



Advanced oxidation (UV-ozone) and cyclodextrin sorption: Effects of individual and combined action on the chemical abatement of organic pollutants in industrial effluents

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ABSTRACT

Among organic pollutants, four families have been listed as priority substances by the European Agency, namely polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), chlorophenols (CPs) and alkylphenols (APs). In this study, sorption onto a non-conventional cyclodextrin-based material alone as well as in combination with advanced oxidation using a UV-ozone process as pre-treatment was applied for the removal of PAHs, VOCs, CPs and APs from industrial effluents. After the various treatments proposed, we present the abatements obtained in the levels of chemical pollution monitored by a complete chemical analysis, and total organic carbon (TOC) and chemical oxygen demand (COD) measurements. High levels of pollutant removal were attained with the combined use of oxidation and sorption. The treatment led to the almost total elimination of organics such as chloroform, 1,2-dichlorobenzene, 2,4,6-trichlorophenol, nonylphenol and phenanthrene. The treatment also lowered TOC and COD by more than 84% and 93%, respectively. This combined lab-scale process using a non-conventional material could constitute an advantageous technology for removing organic pollutants when scaled up to treat polycontaminated industrial effluent.

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1. Introduction

To limit the environmental impact of industrial effluent, wastewater must be treated before it is discharged. Even though the effluent respects the statutory limits, the industrial sector is nevertheless considered to be one of the sectors of human activities that generates the most water-borne pollution. However the regulations are becoming increasingly strict and industry now has to find better treatment and/or reduce the quantity of effluent released. From an environmental point of view, the ideal solution is to tend towards zero pollution by perfecting conventional systems of water purification by adding further stages to the treatment [1]. For instance, the surface finishing industry can complete the

standard physical-chemical installations used to treat their waste water before release using the series: microfiltration + reverse osmosis + evaporation to reach the goal of zero liquid effluent release. However, owing to technical and especially economic limitations, zero release is not frequently practiced by European industry [1–4]. The choice made generally consists of treating the effluent to below the regulatory limits then discharging the effluent into the nearest water body or the drains for treatment in the urban wastewater treatment plant. However, even though the effluent satisfies legal requirements, it still contains non-negligible amounts of a heterogeneous pollution that is, in particular, variable in time. Complementary methods are therefore required to efficiently eliminate this residual pollution. However, the problem is not straightforward as it is difficult to remove the last pollutants, especially organic substances that are present at low or very low concentrations in complex polycontaminated effluent [2,3], in an economically feasible way. There is therefore a demand for

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innovation in the treatment of wastewater, to find new methods that are both chemically efficient and that are useable on an industrial scale.

Recently, various materials based on beta-cyclodextrin (beta-CD), which is a natural molecule derived from starch by enzymatic alteration, have been proposed for this purpose. This substance has a remarkable capacity to form inclusion complexes in solution with organic molecules through host-guest interactions [5,6]. Numerous recent studies on the removal of pollutants by crosslinked gels or CD beads based on oriented-sorption processes have shown that these materials are efficient for the treatment of synthetic solutions of phenolic or other aromatic compounds, mainly containing a single contaminant molecule [7–15]. The removal of the pollutants is mainly accounted for by the formation of inclusion processes due to the presence of the cyclodextrin motifs and the specific crosslinked structure of the CD. However, only few studies have reported the use of CD polymers for the treatment of industrial effluent polycontaminated with organic substances such as polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), chlorophenols (CPs) or alkylphenols (APs).

In the present study, we report the performance of a non-conventional material based on CD to treat a mixture of organic substances (PAHs, VOCs, CPs, APs) present in industrial effluents using an oriented-sorption process. We present the chemical abatements obtained using the process alone or combined with a pre-treatment using advanced oxidation. We also compare the performance of the CD material with that obtained using a crosslinked starch, in order to highlight the role of the formation of inclusion complexes.

2. Materials and methods

2.1. Industrial effluents

Polycontaminated industrial effluents were collected from EEA Industry located in Vitreux (Jura, France). Their analytical characteristics are described in Table 1 for three sampling campaigns. The values described in the table represent the minimal and maximal concentrations obtained for the 5 effluents studied.

2.2. Materials

Two non-conventional crosslinked polysaccharides (abbreviated as beta-CD and starch) were used in this study. Their general

description is given in Table 2. Beta-CD and starch are two crosslinked polymers, prepared in two steps. Firstly, reticulating commercial biopolymer using 1,4-butanediol diglycidyl ether in the presence of NH_4OH and 2,3-epoxypropyltrimethylammonium chloride and secondly carboxymethylating it by means of a chloroacetic acid solution. The synthesis and characterisation have already been described in detail in previous works [16,17].

2.3. Analytical methods

Pollutant removal from effluents by sorption on materials was studied by the batch method without changing the initial pH of the effluent [18]. In each experiment, 5 g of material were mixed with 5 L of effluent in a flask at room temperature ($21\text{ }^\circ\text{C} \pm 1$). The mixture was then mechanically stirred for 1 h at a constant speed of 250 rpm. After treatment, the material and solution were separated by filtration. The parameters (COD and TOC) and pollutant concentrations in the initial effluents and in the treated effluents were determined by chemical analysis as described in detail elsewhere [17–19]. The measurements were repeated three times and average values taken as the amount of pollutant remaining in the effluents. Results are expressed in mg/L or in $\mu\text{g/L}$. The COD was determined by the dichromate COD method based on the use of colorimetric measurement using standards (model COD Vaxio, Aqualytic PCCompact, Dortmund, Germany). Concentrations of TOC were measured by a portable photometer (Spectroflex 6100 model, WTW, Alès, France) using test kits (TOC Cell test, Merck, Darmstadt, Germany). Organics were analysed by an accredited analysis laboratory (LCDI, Marange, France) using standard French protocols [17–19].

2.4. Experimental setup for oxidation

All oxidation-based reaction runs were carried out in a cylindrical glass reactor (75 mm ID \times 230 mm H) equipped with a magnetic stirrer and a thermostat [19]. At the beginning of each run, the reactor was almost completely filled with the effluent (1 L) in order to minimise headspace and thus loss of volatile substrates. Ozone was produced from dried air by an ozone generator (Anseros COM-AD-01). It was continuously bubbled through the effluent, by means of a ceramic sparger, at a flow rate of 10 L/h, providing an O_3 dose of 1.00 ± 0.02 mg/min. The reactor was also equipped with a low-pressure mercury lamp, emitting UV radiation at 254 nm with a light intensity of 4.5×10^{-6} Einstein/L/s. The UV lamp was placed centrally in the internal quartz well of the reactor (immersed in the solution). All runs were carried out at the initial pH of the effluent

Table 1
Maxima and minima (\pm standard deviation) for several parameters and pollutants over 5 industrial effluents taken during the three sampling campaigns (five samples taken on five consecutive days; samples characteristic of that day's activity; for COD and TOC measurements the concentrations are expressed in mg/L and for the organics in $\mu\text{g/L}$; pH at $20\text{ }^\circ\text{C}$).

Pollutant/parameter	Campaign 1	Campaign 2	Campaign 3
pH	7.9–8.5 (± 0.2)	8.0–8.5 (± 0.2)	8.0–8.4 (± 0.2)
Chemical oxygen demand (COD)	125–175 (± 21)	165–270 (± 41)	133–172 (± 15)
Total organic carbon (TOC)	27–44 (± 7)	30–85 (± 22)	37–53 (± 7)
Anthracene	<0.01	<0.01	<0.01–0.35 (± 0.15)
Naphthalene	<0.01–0.26 (± 0.12)	<0.01	<0.01–0.2 (± 0.09)
Phenanthrene	<0.01	2.4–17.8 (± 6.8)	<0.01
Chloroform	9.1–71 (± 25.7)	25.0–180.0 (± 68.8)	11.0–62.0 (± 20.4)
Toluene	<0.5	3.9–20.2 (± 7.1)	<0.5
1,2-Dichlorobenzene (1,2-DCB)	<0.01	7.2–139.7 (± 57.5)	<0.01
2-Chlorophenol (2-CP)	<0.01–0.5 (± 0.22)	<0.01	<0.01–0.3 (± 0.13)
4-Chlorophenol (4-CP)	<0.01	<0.01–1.1 (± 0.49)	<0.01
2,4-Dichlorophenol (2,4-diCP)	<0.01	<0.01	<0.01–0.4 (± 0.20)
2,4,6-Trichlorophenol (2,4,6-triCP)	<0.01–0.7 (± 0.30)	<0.01–1.9 (± 0.82)	<0.01
Nonylphenol (NP)	<0.1–0.11 (± 0.05)	8.1–30.7 (± 9.3)	4.5–7.3 (± 1.1)
Octylphenol ethoxylate (OP1EO)	0.14–1.9 (± 0.72)	<0.1	<0.1
Octylphenol diethoxylate (OP2OE)	0.88–3.0 (± 0.96)	<0.1	<0.1

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