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Comparison of Activated Carbon and Hydrophobic Zeolite Efficiencies in 2,4-Dichlorophenol Advanced Ozonation

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This study aims at comparing the removal of 2,4-dichlorophenol (2,4-DCP) by 3 methods; adsorption using hydrophobic zeolite (faujasite) or activated carbon (S-23 and L-27), conventional ozonation and hybrid adsorption/ozonation treatment. On the one hand, the three materials correctly adsorb 2,4-DCP; however the adsorption kinetics using zeolite is very low. On the other hand, ozonation totally removes 2,4-DCP after 1 h experiment and the simultaneous combination of adsorbent and ozone does not change the 2,4-DCP degradation. But, though ozonation and hybrid process appear to be equivalent for 2,4-DCP removal, activated carbons are able to decompose ozone and to improve chemical oxygen demand (COD) removal, whereas the zeolite does not show this catalytic effect. Similar results were also observed in a former study with nitrobenzene. Adsorbent degradation is evaluated by Brunauer, Emmet and Teller (BET) and differential thermogravimetric (DTG) analysis, which evidence that Faujasite and S-23 activated carbon are resistant to ozone exposure whereas the pore volume and the surface area of L-27 activated carbon decrease during ozonation.

Keywords Ozone, Zeolite, Activated Carbon, 2,4-dichlorophenol, Adsorption

INTRODUCTION

Nowadays, industrial wastewater is mainly purified by biological treatment. Yet some effluents cannot undergo biological treatment for they contain many bio-recalcitrant organics or toxic compounds. In these cases, expensive shock treatments are often required such as incineration or advanced oxidation processes (AOPs). Indeed, radicals (especially HO●) involved in these AOPs increase the oxidation efficiency (Hoigné and Bader, 1976).

Jans and Hoigné (1998) have shown that the decomposition of ozone into hydroxyl radicals is increased by activated

carbon. Zeolites were also proven to improve refractory compounds removal (Fujita et al., 2004; Sano et al., 2007). Even though activated carbon is a cheaper adsorbent, its properties can be affected whereas zeolites are supposed to be stronger facing ozonation. Thus, this study compares activated carbon and zeolite media in terms of resistance to ozone treatment and efficiency to remove bio-recalcitrant compounds.

MATERIAL AND METHODS

2,4-DCP Reagent and Organic Molecular Analyses

Analytical grade 2,4-dichlorophenol (2,4-DCP) was purchased from Acros chemicals. The kinetic diameter is 6.3 Å and was calculated by the method of Reid et al. (1977). The chemical oxygen demand (COD) of the solutions was measured by Hanna Instrument test tube (COD MR Reagent, Woonsocket, RI, USA) and total organic carbon (TOC) concentration was determined using a Shimadzu TOC-VCSH analyzer. COD and TOC samples were filtered using a 0.45 µm filter before analyses.

The 2,4-DCP residual concentration was determined by high pressure liquid chromatography using HP 1050 series chromatograph with a C-18 column (EQUISORB ODS2 5 µm) and a diode array detector (Agilent Technologies model HP 1200, Santa Clara, CA, USA).

Adsorbents and Characterization

Three adsorbents were used in this study: 2 granular activated carbon (supplied by PICA Corporation, France) called S-23 and L-27 and 1 hydrophobic zeolite called faujasite (FAU supplied by TOSOH Corp., Japan). First, their physical properties were characterized through the measurement of the nitrogen adsorption isotherms at 77 K using a Micrometrics ASAP 2010 device. The Brunauer, Emmet and Teller (BET) surface area and the external surface area were determined

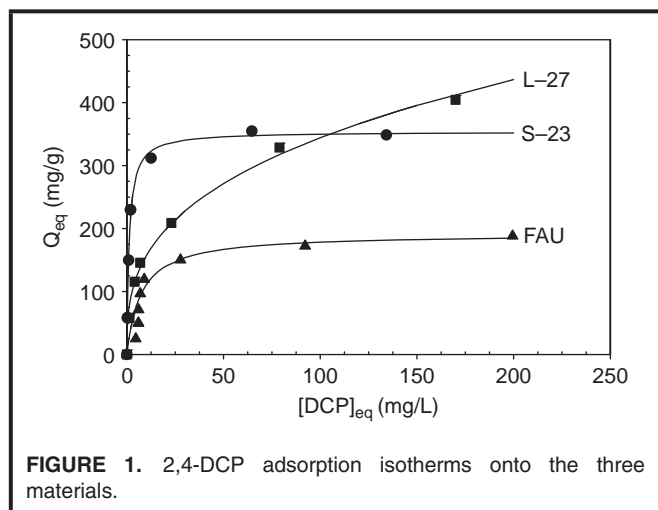
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TABLE 1. Main Characteristics of the Adsorbents

	Activated carbon		Zeolite
	S-23	L-27	FAU
Specific area ($\text{m}^2.\text{g}^{-1}$)	1374	2337	614
Microporous volume ($\text{cm}^3.\text{g}^{-1}$)	0.56	0.85	0.21
Mesoporous volume ($\text{cm}^3.\text{g}^{-1}$)	0.05	0.53	0.26
Mean pore diameter (\AA)	17	25	7.48
Granular diameter (mm)	1.46	1.79	3.0
Si/Al ratio	–	–	95
Binding amount (%)	–	–	25

using the BET method whereas mesoporous and microporous volumes were calculated with the t-plot method. The corresponding results are reported in Table 1.

Second, 2,4-DCP adsorption isotherms were determined for the 3 materials at 25°C adding increasing quantities (between 10 and 900 mg) in 100 mL deionized water loaded with $233 \pm 3 \text{ mg.L}^{-1}$ 2,4-DCP. They exhibit classical shapes as shown in Figure 1. The isotherms onto faujasite and S-23 activated carbon could be described through the Langmuir's model (Equation 1), whereas L-27 activated carbon behavior was better described through the Freundlich's model (Equation 2). The parameters for both models are given in Table 2. Adsorption of 2,4-DCP is favored onto the three materials and, for 2,4-DCP equilibrium concentrations below 100 mg.L^{-1} , the adsorption capacity is relatively low for faujasite, intermediate for L-27 activated carbon and higher for S-23 activated carbon.

**FIGURE 1.** 2,4-DCP adsorption isotherms onto the three materials.**TABLE 2.** Langmuir and Freundlich Parameters

S-23 (Langmuir)		L-27 (Freundlich)		FAU (Langmuir)	
Q_{Max} (mg/g)	K	F	1/n	Q_{Max} (mg/g)	K
354	0.83	70.9	0.34	192	0.14

$$\text{Langmuir model: } Q_{\text{Eq}} = Q_{\text{Max}} \times (K \times C_{\text{Eq}}) / (1 + K \times C_{\text{Eq}}) \quad [1]$$

$$\text{Freundlich model: } Q_{\text{Eq}} = F \times (C_{\text{Eq}})^{1/n} \quad [2]$$

with:

- $Q_{\text{Eq}}, Q_{\text{Max}}$ equilibrium [resp. maximum] adsorbed quantity;
- C_{Eq} equilibrium concentration in the liquid phase;
- K Langmuir constant;
- F Freundlich constant;
- n Freundlich coefficient

At last, differential thermogravimetric (DTG) analyses were carried out using a thermo balance system (TA instruments STD 2960 and STD Q600, New Castle, DE, USA) by heating about 10 mg adsorbent from 303 K up to 1173 K at a rate of 10 K.min^{-1} under flowing argon (100 mL.min^{-1}).

Experimental Setup

All the experiments described in this study were carried on using the device presented in Figure 2. It consists in a 2 L liquid capacity semi-batch reactor. Mixing was ensured by a 6-blades Rushton turbine and allowed to prevent any limitation of the process by the external mass transfer resistance. The gas was fed through a pipe located below the stirrer and collected through another pipe located at the top of the reactor. Ozone was produced from pure oxygen using an ozone generator (Trailgaz model Labo-Lox-sp, Paris, France), the nominal capacity is $16 \text{ g O}_3.\text{h}^{-1}$ for a concentration equal to 50 mg.L^{-1} and the gas flow rate and ozone concentrations could be varied according to the values required.

A set of valves and a flowmeter ensured a constant 0.5 L.min^{-1} input flow into the reactor. The excess gas flow, as well as the off-gas flow, was driven to an ozone destructor before atmospheric release. A UV absorbance analyzer (Trailgaz model UVOZON TLG 200) allowed 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, Loveland, CO, USA) mounted on a circulation loop allowed to measure continuously the dissolved ozone concentration. At last, when solid materials were used, they were inserted into a stainless steel grid basket in order to avoid both attrition and floatation. A series of blank tests (Merle, 2009) allowed verifying that the reactor itself

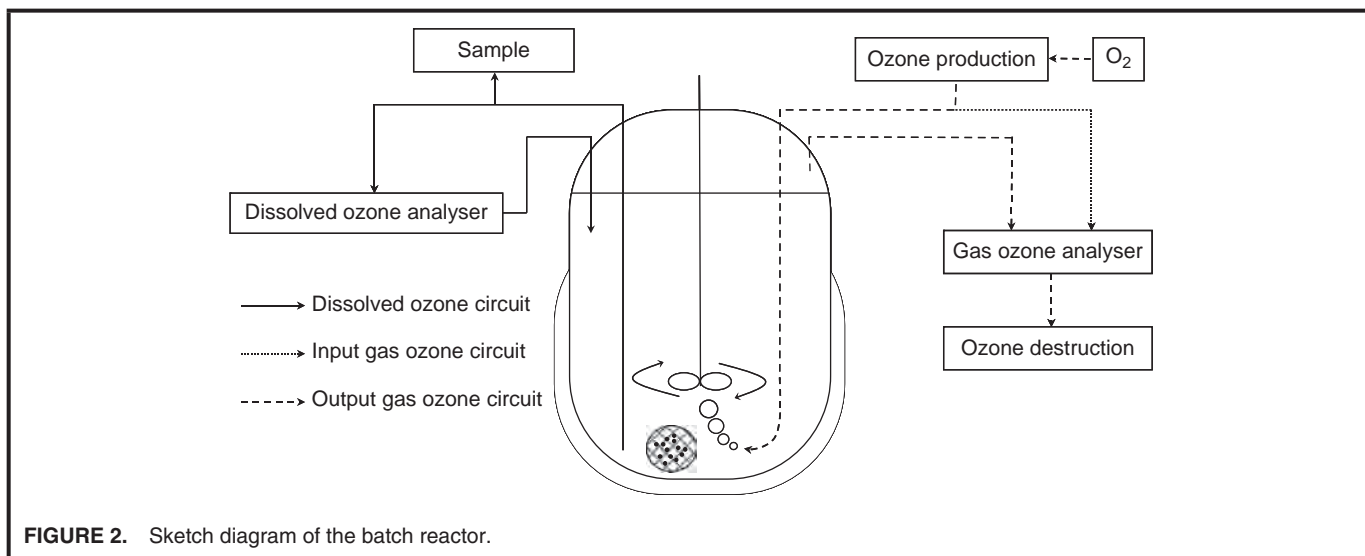


FIGURE 2. Sketch diagram of the batch reactor.

and its various accessories were inert with respect to ozone decomposition.

Determination of Ozone Transfer and Self-decomposition Parameters in the Presence of Materials

Ozonation of the adsorbents was carried out into this batch reactor (Figure 2) with 2 g adsorbent into 2 L deionized water. A $0.5 \text{ L}\cdot\text{min}^{-1}$ gas input flow was used with a $63 \pm 4 \text{ mg}\cdot\text{L}^{-1}$ ozone concentration in order to enhance the possible effect of ozone onto the materials. The experiments were run during two 7.5 h cycles.

The volumic ozone transfer coefficient, $k_{L,a}$, and the self-decomposition kinetic constant, k_C – pseudo first order – were measured through mass balances established simultaneously in both the gas and the liquid phases during ozone dissolution into water, according to the method proposed by Lopez-Lopez et al., 2009. As shown in Figure 3 (S-23 and FAU), an experiment of ozone dissolution in water starts by an unsteady state period – about 10 min – during which ozone accumulates into the liquid, then followed by a steady state period. During the unsteady state period, the mass balance for ozone in the liquid phase provides, after integration, the expression of the volumic ozone transfer coefficient, $k_{L,a}$. Once the steady state has been reached, the rate of ozone self-decomposition equals the rate of dissolution, which is obtained from the gas phase balance, thus providing an expression for the rate constant, k_C .

Adsorption, Ozonation and Simultaneous Process Experiments in the Presence of 2,4-DCP

All experiments were carried out into the batch reactor during 4 h at 25°C with a $240 \pm 10 \text{ mg}\cdot\text{L}^{-1}$ concentration 2,4-DCP solution (equivalent to a COD load of $280 \pm 10 \text{ mg O}_2\cdot\text{L}^{-1}$). For adsorption experiments, 2 g material was mixed with 2 L 2,4-DCP solution. Ozonation experiments

were conducted with an ozonated oxygen gas flow (flow rate: $0.5 \text{ L}\cdot\text{min}^{-1}$; ozone concentration: $39 \pm 3 \text{ mg}\cdot\text{L}^{-1}$). At last, the simultaneous process experiments consisted in ozonation experiments in the presence of $2 \text{ g}\cdot\text{L}^{-1}$ adsorbent.

Sequential Adsorption/Ozonation Experiments

Sequential adsorption/ozonation experiments were also carried on into the batch reactor, under the conditions described below. After a 4 h adsorption period, ozone process was turned on during 2.5 h (flow rate: $0.5 \text{ L}\cdot\text{min}^{-1}$; ozone concentration: $39 \pm 3 \text{ mg}\cdot\text{L}^{-1}$). This duration was chosen because it corresponds to the time required for the total oxidation of a $240 \text{ mg}\cdot\text{L}^{-1}$ 2,4-DCP solution by ozone under these experimental conditions. The experiment was repeated twice with the same material but a fresh 2,4-DCP solution was loaded before beginning the second run.

RESULTS AND DISCUSSION

Ozone Decomposition in the Presence of Adsorbent Materials

The evolution of ozone concentrations either in the liquid phase or in the outlet gas phase are reported in Figure 3. The results for ozone decomposition in water were determined from these curves and are reported in Table 3.

The values of the volumic ozone transfer coefficient, $k_{L,a}$, are much lower than the values usually observed in bubble columns. However, these results are consistent with the results published by Bouafi et al., 2001; the very low superficial velocity of the gas – about $1.0 \cdot 10^{-3} \text{ m}\cdot\text{s}^{-1}$ – provides a limited gas hold-up and interfacial area despite the mechanical stirring.

First, the results show that ozone transfer kinetics is not modified in the presence of the solid materials. This result was anticipated since this parameter only depends on

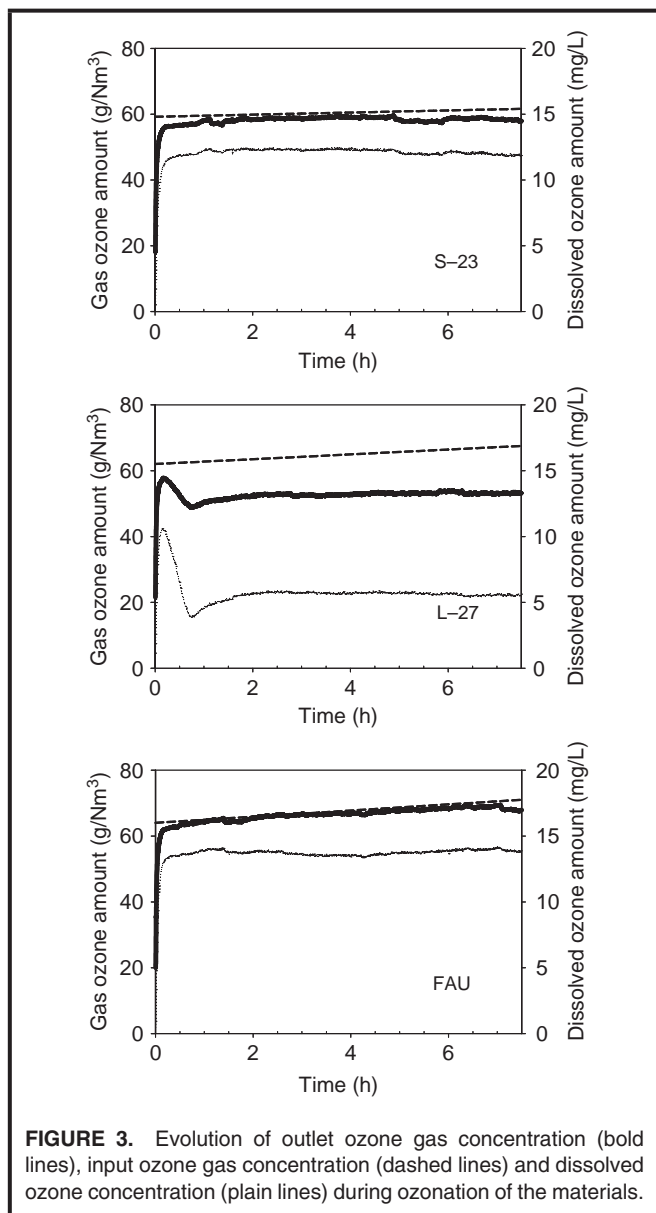


FIGURE 3. Evolution of outlet ozone gas concentration (bold lines), input ozone gas concentration (dashed lines) and dissolved ozone concentration (plain lines) during ozonation of the materials.

TABLE 3. Volumic Ozone Transfer and Self-Decomposition Kinetics Parameters in the Presence of Materials

Material	$k_{L,a} \times 10^3 \text{ (s}^{-1}\text{)}$	$k_C \times 10^4 \text{ (s}^{-1}\text{)}$
None – pH = 5	4.8	3.8
1 g.L ⁻¹ S-23	4.0	5.0
1 g.L ⁻¹ L-27	–	90.0
1 g.L ⁻¹ FAU	5.0	2.5

physico-chemical conditions which are similar with or without material (same liquid phase composition, gas velocity and gas-liquid interfacial area . . .). The volumic ozone transfer coefficient for the L-27 experiment could not be calculated because the ozone concentration profile was modified in

relation with the catalytic effect of the activated carbon and, thus, did not follow the evolution expected (see Figure 3).

Ozone self-decomposition kinetics is not changed in the presence of Faujasite whereas it is increased about 1.3 times with S-23 and about 24 times with L-27. This result is not surprising since activated carbons are known for their ability to decompose ozone into hydroxyl radicals. The difference between the two activated carbons can be linked to a difference in their active surface (as shown in Table 1) but also in the chemical composition of the material itself. As already mentioned for L-27 activated carbon, an unexpected decrease in ozone concentration was observed after about 10 minutes. Among the various hypotheses which can help explaining this behavior, the more likely is a change in the L-27 structure leading to higher ozone decomposition, since similar behaviors were observed by Reungoat, 2007, during ozonation of nitrobenzene in solutions buffered at pH 2.2. Moreover, the change in L-27 activated carbon structure is confirmed by BET and DTG measurements (see Table 4 and Figure 4).

Evolution of the Material Structure after Exposure to Dissolved Ozone

Table 4 reports the main physical characteristics of the materials before ozonation (V), after 15 h exposure to ozone (O) and after sequential adsorption/ozonation process (SP). Figure 4 reports the DTG analyses for the three materials after the same treatment conditions. The results for adsorption and oxidation kinetics during the SP treatment will be discussed later.

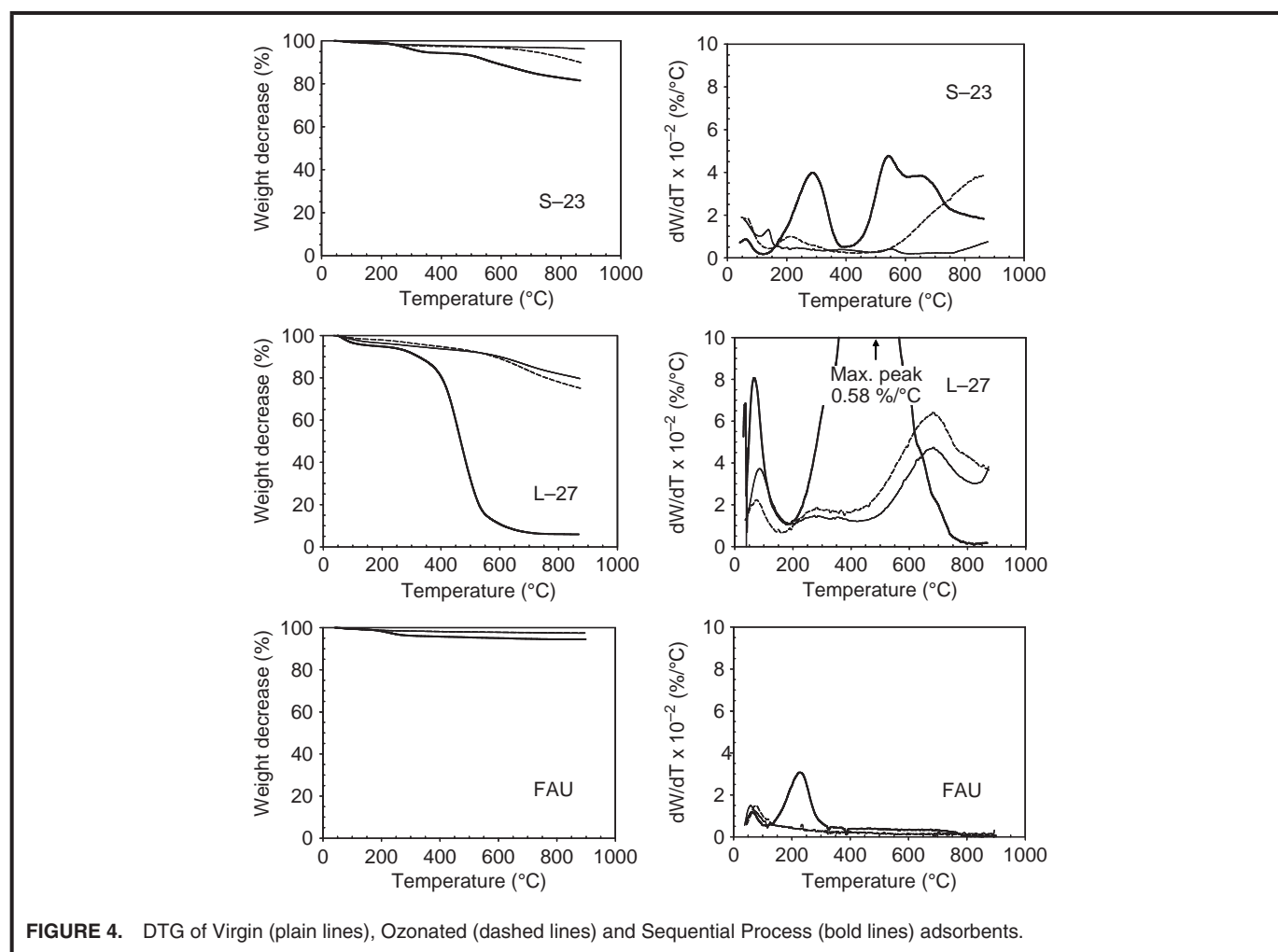
The comparison of the first two columns (V and O) for each material in Table 4 leads to the following remarks. Both S-23 activated carbon and faujasite structures were not changed after exposure to ozone whereas L-27 activated carbon was degraded after exposure ozone. Its total surface area was decreased by about 26% and its porous volume was reduced by about 47% (89% for mesoporous volume and 18% for microporous volume). The material also became very friable. Moreover, the DTG curves for virgin (V) and ozonated (O) materials (Figure 4) were quite similar except for very high temperatures, where ozonated S-23 seems to decompose whereas virgin S-23 does not. The peak close to 100°C corresponds to water desorption.

The ageing of the materials after the Sequential Process is more difficult to interpret. As shown by the results in Table 4, for each material, SP surface area was different from the two other values (V and O), probably indicating that the material regeneration by ozone was not complete. This was confirmed by DTG curves where a peak around 210°C appeared which corresponds to 2,4-DCP desorption. As can be seen for this temperature, there was an approximately 10% mass loss for FAU and S-23 due to 2,4-DCP desorption. A second desorption peak appeared for S-23 around 600°C probably indicating a slight degradation of the material. On the other hand the mass loss for L-27 activated carbon was

TABLE 4. Characteristics of Virgin (V), Ozonated (O) and Sequential Process (SP) Media

	Activated carbon						Zeolite		
	S-23			L-27			FAU		
	V	O	SP	V	O	SP	V	O	SP
Total surface area	1374	1426	704	2337	1716	1745	614	617	556
Microporous area	1373	1424	695	2313	1708	1722	515	533	477
External area	1	2	9	24	8	23	99	84	78
Total porous volume	0.58	0.59	0.31	1.36	0.72	1.07	0.45	0.49	0.44
Mesoporous volume	0.05	0.04	0.08	0.53	0.06	0.46	0.26	0.29	0.24
Microporous volume	0.56	0.58	0.29	0.85	0.70	0.57	0.21	0.21	0.20

Areas are in $\text{m}^2 \cdot \text{g}^{-1}$.
 Volumes are in $\text{cm}^3 \cdot \text{g}^{-1}$.

**FIGURE 4.** DTG of Virgin (plain lines), Ozonated (dashed lines) and Sequential Process (bold lines) adsorbents.

continuous between 200 and 800°C and was quite 100% for the latter temperature. Here again, it is confirmed that L-27 activated carbon is strongly degraded by ozone and that this material is not suited for a combined adsorption/oxidation process.

Removal of 2,4-DCP by Adsorption, Ozonation and Simultaneous Adsorption/Ozonation Process

Figure 5 shows 2,4-DCP removal by adsorption (A), single ozonation (O) and simultaneous adsorption/ozonation process (AO). In a first approach, the evolution of the

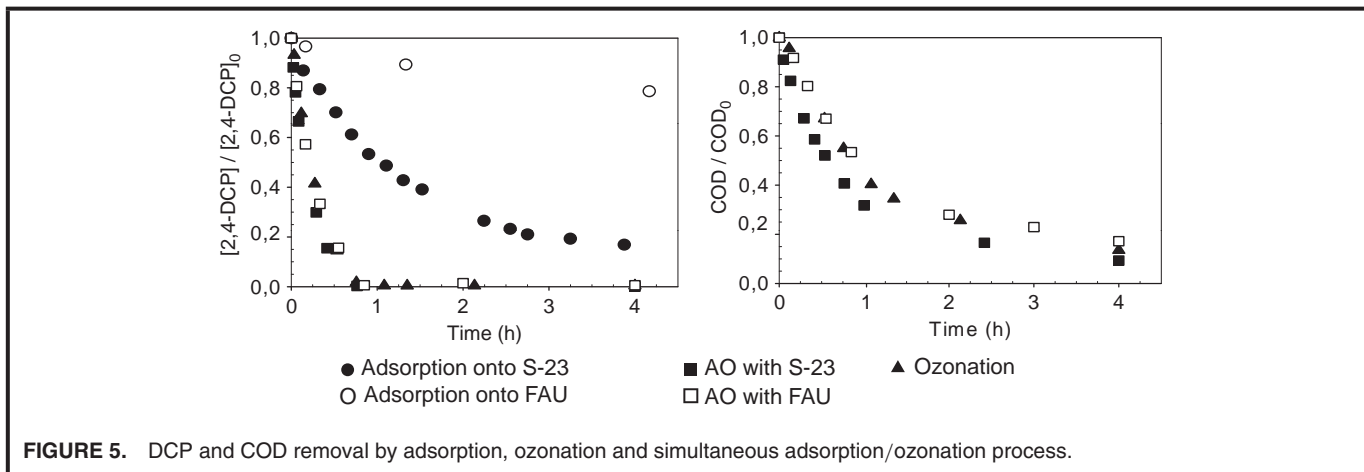


TABLE 5. Adsorption and Ozonation Pseudo-first-order Constant with 2,4-DCP

Without adsorbent	S-23		FAU	
	k_{Ads}	k_{Ozo}	k_{Ads}	k_{Ozo}
k_{Ozo}				
77	9.0	110	0.88	59

All constants are in 10^{-3} min^{-1} .

concentrations can be modeled by a pseudo-first-order kinetics law as described by Equation 3. The values of the corresponding kinetic constants are reported in Table 5.

$$C = C_0 \times e^{-k \times t} \quad [3]$$

with:

- C, C_0 current [resp. initial] concentration in the liquid phase (either 2,4-DCP or COD);
- t time;
- k 1st-order kinetic constant (either adsorption k_{Ads} or ozonation k_{Ozo})

The 2,4-DCP adsorption onto Faujasite was about 10 times slower than 2,4-DCP adsorption onto S-23, as proven by the corresponding kinetic constants in Table 5. This is easily explained by a higher granular diameter which induced slower diffusion phenomena. Above this, pore diameter and BET surface are lower for the zeolite than for activated carbons.

Ozonation – single or combined – is a more efficient process than adsorption. However, the addition of either S-23 activated carbon or faujasite during ozonation does not improve 2,4-DCP removal since the kinetic constants remain in the same order of magnitude. In the case of this molecule, single ozonation is efficient enough for a fairly quick removal; thus the catalytic material considered during this study did not exhibit any dramatic increase in the reactivity.

Yet, the interest of the combined S-23 ozonation process is proven when the COD abatement is followed (Figure 5, right side). The radical process induced by S-23 activated

carbon allowed a faster oxidation of 2,4-DCP degradation by-products and a better efficiency at the end of the reaction period. Comparable conclusions were observed by Reungoat et al. (2007a, 2007b), during additional experiments with nitrobenzene and it was established that ozone consumption was lower during the combined process than during classical ozonation.

Removal of 2,4-DCP by Sequential Adsorption/Ozonation Process (SP)

Figure 6 shows the evolution of 2,4-DCP and of COD concentrations during two successive cycles of the sequential adsorption/ozonation process. The kinetics of the two adsorption steps were once again modeled through pseudo-first-order laws and the corresponding constants are given in Table 6.

The values for the first adsorption step are consistent with the adsorption kinetics constants given in Table 5. As regards the second adsorption step (i.e., after exposure to ozone during 2.5 h), the kinetics seemed to be quite slowed down for the two activated carbons, whereas it was not changed for faujasite. Two phenomena can explain this behavior: first, the surface regeneration during the ozonation steps are not complete as discussed in the following paragraph. Indeed, DTG measurements after the two cycles as well as BET surface determinations (Table 4) showed that an amount of molecules remained adsorbed onto the solids surface. This amount was low for Faujasite, higher for S-23 and far higher for L-27 activated carbon. This result is consistent with the decrease in the adsorption kinetics. Secondly, the porous volume of the two activated carbons was also decreased after the two SP cycles, which can also explain the decrease in the adsorption kinetics.

As regards the ozonation of adsorbed pollutants, it allowed a total removal of 2,4-DCP for each material. A little difference could be found in terms of duration: for S-23 experiments, ozonation time to reach zero DCP in water was lower than for AO experiments (30 min versus 45 min); on

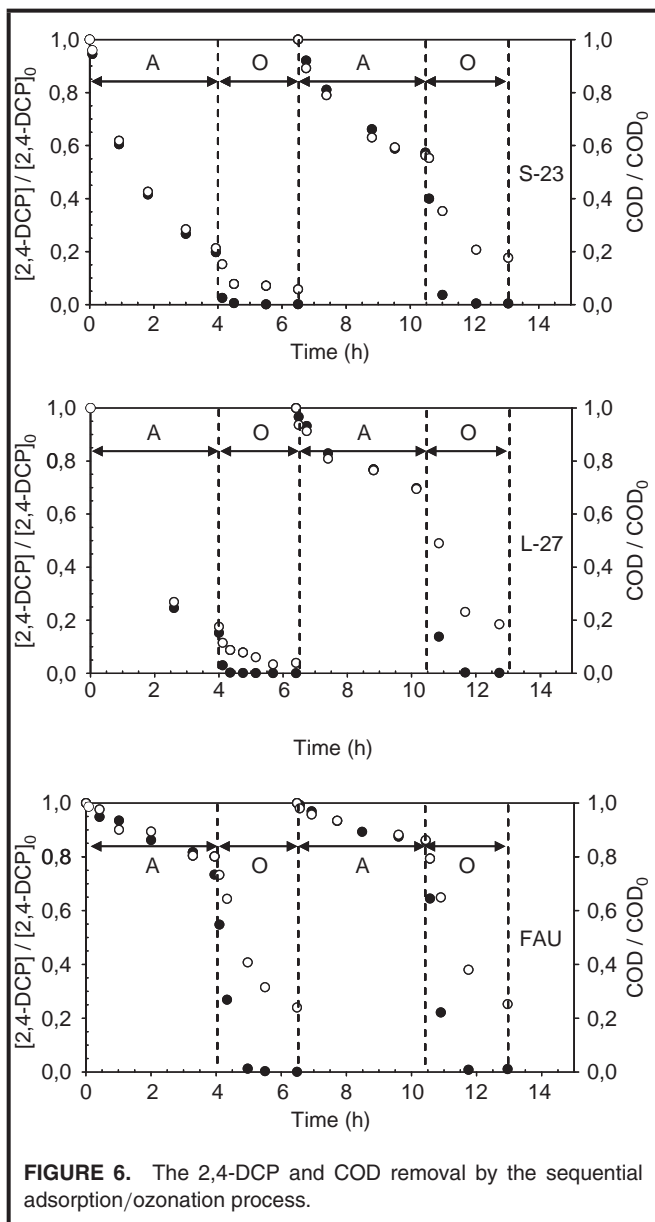


FIGURE 6. The 2,4-DCP and COD removal by the sequential adsorption/ozonation process.

TABLE 6. Evolution of the First-Order Constants During the Two 2,4-DCP Adsorption Steps in the Sequential Process

S-23		L-27		FAU	
$k_{Ads\ 1}$	$k_{Ads\ 2}$	$k_{Ads\ 1}$	$k_{Ads\ 2}$	$k_{Ads\ 1}$	$k_{Ads\ 2}$
7.3	2.4	8.0	1.5	1.2	0.9

All constants are in 10^{-3} min^{-1} .

the contrary, this time was higher for SP experiments on FAU (1 h) than for AO experiments on FAU (45 min) and, at last, L-27 behaved like S-23. However, considering global pollution, the efficiency was not total for the 3 materials: a residual value of COD still remained after ozonation. This value seemed to be weaker than for AO experiments, as well

for S-23 as for FAU: about 14% for AO experiments versus 5% for SP experiments.

A concentration effect must account for this result. At last, after the second cycle, a slight difference between the materials could be noticed in terms of COD but not for DCP removal. The residual COD value for FAU experiments was 26% whereas this COD value was 17% after ozonation of S-23 or of L-27. But these were not significant differences according to experimental and measurement standard deviations.

CONCLUSIONS

This work investigated a hybrid process coupling adsorption and oxidation by ozone for pollutants removal in water. An aqueous solution of 2,4-dichlorophenol was used as a model pollutant accounting for industrial wastewater. Two granular activated carbons (microporous S-23 and micro/mesoporous L-27) and a de-aluminized zeolite (FAU) were chosen for adsorbents. All materials exhibited good adsorption capacities towards 2,4-DCP. The adsorption kinetics was faster for the activated carbons than for zeolite, due to both lower particle diameters and higher pore diameters and surface areas.

As expected, the two activated carbons showed good ability to decompose ozone whereas the zeolite did not exhibit such a catalytic effect. On the other hand, the short term stability of Faujasite towards ozone could be proved. S-23 activated carbon also seemed to hold its adsorption capacities after 15 hours exposure to ozone, whereas L-27 activated carbon seemed to be degraded by ozone: decrease of surface area, dramatic loss of either meso and micro-porosities and increased mechanical fragility. Hence, despite its good catalytic properties, this material was withdrawn of the rest of the study.

The simultaneous combination of adsorbent and ozone did not improve 2,4-DCP removal kinetics compared to classical ozonation. It appeared that 2,4-DCP ozonation was fast enough not to need any catalysis. Yet, the combined process with S-23 activated carbon seemed to enhance COD removal; this is probably related to HO° radicals production which improves the further oxidation of 2,4-DCP decomposition products. These results were comparable to results obtained with nitrobenzene (9, 10 and 11). Ozone consumption was not determined in this work but it is expected to be improved in the Combined Process compared to classical ozonation.

The solids regeneration by ozone was also investigated in a 4 hours adsorption and 2.5 hours ozonation Sequential Process. Two successive cycles were performed with both S-23 and FAU. For the durations used in this work, it was evidenced that 2,4-DCP was completely removed through the ozonation stage but that incomplete COD oxidation was achieved. Moreover, DTG analyses showed the persistence of residual molecules onto the solid surfaces. Thus, the duration of the two phases should still be optimized in order to

reduce ozone consumption along with improving the oxidation efficiency. At last, the materials submitted to two cycles seemed to keep correct adsorption capacities. A long-term investigation is underway to better characterize the materials ageing.

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