special treatment was applied. The major properties of these materials are summarized in Table 1. For all materials, the pore diameter is greater than the kinetic diameter of NB that was calculated at 5.9 Å using the Lennard-Jones theory (13), thus making adsorption possible.

Analytical Methods

The concentration of pure NB solutions was assessed by 267 nm UV-absorbance using a JascoV-530 spectrophotometer. Absorbance proved to be proportional to the NB concentration in the range 0 to 30 $mg \cdot L^{-1}$ with an error of 0.1 $mg \cdot L^{-1}$.

High Pressure liquid chromatography (HPLC) was performed, using a Hewlett-Packard 1050 series controlled by HP Chemstation software, for assessing the concentration of NB in the samples collected during the oxidation process but the various by-products obtained during oxidation were neither identified nor quantified. Analysis conditions for NB are listed in Table 2.

Ozone concentration in the gas flow was determined using a Trailigaz UV analyzer model TLG 200 connected to a computer for data acquisition. Ozone concentration in the liquid phase was determined using the colorimetric indigo trisulfonate standard method (14).

Adsorption Equilibrium Isotherms

The adsorption isotherms were determined weighing various amounts of adsorbent powder in a 125 mL bottle and adding 50 mL of a feedstock

Table 1. Properties of the various adsorbents tested in this study

Type	Commercial name	Supplier	Structure IZA[b]	SiO_2/Al_2O_3 ratio	Pore size (Å)	Countercation	BET specific area ($m^2 \cdot g^{-1}$)
Silicalite	PZ2/900	Zeochem	MFI	900	6 (7)	Na^+	300
	PZ2/400			400	6 (7)	Na^+	300
	PZ2/100			100	6 (7)	Na^+	300
	PZ2/100H			100	6 (7)	H^+	300
	PZ2/40			40	6 (7)	Na^+	300
Faujasite	390HUA	Tosoh	FAU	200	7.4 (16)	H^+	750
Beta	TZB-513	Tricat	*BEA	49	7–7.4 (7)	H^+	700
	TZB-213			21	7–7.4 (7)	H^+	537
Mordenite	TZM-1013		MOR	13	6.7–7 (16)	H^+	442
	TZM-1023			18,4	6.7–7 (16)	H^+	489
MCM	MCM-41	ENSCMu[a]	Amorphous	∞	22		610
Activated carbon	S-23	Pica	/	/	8	/	1250
	L-27				14		1800

[a]ENSCMu: Ecole Nationale Supérieure de Chimie–Mulhouse (France).
[b]IZA: International Zeolite Association–Zurich (Switzerland).

Table 2. HPLC analysis conditions

Column	C18 Equisorb ODS2 5 μm 250 × 4.6 mm
Eluent	35% acetonitrile 65% water acidified at pH = 2 with H_3PO_4
Flow	1 mL · min^{-1}
Temperature	40°C
Detection	UV detection at λ = 267 nm
Retention time	About 15 min
Range	0–250 mg · L^{-1}; ± 1 mg · L^{-1}

solution containing about 600 mg · L^{-1} NB in demineralized water. The pH was not controlled. The bottles were sealed and agitated overnight using a "rotator" at 20 ± 1°C. Then a sample was collected from each bottle, filtered through 0.45 μm filters and the residual aqueous NB concentration was determined by spectrophotometry, after dilution when necessary to match the analytical range.

Ozonation Experiments

Ozonation experiments were carried out at room temperature (around 20°C) in a 2 L reactor (Fig. 1) filled with 1.5 L NB solution buffered at pH 2.2 and fed with an ozonated oxygen gas flow. During the experiments conducted with zeolites, a known amount of powder was suspended in the solution. The ozone generator was an Ozone Technology OT 40 model with an ozone production capacity of 40 g · h^{-1} and was fed with pure oxygen. Before starting the experiments, the gas flow rate was set to 30 L · h^{-1} and the ozone concentration in the gas was fixed at 30 ± 1 g · Nm^{-3}. During the experiments,

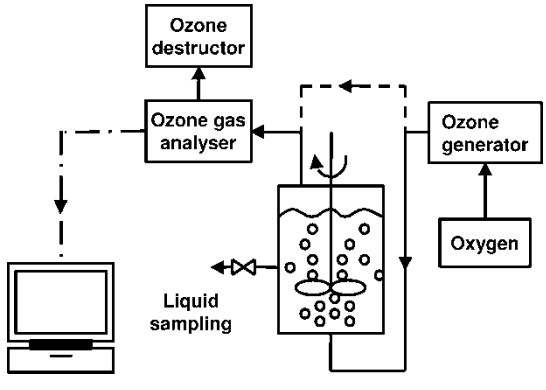

Figure 1. Sketch diagram of the ozonation device.

ozonated oxygen was bubbled at the bottom of the reactor through a porous medium, just below a three-blade impeller (40 mm diameter, 1560 rpm), which enabled bubble dispersion and solution mixing. The exhaust gas was collected at the top of the reactor for ozone concentration measurement and destruction before venting out. Liquid samples collected from the reactor were filtered through 0.45 μm filters resistant to ozone and the residual ozone was rapidly stripped out by nitrogen.

RESULTS AND DISCUSSION

Nitrobenzene Adsorption onto Zeolites

In order to select the best adsorbent suitable for NB removal from water, the adsorption isotherms of NB onto zeolites were determined; they are presented in Fig. 2. Adsorption isotherms onto mordenite are not reported here because they did not show any significant NB adsorption capability. All isotherms reached a plateau in the concentration range used, which means that the maximum adsorption capacity of the zeolites was reached. Figure 2 shows that the adsorption capacity is strongly dependent on the zeolites' structure and on their SiO_2/Al_2O_3 ratio. Faujasite had the greatest adsorption capacity with 267 $mg \cdot g^{-1}$, far above the other zeolites. Next, silicalites showed capacities varying from 84 $mg \cdot g^{-1}$ to 148 $mg \cdot g^{-1}$ depending on their SiO_2/Al_2O_3 ratio. Finally, beta-type zeolites had adsorption capacities similar to the silicalites with low SiO_2/Al_2O_3 ratios. Moreover, the comparison of PZ2/100 and PZ2/100H revealed that the zeolite countercation had no influence on the adsorption capacity.

All isotherms were type 1, which means that they followed a Langmuir-type model, as presented in equation (1), where Q_E is the adsorbed quantity

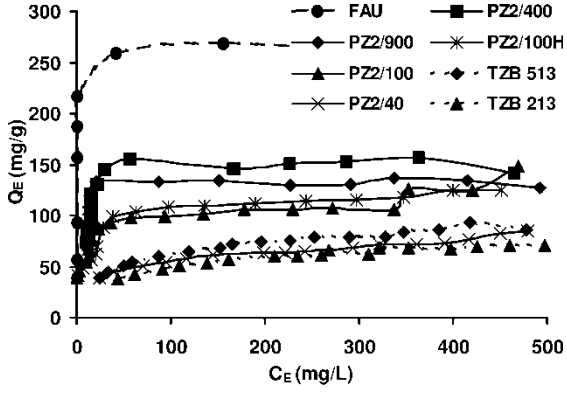

Figure 2. Adsorption isotherms of NB onto various zeolites.

($mg\ NB \cdot g^{-1}$), Q_{MAX} is the adsorption capacity ($mg\ NB \cdot g^{-1}$), K_L is the Langmuir constant ($L \cdot (mg\ NB)^{-1}$) and C_E is the equilibrium concentration in the liquid ($mg\ NB \cdot L^{-1}$). The model parameters were adjusted in order to fit this model to the experimental adsorption isotherms.

$$Q_E = Q_{MAX} \times \left(\frac{K_L \times C_E}{1 + K_L \times C_E} \right) \quad (1)$$

For the various zeolites, these parameters are listed in Table 3 and the results are plotted in Figure 3, which shows the variations in the adsorption capacity with the zeolite structure and its SiO_2/Al_2O_3 ratio. For SiO_2/Al_2O_3 ratios lower than 100, the adsorption capacity increased with increasing the SiO_2/Al_2O_3 ratio. Moreover, the comparison of silicalites and beta-type zeolites showed that in this range of low silicate content, the adsorption capacity was quite independent of the crystalline structure. Indeed, silicalites have a three-dimensional porous structure (15) with two kinds of ten-membered channels, straight channels having an elliptical cross section of 5.7–5.8 × 5.1–5.2 Å and zigzag channels having a nearly circular cross section of 5.4 Å free diameter. On the other hand, beta-type zeolites also have a three-dimensional porous structure with twelve-membered straight channels intersecting perpendicularly to each other. The pore opening of the linear channels is approximately 5.7 × 7.5 Å and the tortuous channels formed by the intersection of linear channels (9) have an approximate pore opening of 5.6 × 6.5 Å. These results are consistent with the literature since

Table 3. Parameters of the Langmuir or Freundlich equations for the various zeolites and activated carbons tested in this study

Type	Commercial name	Q_{MAX} ($mg\ NB \cdot g^{-1}$)	K_L $L \cdot (mg\ NB)^{-1}$
Zeolite	PZ2/900	135.7	0.174[a]
	PZ2/400	147.6	0.148[a]
	PZ2/100	118.7	0.104[a]
	PZ2/100H	125.7	0.070[a]
	PZ2/40	83.9	0.022[a]
	Faujasite	267.2	0.753[a]
	TZB-513	95.0	0.021[a]
	TZB-213	75.6	0.019[a]
Activated carbon	Microporous S-23	550.8	0.090[a]
	Mesoporous L-27	$1/n = 0.527$	$K_F = 22.8$[b]

[a]Langmuir isotherm.
[b]Freundlich isotherm—K_F in $(mg\ NB)^{1-1/n} \cdot L^{1/n} \cdot g^{-1}$.

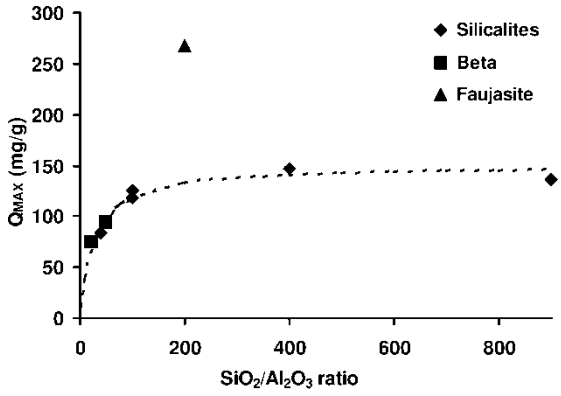

Figure 3. Variation of the NB adsorption capacity with the zeolite structure and SiO_2/Al_2O_3 ratio.

several authors reported the same dependence of the adsorption capacity on the SiO_2/Al_2O_3 ratio for several molecules and various zeolites (9, 10, 11).

On the contrary, for SiO_2/Al_2O_3 ratios over 100, the adsorption capacity of silicalites seemed to become independent of the SiO_2/Al_2O_3 ratio. When studying the adsorption of phenol, 3-chlorophenol and 4-chlorophenol onto silicalites—with SiO_2/Al_2O_3 ratios of 252, 1126, and 2116—Shu (9) could show that the adsorption capacities increased by more than 30% when the ratio increased from 252 to 1126 but then there was only a small difference between 1126 and 2116. The present study confirms this behavior in the case of NB adsorption.

Figure 3 also shows that faujasite had a far higher adsorption capacity than silicalites; this is probably related to a structure effect. Faujasite exhibits large 13 Å diameter cages (α cages), each one being connected to four other cages with twelve-membered rings of about 7.4 Å (β cages). The resulting structure is very open with a large porous volume accounting for about 50% of the total volume (16), which produces a large specific area and large adsorption capacities.

Hence it appeared that for low SiO_2/Al_2O_3 ratios, the zeolite adsorption capacity was fixed by its hydrophobicity—as hydrophobicity increases with the SiO_2/Al_2O_3 ratio—whereas for higher values of SiO_2/Al_2O_3 the structure effect became predominant.

Nitrobenzene Adsorption onto other Materials

Figure 4 compares the adsorption isotherms onto faujasite with the ones obtained with the other porous materials tested. This figure indicates that both S-23 and L-27 activated carbons have a far higher adsorption capacity

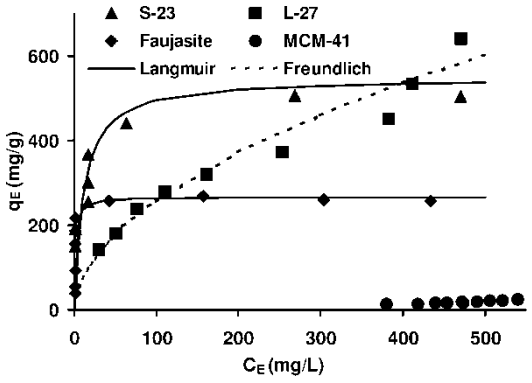

Figure 4. Adsorption equilibrium isotherms of NB onto various zeolites and activated carbons.

than faujasite whereas mesoporous MCM shows barely any adsorption of NB. For S-23 activated carbon, the Langmuir model presented in equation (1) fits conveniently the adsorption isotherm whereas for L-27, the Freundlich model presented in equation (2) is preferred. In this equation, Q_E is the adsorbed quantity (mg NB $\cdot$ g^{-1}), K_F is a constant ((mg NB)$^{1\text{-}1/n} \cdot$ L$^{1/n} \cdot$ g^{-1}), $1/n$ is a dimensionless constant and C_E is the equilibrium concentration in the liquid (mg NB $\cdot$ L^{-1}). These parameters are also listed in Table 3.

$$Q_E = K_F \times (C_E)^{1/n} \tag{2}$$

The better adsorption of NB by activated carbons S-23 and L-27 can be explained by their higher specific area, which usually exceeds 1000 m$^2 \cdot$ g^{-1}, and their larger porous volume. Two different behaviors are observed for low concentrations (under 100 mg $\cdot$ L^{-1}): whereas faujasite and S-23 activated carbon have good adsorption capacities even for very low concentrations, the L-27 activated carbon is less efficient. This is related to the porosity of the materials: Table 4 compares the porous volumes for both the activated carbons and faujasite. The porous volumes for activated carbons were measured by the supplier (Pica) whereas for faujasite they were calculated according to the method proposed by Clausse (17). Finally, the maximum adsorbable NB quantity was determined assuming condensation of pure liquid nitrobenzene in the pores (liquid density 1.2 kg $\cdot$ L^{-1}). The results show that faujasite and S-23 have only micropores whereas L-27 has a larger mesoporous volume and probably macropores as well, which were not measured. The theoretical NB maximum adsorbable quantities were consistent with the experimental values, which correspond to the plateau in the Langmuir-type adsorption isotherms.

As adsorption is mainly related to physical bonds between the adsorbent and the adsorbate, narrower pores in microporous solids lead to stronger physical

Table 4. Comparison of porous volumes and NB adsorption capacities for activated carbons Pica S-23 and L-27and for faujasite

	Porous volume ($cm^3 \cdot g^{-1}$)			Maximum adsorbed NB (mg NB · (g CA)$^{-1}$)			
Adsorbent	Micropores		Mesopores	Theoretical (micropores)			Experimental (Q_{MAX})
S-23	0.5		0.05	600			550.8
L-27	0.7		0.35	840			nd
Faujasite	α cages	β cages	0	α cages	β cages	total	267.2
	0.297	0.065		356	78	434	

interactions and thus to better adsorption. Activated carbons usually have a large pore distribution with micro, meso, and macropores; so, in spite of a lower adsorption capacity, faujasite may be more efficient than some activated carbons at low concentrations. In contrast, MCM-41, a pure amorphous silica with only mesopores, has a very low adsorption capacity.

Catalytic Ozonation

The second part of the study consisted in investigating the influence of zeolite on the ozonation kinetics. Firstly, ozone decomposition in the presence of zeolite was focused on and then NB solutions were oxidized by ozone in the presence or absence of zeolites. The catalytic activity of faujasite and PZ2/900 towards ozone decomposition was investigated by bubbling ozone gas in a NB free solution containing 1 $g \cdot L^{-1}$ suspended zeolite powder. Ozone concentrations in the outlet gas at steady state were found to be similar to the reference case—ozone dissolution in pure water. This confirms that these zeolites are not effective catalysts for aqueous ozone decomposition, as previously reported by Fujita (10, 18) and Lin (19).

The following experiments consisted in the ozonation of NB solutions in the presence of suspended zeolite once the adsorption equilibrium was reached. These experiments were compared to ozonation of NB solutions under the same concentration conditions but without zeolite. In all cases the adsorption kinetics proved to be far higher than the oxidation kinetics, hence two experimental procedures were adopted. The first experiments (Fig. 5) were carried out using a constant initial amount of NB corresponding to a 250 $mg \cdot L^{-1}$ concentration in the solution before adsorption. In the second procedure (Fig. 6), NB amounts were varied in order to achieve a 100 $mg \cdot L^{-1}$ concentration in the solution at the end of the adsorption step. During all experiments, the presence of a few $mg \cdot L^{-1}$ dissolved ozone in the liquid phase was maintained in order to ensure that reaction kinetics were not limited by gas-liquid mass transfer.

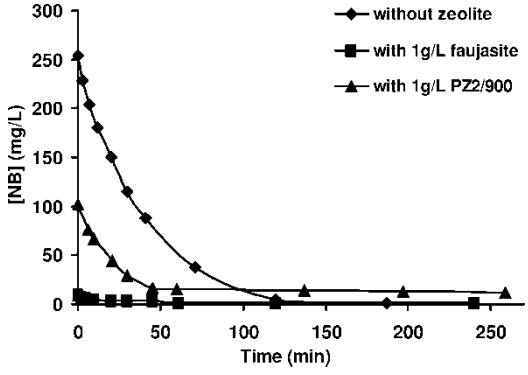

Figure 5. Ozonation of NB solutions in the presence of zeolites after preliminary adsorption. Comparison with ozonation alone. NB concentration before adsorption is 250 mg/L.

Figure 5 shows that without any adsorbent, NB concentration decreases below the detection limit after 180 min ozone bubbling. In the experiments with zeolites, a large amount of NB was removed from the solution by adsorption prior to ozonation, over 95% with faujasite. In both experiments, the adsorbed quantities matched the adsorption isotherms—$C_E = 9.9\ mg \cdot L^{-1}$ and $Q_E = 236.2\ mg \cdot g^{-1}$ for faujasite and $C_E = 102.1\ mg \cdot L^{-1}$ and $Q_E = 134.2\ mg \cdot g^{-1}$ for silicalite PZ2/900. In the case of PZ2/900, NB concentration after adsorption verged on $100\ mg \cdot L^{-1}$ and it decreased to $15\ mg \cdot L^{-1}$ within the first 60 minutes of ozonation. However, a few $mg \cdot L^{-1}$ NB remained in the solution even after 360 minutes ozonation. A similar behavior was observed with faujasite since NB traces still remained after 360 minutes ozonation, but at a lower concentration level.

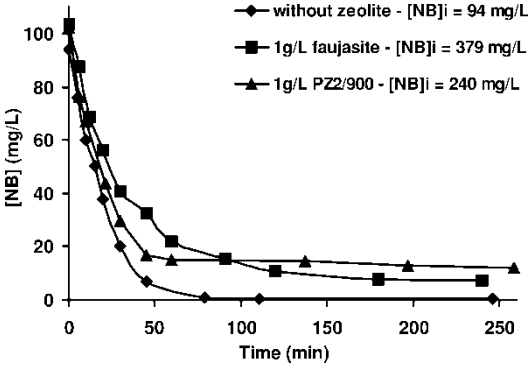

Figure 6. Ozonation of NB solutions in the presence of zeolites after preliminary adsorption. Comparison with ozonation alone. NB concentration remaining after adsorption is 100 mg/L.

The second set of experiments, reported in Fig. 6, exhibited the same behaviors. During ozonation alone, 99% of NB was removed within 80 minutes of ozonation whereas the tests with PZ2/900 and faujasite led to residual NB concentrations in the solution reaching 15 $mg \cdot L^{-1}$ and 20 $mg \cdot L^{-1}$ respectively after the same oxidation time. Afterwards, the concentration of NB in the aqueous phase decreased very slowly. Thus, these experiments indicated that NB remaining in the solution was oxidized by ozone but was not removed faster in the presence of zeolite, which means that there was no catalytic effect as previously reported (11, 18, 19). On the contrary, the remaining NB concentration seemed to indicate that it was oxidized only in the aqueous phase. Thus, in the presence of zeolites, the adsorbed NB would be continuously desorbed as fast as it was removed from the solution by oxidation.

This is in contradiction with the results obtained by Fujita (10) for trichloroethylene and Sagehashi (11) for 2-methylisoborneol, which found that the adsorption of organic molecules onto high silica zeolites enhanced ozonation by means of a concentration effect. However, these authors worked by flowing ozone-saturated solutions through fixed beds of zeolites. This situation corresponded to using a large amount of adsorbent and led to a concentration of organics within the liquid as low as 0.05 $mg \cdot L^{-1}$ and about 10^7 greater within the pores. The authors (10, 11) concluded that oxidation occurred mainly within the pores and that the rate was limited by resistance to mass transfer from the bulk liquid to the surface of the solid. On the contrary, the present study refers to semi-batch experiments using small amounts of adsorbent suspended in the liquid. The concentration of dissolved NB can reach 20 $mg \cdot L^{-1}$ while the concentration within the pores, computed from the data presented in Table 4, is about 5×10^4 times greater. During the present study, the concentration values and the shape of the curves presented in Figs. 5 and 6 indicate that the NB previously adsorbed migrates towards the bulk liquid where it is oxidized. The actual concentration of NB within the liquid is linked to the adsorption/desorption phenomena and to oxidation. Further investigations in a fixed bed system are now underway before any conclusion can be reached.

Regeneration

Regeneration experiments were carried out for faujasite, using a solution containing around 170 $mg \cdot L^{-1}$ NB, and a zeolite concentration of 0.5 $g \cdot L^{-1}$. First, the NB solution and zeolite powder were mixed in the reactor until the adsorption equilibrium was reached; under these conditions, the zeolite was saturated with NB and the NB concentration remaining in the solution was around 30 $mg \cdot L^{-1}$. Then, ozone bubbling in the reactor was started for a given time. At the end of the period, residual ozone in the reactor was stripped with air and the aqueous NB residual concentration

was assessed. Then, a new aliquot of NB was added to the solution and, once the adsorption equilibrium was reached again, the new adsorption capacity was calculated.

The adsorption capacity Q_{MAX}, expressed as a percentage of the initial adsorption capacity, is presented in Fig. 7 versus the ozonation time. This Fig. 7 shows that the total regeneration of the adsorption capacity was achieved within 2 hours of ozonation. For longer ozonation times, it appears that the adsorption capacity increased slightly after ozone treatment, reaching even more than 100% of the initial capacity. This phenomenon is probably related to a "cleaning effect" of the pores of the zeolite by ozone. Indeed, during the synthesis process, a template molecule is used to give the zeolites their structure and is then removed, usually by calcination at a temperature of several hundred degrees, but traces of organic molecules might still be present in the zeolite pores as no further treatment was applied to the zeolites before use in this study.

For comparison purposes, Fig. 8 also shows the behavior of a NB solution during ozonation under similar conditions, but without adsorbent, and Fig. 9 shows the total amount of ozone then used versus time. The initial concentration was $170\,mg \cdot L^{-1}$ NB instead of $30\,mg \cdot L^{-1}$ when faujasite was added; but, as indicated previously, the adsorption of NB onto faujasite has to be taken into account and the same quantity of NB was used in both experiments. Figure 8 shows that the same time, about 2 hours, was necessary for the complete removal of NB from an aqueous solution using similar ozonation conditions, but without zeolite. Figure 9 establishes that about 640 mg O_3 was then necessary to remove this quantity of NB. Meanwhile less than 430 mg O_3 were consumed during this 2 hour period when using the zeolite and the regeneration process for removing the same quantity of NB. This corresponded to a saving in the

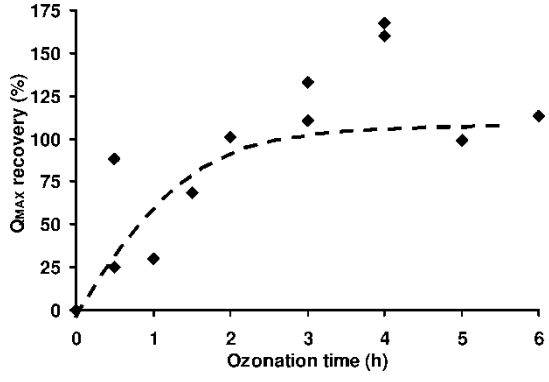

Figure 7. Regeneration of the initial adsorption capacity Q_{MAX} of faujasite with ozone. Adsorption capacity recovery with ozonation time.

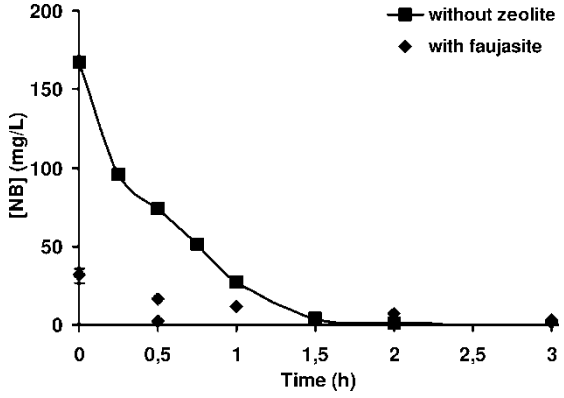

Figure 8. NB aqueous concentration during regeneration. Comparison between adsorption onto faujasite and regeneration by ozone and ozonation alone.

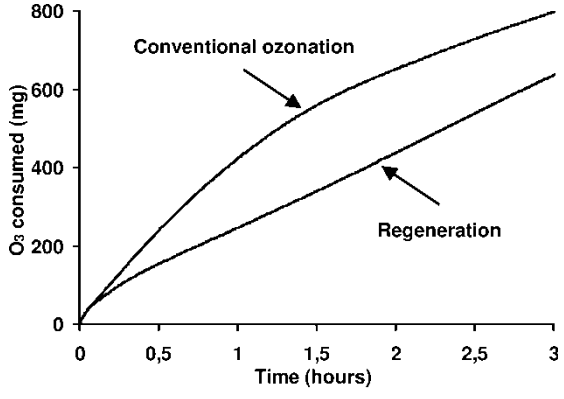

Figure 9. Comparison of the quantity of ozone necessary for adsorption onto faujasite and regeneration by ozone to the quantity necessary for ozonation alone.

required ozone amounting to about 30%, thus establishing the practical value of such a coupled procedure.

CONCLUSION

While investigating the removal of nitrobenzene (NB) from water—a model molecule for non-biodegradable and refractory organic compounds—this paper establishes that high silica zeolites have a satisfactory adsorption capacity for removing NB from water. Equilibrium adsorption isotherms corresponded to a Langmuir-type model. The adsorption capacity depended on

the Si/Al ratio for ratios lower than 100 and adsorption capacity depended on the zeolite structure for higher ratios. Faujasite turned out to be the zeolite with the highest adsorption capacity (267 $mg \cdot L^{-1}$). This capacity had the same order of magnitude as that of activated carbon, lower at high NB concentrations and higher at low NB concentrations.

During ozonation experiments, no catalytic effect of the zeolites on the oxidation rate of NB by ozone was observed, contrary to the results previously published (10, 11) and ozonation seemed to occur within the liquid phase after desorption of the adsorbed NB molecules. However, because of the concentration effect resulting from prior adsorption, the global oxidation rate could be increased and the quantity of ozone necessary appeared to be lower compared to ozonation alone.

Faujasite saturated with NB could be totally regenerated by ozone treatment and the initial adsorption capacity was totally recovered, proving this zeolite to be an easy material to recycle continuously. Indeed, this study established the feasibility of a three-phase process for wastewater treatment; combining adsorption of refractory organics onto hydrophobic zeolites and in situ regeneration of the zeolites by ozone which would oxidize the desorbed molecules.

ACKNOWLEDGMENTS

The authors acknowledge the French National Agency for Research (ANR) for supporting this study through the convention ANR PHARE n°: ANR 05 ECOT 012 03. They are grateful to F. Correia for contributing to the experimental part of this study. Also, they acknowledge Pr. P. Magnoux, Pr. S. Mignard, and Dr. G. Joly (LACCO–Poitiers, France) for fruitful discussions.

REFERENCES

1. IARC, International Agency for Research on Cancer, (1996) *Nitrobenzene*; In IARC Monographs on the Evaluation of Carcinogenic Risks to Humans; 65, 380–408.
2. Cattley, R.C. et al. (1994) Carcinogenicity and toxicity of inhaled nitrobenzene in B6C3F1 mice and F344 and CD rats. *Fundam. Appl. Toxicol.*, 22: 328–340.
3. ATSDR, Agency for Toxic substances and Disease Registry. US Public Health Service (1990) *Toxicological Profile for Nitrobenzene*; ATSDR: Atlanta, GA.
4. Hoigné, J. and Bader, H. (1983) Rate constants of reactions of ozone with organic and inorganic compounds in water-I: non-dissociating compounds. *Water Research*, 17: 173–183.
5. Beltrán, F.J. (ed.) (2004) *Ozone Reaction Kinetics for Water and Wastewater Systems*; Lewis Publishers: Boca Raton, FL.

6. Doré, M. (ed.) (1989) *Chimie des Oxydants et Traitement Des Eaux*; Lavoisier Tech & Doc: Paris, (France).
7. Ruthven, D.M. (ed.) (1984) *Principles of Adsorption and Adsorption Processes*; Wiley Interscience.
8. Khalid, M., et al. (2004) Removal of phenol from water by adsorption using zeolites. *Ind. Eng. Chem. Res.*, 43 (17): 5275–5280.
9. Shu, H., Li, D., Scala, A., and Ma, Y. (1997) Adsorption of small organic pollutants from aqueous streams by aluminosilicate-based microporous materials. *Separation and Purification Technology*, 11: 27–36.
10. Fujita, H. et al. (2004) Decomposition of trichloroethene on ozone-adsorbed high silica zeolites. *Water Research*, 38: 166–172.
11. Sagehashi, M. et al. (2005) Ozone decomposition of 2-methylisoborneol in adsorption phase on high silica zeolites with preventing bromate formation. *Water Research*, 39: 2926–2934.
12. Monneyron, P. et al. (2003) Regeneration of high silica zeolites via advanced oxidation process—; a preliminary study about adsorbent reactivity towards ozone. *Trans IchemE*, 81: 1193–1198.
13. Reid, R.C., Prausnitz, J.M., and Sherwood, T.K. (1977) *The Properties of Gases and Liquids*, 3rd Ed.; Mc Graw Hill Ed: New York, NY.
14. Masschelein, W. (ed.) J. (1991) *Ozone et Ozonation Des Eaux*; Lavoisier—Tec & Doc: Paris, (France).
15. Kärger, J. and Ruthven, D.M. (ed.) (1992) *Diffusion in Zeolites and other Microporous Solids*; Wiley Interscience.
16. Breck, D.W. (ed.) (1974) *Zeolite Molecular Sieves, Structure, Chemistry and Use*; Wiley Interscience.
17. Clausse, B. (1997) *Adsorption/co-adsorption de composés organochlorés par une faujasite Y hydrophobe/organophile dans un contexte de dépollution de l'air et de l'eau,* Ph. D. Thesis, Université de Bourgogne: Dijon (France).
18. Fujita, H. et al. (2004) Adsorption and decomposition of water dissolved ozone on high silica zeolite. *Water Research*, 38: 159–165.
19. Lin, J., Kawai, A., and Nakajima, T. (2002) Effective catalysts for decomposition of aqueous ozone. *Applied Catalysis. B. Environmental*, 39: 157–165.