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Eprints ID: 5970

To link to this article: DOI:10.2166/WST.2009.711
URL: <http://dx.doi.org/10.2166/WST.2009.711>

To cite this version: Merle, Tony and Pic, Jean-Stéphane and Debellefontaine, Hubert and Manero, Marie-Hélène (2009) Enhanced bio-recalcitrant organics removal by combined adsorption and ozonation. *Water Science and Technology*, vol. 60 (n°11). pp. 2921-2928. ISSN 0273-1223

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Enhanced bio-recalcitrant organics removal by combined adsorption and ozonation

T. Merle, J. S. Pic, M. H. Manero and H. Debellefontaine

ABSTRACT

Removal of bio-recalcitrant and toxic compounds from wastewaters has been a major objective of industrial manufacturers for a few years. Due to the potential risk toward public health, regulations are becoming increasingly strict and classical treatments like biological treatments are not efficient. Other techniques such as incineration, oxidation or adsorption provide higher levels of removal but with a high energy and capital cost. A coupled process involving adsorption and oxidation is studied. Four adsorbents are tested and compared according to two objectives, their adsorption capacity and their capability to decompose ozone into powerful hydroxyl radicals. Two model compounds were chosen: 2,4-dichlorophenol and nitrobenzene. Experimental results allow comparing coupled process with results obtained during ozonation alone. Zeolite (Faujasite Y) gave disappointing results in term of both adsorption kinetics and ozone decomposition. On the contrary, activated carbons showed fast adsorptions and important capabilities to decompose ozone into radicals, almost in nitrobenzene experiments. S-23 activated carbon proved to be the most interesting adsorbent for better mechanical and chemical stabilities over time. Sequential adsorption/ozonation experiments were conducted, showing a strong loss of adsorption efficiency after the first operation, but the positive point is that the adsorption capacity remains almost constant during further cycles.

Key words | activated carbon, adsorption, bio-recalcitrant, coupled process, ozonation, zeolite

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INTRODUCTION

Many industrial wastewaters contain bio-recalcitrant organic compounds. The removal efficiency of conventional processes is not sufficient and an additional treatment must be installed; activated carbon adsorption is often considered among various techniques. But all of them being complex and/or expensive, numerous investigations have been developed for a few years, looking for new powerful processes to remove these toxic compounds. The coupling of techniques can be an interesting solution. Previous studies have showed the interest of granular adsorption combined with ozone oxidation (ADOZ) (Monneyron *et al.* 2003; Fujita *et al.* 2004; Reungoat *et al.* 2008).

Indeed, activated carbon or zeolite seem to allow molecular ozone to be transformed into several radicals like hydroxyl radical (HO[•]) in water (Hoigné & Bader 1976; Fujita *et al.* 2004). This hydroxyl radical has better oxidation properties than ozone and therefore can oxidise organic compounds with better efficiencies. However, some studies showed that activated carbon can be degraded in contact with ozone (Valdés *et al.* 2002; Merle *et al.* 2008). In order to better understand these phenomena, this study focuses on the treatment of two bio-recalcitrant organic compounds by coupled processes ADOZ involving several activated carbons or zeolite.

MATERIALS AND METHODS

Chemical reagents and organic molecular analyses

Analytical grade 2,4-dichlorophenol (2,4-DCP) and nitrobenzene (NB) were purchased from Acros chemicals. Their kinetic diameters, respectively 6.3 Å and 5.9 Å, were calculated by the method of Reid *et al.* (1977). The Chemical Oxygen Demand (COD) of the solutions was measured by Hanna Instrument test tubes (COD MR Reagent). COD samples were first passed through a 0.45 µm filter before analyses in order to remove undissolved compounds. 2,4-DCP, NB and oxidation products concentrations were determined by High Performance Liquid Chromatography using a HP 1050 series chromatograph equipped with a Diode Array Detector (Agilent Technologies HP 1200) and a C-18 column (EQUISORB ODS2 5 µm).

Adsorbents and characterization

Four adsorbents were used in this study: 3 granular activated carbons (supplied by PICA Corp., France) called S-23, L-27, F-22 and one hydrophobic zeolite called faujasite (FAU supplied by TOSOH Corp., Japan). Their physical properties were characterized (Table 1). Among the activated carbons, S-23 exhibits the pH of zero charge ($\text{pH}_{\text{ZC}} = 9.1$) the less acidic: when contacted with a solution whose pH is smaller than 9.1, H_3O^+ ions of the solution will adsorb onto the surface of the activated carbon and the pH of the solution will increase. The number of basic sites was estimated using

Table 1 | Characteristics of the adsorbents

	Activated carbon			Zeolite
	S-23	L-27	F-22	FAU
pH of zero charge (pH_{ZC})	9.1	6.1	7.1	4.4
Basic sites after ozonation ($\mu\text{eq g}^{-1}$)	170	345	102	–
Specific area ($\text{m}^2 \text{g}^{-1}$)	1,374	2,337	1,005	614
Microporous volume ($\text{cm}^3 \text{g}^{-1}$)	0.56	0.85	0.38	0.21
Mesoporous volume ($\text{cm}^3 \text{g}^{-1}$)	0.05	0.53	0.10	0.26
Mean pore diameter (Å)	17	25	9	7.48
Granular diameter (mm)	1.46	1.79	≈ 1.00	3.0
Si/Al ratio	–	–	–	95
Binder amount (%)	–	–	–	25

the titration method published by Boehm (1966): after 1 hour ozonation, L-27 exhibits a number of basic sites which is more than twice the number of sites of S-23 and F-22.

Experimental setup

Adsorption experiments regarding both equilibrium isotherms determination and saturation steps in the sequential process were run in a rotary beater, in a 25°C controlled room. Adsorption kinetics measurements, as well as oxidation runs (either single or combined ozonation in the presence of materials) were carried out using the device presented in Figure 1, consisting in a 2 L liquid capacity semi-batch reactor. A 6-blades Rushton turbine ensures mixing. The gas is fed through a pipe located below the stirrer and collected at the top of the reactor. In most experiments, pH was not controlled. Yet a few measurements were performed at pH 7 using proper phosphate buffers.

Ozone is produced from pure oxygen using a Trailigaz generator (model Labo-Lox-sp). A set of valves and a flow-meter ensure a constant 30 L/h input flow into the reactor, with a concentration equal to 30 mg O_3/NL . Both excess gas and off-gas flows are driven to an ozone destructor before atmospheric release. A UV absorbance analyzer (Trailigaz model UVOZON TLG 200) allows the measurement of ozone concentration either in the inlet or in the outlet gas flow. Moreover, a polarographic probe (Orbisphere model 410/probe 31330.15xx) mounted on a circulation loop allows dissolved ozone concentration measurement. At last, when solid materials are used, they are inserted into a stainless steel grid basket in order to avoid both attrition and flotation. The ozone dose consumed during the experiments ranges from 0.05 up to 0.5 mg O_3/mg solid material.

RESULTS AND DISCUSSION

Adsorption isotherms

Equilibrium adsorption isotherms for the two target molecules onto the 4 materials were determined and are reported in Figure 2. They all show favourable shapes and can be described either through Langmuir (S-23, F-22 and FAU) or Freundlich (L-27) models (Reungoat 2007; Merle *et al.* 2008). The behaviours are quite similar for the

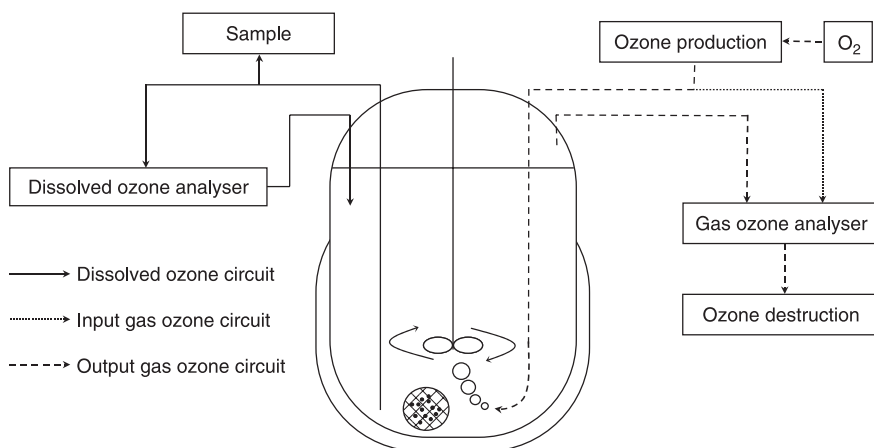


Figure 1 | Batch reactor diagram.

two components 2,4-DCP and NB: adsorption capacity is relatively low for faujasite, intermediate for L-27 and F-22 activated carbons and higher for S-23 activated carbon. It appears that, despite a favourable specific area (Table 1), the low pH of zero charge of L-27 should have a detrimental effect on NB adsorption. The same phenomenon was observed for phenol adsorption on L-27 (Ayril 2009).

Adsorption kinetics

Adsorption kinetics onto the different adsorbents were measured in the semi-batch reactor described in Figure 1 using an initial pollutant concentration of 250 mg L^{-1} , either for 2,4-DCP and NB. The corresponding results are shown in Figure 3. Adsorption kinetics using FAU are lower than onto the activated carbons. Indeed, in the case of 2,4-DCP, the equilibrium was achieved after 10 h

using granular activated carbon whereas using zeolite the equilibrium was still not achieved after 30 h experiment. This phenomenon is due to the structure of faujasite, which consists in microscopic zeolite crystals bound together by clay. Hence, molecules have to diffuse through these two levels of porosity, which induces a lower diffusion coefficient for the zeolite.

Comparison of single ozonation with the combined process for pollutants removal

Figure 4 compares the oxidation kinetics of NB and 2,4-DCP obtained during single ozonation or combined ozonation, which means in the presence of adsorbent media. The results are divided in 3 parts. First of all, Figure 4a and d show the pollutants decay versus time. In addition, global organic matter removal (COD) is plotted

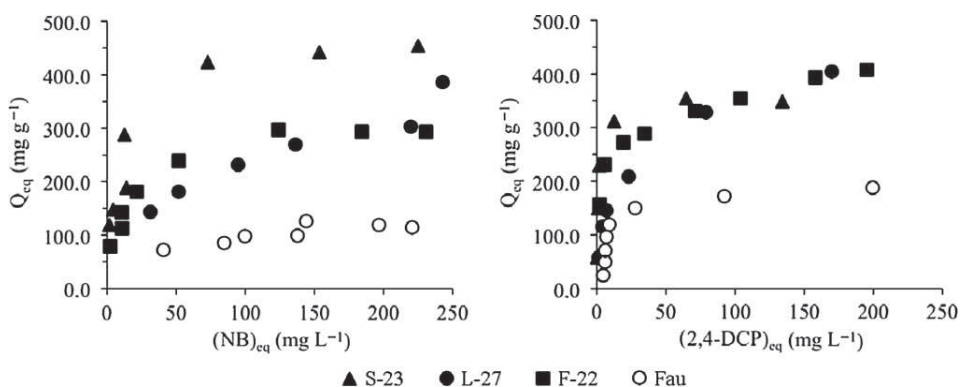


Figure 2 | Adsorption equilibrium isotherms of the pollutants onto several materials.

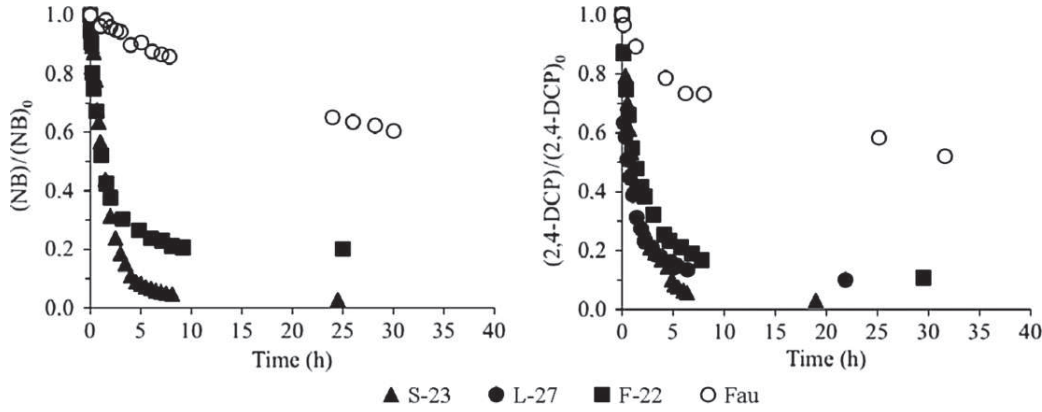
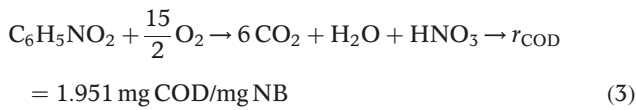
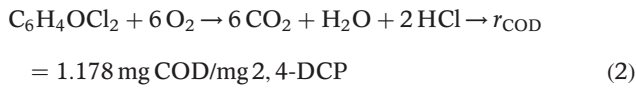


Figure 3 | Adsorption kinetics of the pollutants onto the different materials.

in Figure 4b and e. At last, COD induced by target molecules can be subtracted from total COD as shown in Equation 1, which allows a quantification of by-products amount (Figure 4c and f). To that end, it is necessary to evaluate the ratio r_{COD} defined as the COD amount equivalent to 1 mg organic molecule thanks to the theoretical equation for the molecule total oxidation (Equation (2) for 2,4-DCP and Equation (3) for NB).

$$\text{COD}_{\text{by-products}} = \text{COD} - [\text{Pollutant}] \cdot r_{\text{COD}} \quad (1)$$



On the one hand, NB total removal by single ozonation is achieved in 3.5 h (Figure 4a). The addition of FAU slightly enhances the oxidation kinetics. Activated carbons better improve NB removal; the performances of F-22 and L-27 are similar and higher than those of S-23. The same behaviour is observed for the removal of global organic pollution (COD) in Figure 4b and by-products in Figure 4c. More precisely, the three activated carbons highly enhance the total oxidation kinetics since COD reaches a very low value after 4 h combined treatment whereas still 30% organic load remains during single ozonation and about 20% in FAU combined treatment. At last, by-products removal follows typical series reaction kinetics; the activated carbons

increase these by-products oxidation rate compared to single ozonation or to FAU combined treatment. In addition, a part of the oxidation products was identified: whatever the oxidation process, the major intermediates are o-, m- and p-nitrophenol with varied proportions depending on the media nature.

As regards 2,4-DCP removal, none of the four media had any beneficial effect (Figure 4d). Indeed, 2,4-DCP is totally removed after only 1 h through either single ozonation or the combined process. COD results (Figure 4e and f) seem to confirm that the addition of the materials does not change the ozonation mechanism. Moreover, it can be noticed that the oxidation treatment is not complete since about 15% COD still remains after 4 h. In this case, the major intermediate products are different position dichloro-dihydroxy and monochloro-dihydroxy-substituted benzene rings as expected (Kwan & Chu 2004). The final oxidation product has been identified as oxalic acid.

In conclusion, the oxidation mechanism seems to be different for the two organic molecules. Thanks to the presence of a hydroxyl group on the aromatic ring, 2,4-DCP is easily oxidised by molecular ozone. Thus, the part of radical reactivity in the oxidation mechanism of this molecule is very low. Yet the addition of activated carbon or zeolite does not improve the global oxidation kinetics. On the other hand, NB oxidation is mainly ensured through a radical pathway, since the nitro substituent deactivates direct ozone attack of the molecule. In this case, the carbon media improve the oxidation kinetics probably through an increase in radical production.

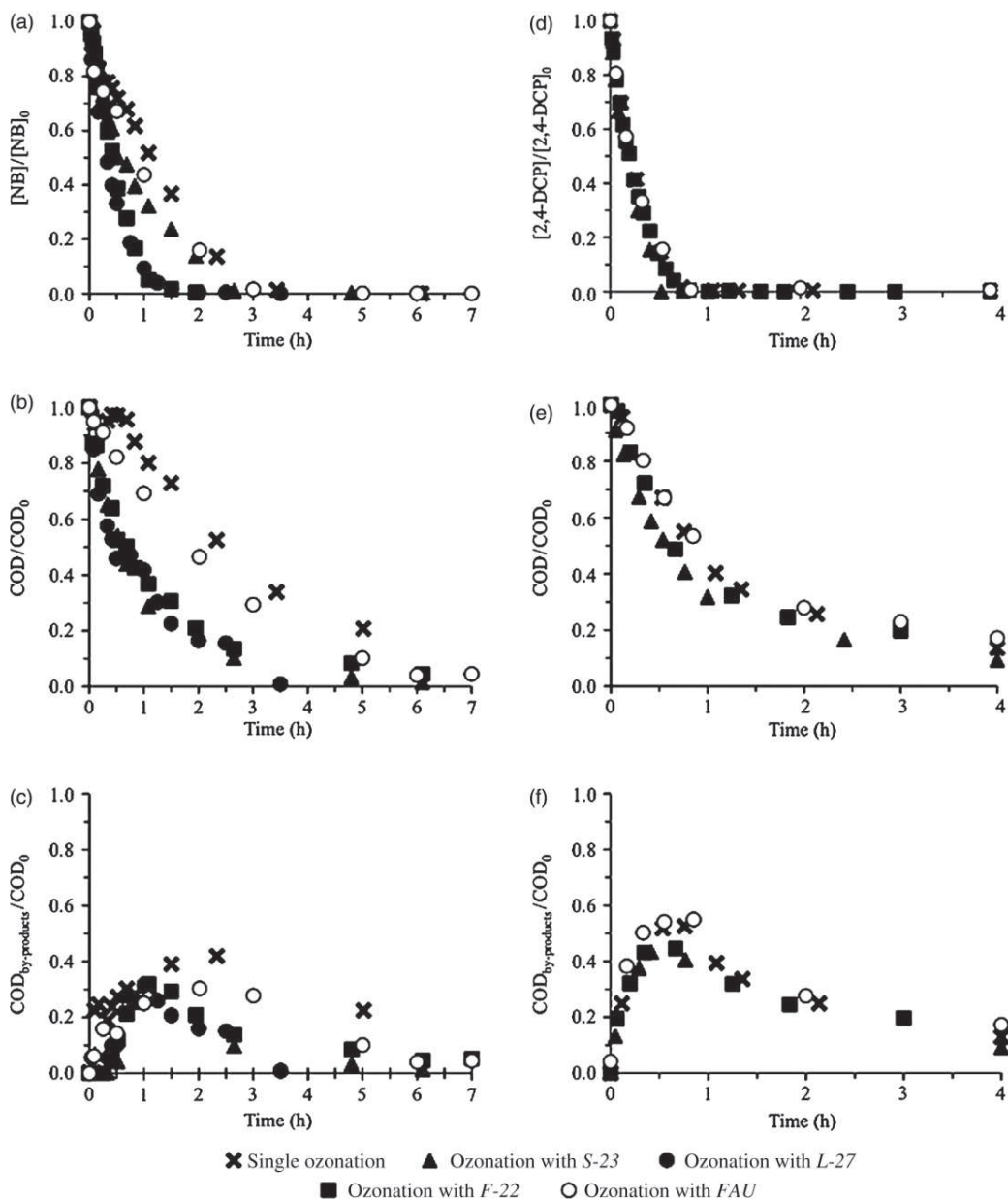


Figure 4 | Ozonation kinetics of NB (a, b, c) and 2,4-DCP (d, e, f) using single ozonation and combined process: pollutants (a, d), COD (b, e) and COD_{by-products} (c, f) removal.

Reaction mechanisms

In order to confirm the former hypotheses regarding the reaction mechanisms, ozone decomposition induced by the materials was investigated. The first order kinetics constant for ozone decomposition was determined according to the protocol published by Lopez-Lopez *et al.* (2007). Thus, Figure 5 shows that an increase in activated carbon

content induces an increase in ozone decomposition rate. For example, the addition of 13.4 g/L F-22 improves 8 times ozone decomposition.

Therefore, the activated carbons are classified according to their relative efficiency towards ozone decomposition: L-27 \gg F-22 > S-23. In homogeneous media, it is well-known that increasing the amount of hydroxyl ions in the solution favours ozone self-decomposition into

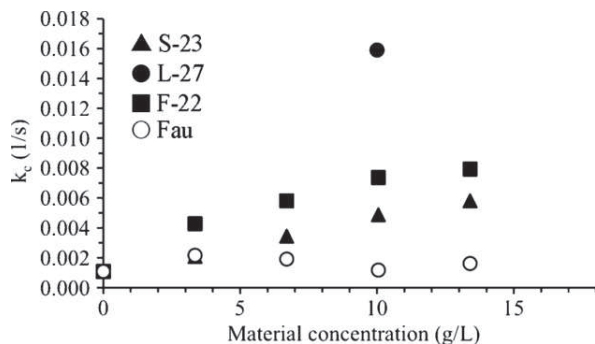


Figure 5 | Effect of the media concentration on ozone decomposition rate constant (k_c). All solutions are buffered at pH 7.

HO[•] radicals (Hoigné & Bader 1976). Thus a similar behaviour is expected with the materials. Yet, it is observed that the efficiency is opposite to the pH_{ZC} , which is a figure of the balance between acidic and basic sites. But, considering the number of basic sites (see Table 1) allows explaining the higher efficiency with L-27, thus confirming the chief importance of basic species for ozone decomposition. As well as the decomposition rate, this number of sites was considered after 1 hour ozonation of the activated carbon. The divergence between F-22 and S-23 efficiencies should be linked to acidic surface groups which could lead to the indirect production of hydrogen peroxide, thus enhancing ozone decomposition for F-22 (Alvarez *et al.* 2006). To confirm this hypothesis, a more complex characterization of the materials would be necessary, which is out of the scope of the present study. On the other hand, zeolite has no apparent effect, at least for this amount range.

Secondly, a radical scavenger, tertibutanol (*t*-BuOH), was used during NB single or combined oxidation. Figure 6 shows that only 35% of NB is removed after 7 h single ozonation in presence of *t*-BuOH against 100% NB removal without *t*-BuOH. Likewise, the addition of *t*-BuOH during the combined process with L-27 dramatically reduces NB removal kinetics. In this case, NB removal is only achieved through adsorption since the two curves are exactly overlaid. This confirms the major role of radicals in NB oxidation mechanism.

Study of the sequential process

The regeneration of saturated faujasite was formerly investigated by Reungoat (2007). The results showed that

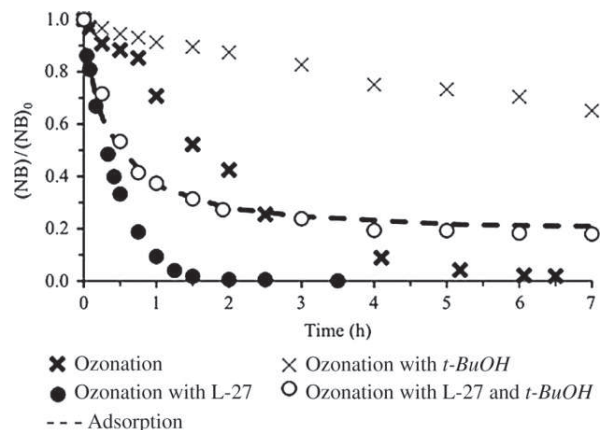


Figure 6 | Effect of a radical scavenger on NB combined adsorption onto L-27/ozonation process.

FAU could be totally regenerated after 3 h ozonation. Moreover, no change in the mineral structure of the zeolite was observed after exposure to ozone (Merle *et al.* 2008). In the present study, the transposition of the sequential process to activated carbon was focused on. Three sets of experiments were carried out with S-23 and 2,4-DCP. This activated carbon was used because of a better mechanical resistance after ozone treatment.

The first protocol consists in saturating the media during a 24 h adsorption step and then regenerating the activated carbon through various length ozonation runs. After regeneration, a second 24 h adsorption step was performed. The remaining adsorption capacity was plotted versus the regeneration time (hollow marks in Figure 7). An optimum regeneration time of 1 h was then determined, corresponding to an ozone dose of 0.055 mg O₃/mg S23. Nevertheless, this optimum duration leads to the recovery of only 40% of the

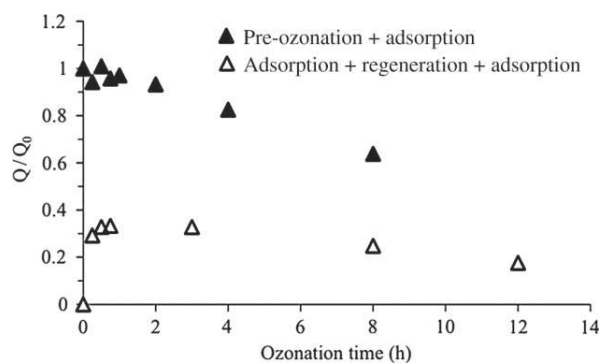


Figure 7 | Effect of ozonation time on S-23 regeneration.

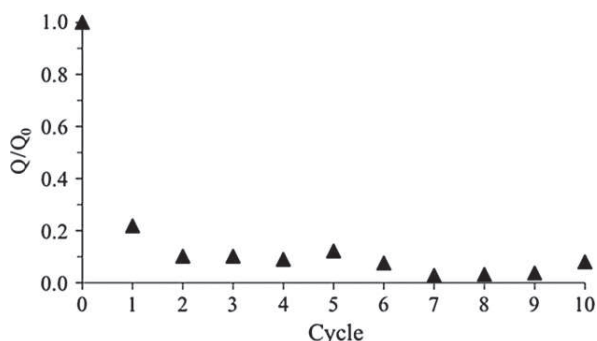


Figure 8 | Evolution of S-23 adsorption capacity during the sequential process.

original adsorption capacity. Two hypotheses are suggested: either a degradation of the S-23 structure or pore clogging by irreversibly adsorbed products. At last, for longer oxidation times, the S23 adsorption capacity decrease is probably due to the chemical degradation of the activated carbon.

In the second set of experiments (plain marks in Figure 7), S-23 was beforehand ozonated for various times and then the solid was submitted to a 24 h 2,4-DCP adsorption step. For oxidation lasting up to 1 h, the adsorption capacity was not changed proving that the material structure was not much modified, the ozone dose being 0.095 mg O₃/mg S23. Here again, for longer oxidation times, chemical degradation of the activated carbon occurred.

At last, ten cycles were run consisting in the succession of 24 h adsorption followed by 1 h ozonation sequences (Figure 8). As observed in previous experiments, 78% of the adsorption capacity was lost after the first regeneration step. The following cycles emphasise the loss of adsorption capacity until an apparent stabilisation occurs around an 8% residual value.

CONCLUSIONS

Experimental results conducted on the simultaneous adsorption/ozonation process showed different behaviours between zeolite and activated carbons. Because of its microporous structure, faujasite leads to low adsorption kinetics and to a limited quantity of pollutants adsorbed. Moreover, faujasite has almost no effect on ozone decomposition and, thus, on ozonation kinetics. On the contrary, fast adsorption and interesting removal kinetics were found with the activated carbons. During simultaneous

adsorption/ozonation, they can increase dramatically the removal kinetics, including COD and by-products. This is not marked for 2,4-DCP because the high electronic density of the aromatic ring allows oxidation by ozone alone but this is clearly evidenced for NB, more recalcitrant to ozone considered alone because of a lack of electrons on the aromatic ring. Tests with a radical scavenger (*t*-BuOH) have evidenced that activated carbons enhance ozone decomposition leading to powerful HO[•] oxidizing radicals. S-23 was preferred to the other activated carbons because of a better mechanical and chemical stability over time.

Sequential adsorption/ozonation tests evidenced that about 80% of the adsorption capacity is lost after the first adsorption/ozonation cycle, but the adsorption capacity remains almost constant during further cycles. This should allow developing a process reusing the same sample of activated carbon for a long time, provided that pilot-plant tests can confirm the stability of the remaining capacity under real conditions and provided that this remaining capacity is enough for a significant adsorption period before regeneration.

Currently ongoing studies aim at identifying and quantifying the various by-products obtained during oxidation. The determinant question of the practical and economical interest of this new process is out of the scope of this paper. This needs a series of pilot plant tests under conditions as close as possible to real industrial conditions. In fact, this should be a later step of this project, conducted in agreement with an industrialist counterpart specializing in the treatment of specific industrial wastewaters for which no satisfying solution exists at the moment.

ACKNOWLEDGEMENTS

ANR (French National Research Agency) supports this work through the PRECODD program (PHARE project).

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