Natural Organic Matter Removal by Heterogeneous Catalytic Wet Peroxide Oxidation (CWPO)

José Herney Ramírez and Luis Alejandro Galeano

Abstract NOM usually reaches drinking water supply sources through metabolic reactions and soil leaching. It has been, in general, considered that NOM is still one of the most problematic contaminants present in this kind of influents. Therefore, in the present chapter, most relevant technologies used for removal of NOM and its constituents from water have been examined, emphasizing in the past few years. An overview of the recent research studies dealing the NOM removal by catalytic wet peroxide oxidation and other closely related heterogeneous Fenton-like AOPs is presented. As revealed from recent literature reports, heterogeneous Fenton processes including CWPO are still emerging, promising catalytic technologies for NOM removal from water. A wide variety of catalytic solids reported within the past few years has been examined focusing on their potential in the NOM removal from water. Main findings offered by several types of catalysts like zeolites, Fe-functionalized activated carbons, carbon nanotubes, but mainly pillared and other clay minerals have been critically discussed emphasizing on the NOM removal by CWPO.

Keywords Al/Fe-pillared clay, Catalytic wet peroxide oxidation, Natural organic matter, Water treatment

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Abbreviations

AC	Activated carbon
AERs	Anion exchange resins
AMR	Atomic metal ratio
AOC	Assimilable organic carbon
AOPs	Advanced oxidation processes
BAC	Biologically activated carbon
BDD	Boron-doped diamond
BDOC	Biodegradable dissolved organic carbon
CNTs	Carbon nanotubes
CWPO	Catalytic wet peroxide oxidation
CEC	Cationic exchange capacity
CC	Chemical coagulation
COD	Chemical oxygen demand
4-CP	4-Chlorophenol
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
EC	Electrocoagulation
EO	Electro-oxidation
GAC	Granular activated carbon
HC	Hydrodynamic cavitation
HDC	Hydro-dechlorination
HMW	High molecular weight
$HO^{\bullet}$	Hydroxyl radical
IMW	Intermediate molecular weight
LC-OCD	Liquid chromatography-organic carbon detector
LMW	Low molecular weight
NA	Nano-adsorbents
NOM	Natural organic matter
PCMC	P-chloro-m-cresol
PILCs	Pillared clays
ROS	Radical oxygen species
THMs	Trihalomethanes
TOC	Total organic carbon

1 Introduction

Waste and surface waters are currently strongly requiring development and application of novel, cost-effective treatments. A number of techniques such as chemical, physical, biological, incineration, etc. and their combinations are available, but each process has its inherent limitations in applicability, effectiveness, and cost. There are many water systems not suitable for biological treatments, mainly due to the presence of some highly refractory and toxic pollutants. Their treatments by conventional chemical processes may have several drawbacks in terms of efficiency and/or cost.

NOM may cause many problems in wastewater treatment processes, for example, undesirable color, taste, and odor, while reacting with common disinfectants to produce a variety of toxic DBPs [1]. Residual NOM can also promote bacterial regrowth and pipe corrosion in drinking water distribution systems [2]. NOM also reduces the overall efficiency of water treatment plants through increased chemical dosages, interference with the removal of other contaminants and filter fouling [3], as well as increased levels of complexed heavy metals and adsorbed organic pollutants [4], among others.

Changes in NOM loading and composition have a significant influence on the selection, design, and operation of water treatment processes. No single process alone can be used to treat NOM due to its very high variability.

2 Conventional Techniques Used in NOM Removal from Water

Diverse processes have been investigated to remove NOM from water such as adsorption, coagulation/flocculation, advanced oxidation processes, biological and electrochemical methods, ion exchange, and membrane technology. These processes are the most common and economically feasible to remove NOM. In the following sections, the removal of NOM by some conventional techniques has been presented and discussed.

2.1 Adsorption

The adsorption process is generally considered as one of the best water treatment technologies because of its convenience, ease of operation, and simplicity of design. The mechanism of NOM adsorption is mainly ligand exchange with the hydroxyl groups of the mineral surface [5]. Different kinds of adsorbents are used to eliminate NOM, including AC [6]. Li et al. [7] showed that constriction of internal pores of the carbon caused a reduction in the diffusion rate of the targeted compounds. By comparison of two carbons, the extent of reduction in the diffusion coefficient caused by adsorption of the same concentration of a pore-blocking compound, mg/g of AC, was found to be less pronounced for the carbon with larger volume of mesopores. AC is often used in drinking water treatment plants to remove or control unpleasant taste and odor, organic compounds, and NOM. Columns are used in municipal treatments to produce potable water as well as in disposable cartridges at industrial, commercial, and residential installations.

AC has been also used in the treatment of municipal wastewater either as a secondary or a tertiary process, with the advantage over other materials of being able to control odor in the water. The carbon may be either powdered or granular, the former being added as slurry into the water before chlorination, whereas the latter used in conventional gravity sand filters alone or together with sand.

GAC is good choice for removing NOM as well as taste and odor compounds. The removal of NOM by GAC is through reversible and irreversible physical adsorption caused by nonspecific mechanisms, such as van der Waals forces, dipole interactions, and hydrophobic interactions [8]. There are two options for locating GAC units in water treatment plants, i.e., (1) post-filtration adsorption, where the GAC unit is located after the conventional filtration process, and (2) filtration-adsorption, in which either all or a fraction of the filter granular media is replaced by GAC. Compared with filter adsorbents, the post-filtration provides higher flexibility for both handling GAC and design of specific conditions of adsorption and thus often allows for lower operational costs.

Many bench-, pilot-, and full-scale studies have shown GAC as a promising method to effectively remove NOM [9, 10]. However, a major constraint in operating GAC contactors is the cost of routinely replacing the GAC media due to the loss of adsorption capacity that occurs once GAC saturates.

2.2 *Coagulation/Flocculation*

The most common and economically feasible process available to remove NOM is coagulation and flocculation followed by sedimentation/flotation and filtration. Most of the NOM can be removed by coagulation, although the hydrophilic, LMW fractions of NOM are apparently removed less efficiently than the hydrophobic, HMW compounds [11]. Coagulation/flocculation in water/wastewater treatment plants involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation [12]. As chemical products, coagulants react with the suspended and colloidal particles in the water, causing them to bind together and thus allowing for their removal in the subsequent treatment processes [13]. The aggregation mechanisms through which particles and colloids are removed include a combination of charge neutralization, entrapment, adsorption, and complexation with coagulant ions into insoluble masses [14].

Coagulation treatment has been employed to decrease turbidity and color and also to remove pathogens [15]. It is well established through the long and large literature that the coagulation process efficiency is highly dependent on hydrophilic and hydrophobic properties (Table 1) of NOM and dissolved organics [16–18].

Coagulation can be induced using chemical salts, such as ferric chloride or alum, or via electrocoagulation (EC) which uses sacrificial electrodes to provide a pure source of cations. Unlike chemical coagulation (CC), EC is not a commonly used water treatment technology. Nevertheless, EC has successfully treated a diverse variety of water types at the bench-scale, including municipal, textile dye, and petroleum refinery wastewaters [20–22].

2.3 Advanced Oxidation Processes (AOPs)

AOPs are based on the production of highly reactive, short-lived hydroxyl radicals, which react with organic contaminants with high reaction rate constants.

AOPs destroy the organic molecules, even the more stable, hard-to-degrade compounds, including carcinogens and mutagens, by means of the generation of highly reactive species which oxidize organic matter; thus, AOPs may be of great interest for public health and turned into a promising study field due to its almost total degradation potential of soluble organic contaminants in waters and soils, some of them under reasonably mild temperature and pressure conditions [23–26].

In AOPs, chemical reactions, electron beams, UV light, or ultrasound pulses are used to obtain high oxidation rates, thanks to the generation of free radicals (mainly hydroxyl radicals). Indeed, highly reactive $HO^{\bullet}$ are traditionally thought to be the main active species responsible for the destruction of the contaminants, including NOM. Their high standard reduction potential of 2.8 V in acidic media enables these radicals to oxidize almost all organic compounds to carbon dioxide and water,

Table 1 NOM fractions and chemical groups (adapted from [19])

Fraction	Chemical groups
Hydrophobic	
Strong acids	Humic and fulvic acids, HMW alkyl monocarboxylic and dicarboxylic acids, aromatic acids
Weak acids	Phenols, tannins, IMW alkyl monocarboxylic and dicarboxylic acids
Bases	Proteins, aromatic amines, HMW alkyl amines
Neutral	Hydrocarbons, aldehydes, HMW methyl ketones and alkyl alcohols, ethers, furans, pyrrole
Hydrophilic	
Acids	Hydroxy acids, sugars, sulfonics, LMW alkyl monocarboxylic and dicarboxylic acids
Bases	Amino acids, purines, pyrimidine, LMW alkyl amines
Neutrals	Polysaccharides, LMW alky alcohols, aldehydes, and ketones

excepting some of the most simple organic compounds, such as acetic, maleic, and oxalic acids, acetone, or simple chloride derivatives as chloroform [27]; however, just these species are of interest because they are typically oxidation products of larger molecules, being continuously generated by chemical, photochemical, or electrochemical reactions.

Among the more used AOPs, photo-Fenton and photocatalysis have been of special interest [28]. The photo-Fenton reaction is well known as an efficient and inexpensive method for wastewater treatment. Photo-Fenton improves the efficiency of dark Fenton or Fenton-like reagents, respectively, by means of the interaction of radiation (UV or Vis) with Fenton reagents. Light exposure increases the rate of $HO^{\bullet}$ formation by photoreactions of H_2O_2 ($\lambda < 360$ nm) and/or Fe^{3+} either producing $HO^{\bullet}$ straightforward or regenerating Fe^{2+} [29].

Photocatalysis is defined as catalytic activation of a given reaction via a mechanism that only proceeds if the system is lighted up. Photocatalytic reactions may operate via a number of different mechanisms. The main well-known mechanisms are (1) photolysis of adsorbates, (2) reactions of adsorbed species with photoelectrons or holes (photo-electrochemical reaction), and (3) injection of electrons from an excited adsorbate into a semiconducting mineral [30].

The efficiency of NOM removal using AOPs strongly depends on water characteristics, including the concentration of organic matter. Therefore, characterization of the NOM in water should necessarily anticipate the design and optimization of any AOP treatment. The characteristics of the organics in the treated water must be also determined to assess their influence on downstream processes.

The reactions of $HO^{\bullet}$ with NOM proceed at least by means of three different ways: (1) $HO^{\bullet}$ addition on double bonds; (2) H-atom abstraction, which yields carbon-centered radicals; and (3) the $HO^{\bullet}$ gaining an electron from an organic substituent. The carbon-centered radicals then react very rapidly with oxygen to form organic peroxyl radicals. The mutual reactions of peroxyl radicals can lead to the production of ketones or aldehydes and/or carbon dioxide. The rate of oxidation depends on radical, oxygen, and pollutant concentrations. Other factors affecting formation of the radicals are pH, temperature, the presence of ions, the type of pollutant, and the presence of scavengers such as bicarbonate ions [31].

Finally, $HO^{\bullet}$ can also be produced without using chemicals by means of cavitation. Generally it is a phenomenon of formation, cyclic growth, and rarefaction with the terminal implosive collapse of vapor bubbles in the liquid phase. Cavitation, caused by pressure gradients of water due to the influence of geometry, is called hydrodynamic cavitation (HC). Recent studies show beneficial effectiveness of HC for degradation of various recalcitrant organic contaminants (pharmaceuticals, synthetic and persistent organic chemicals, micropollutants, etc.) from water and wastewater [32].

2.4 Ion Exchange

Important properties of AERs include polymer composition, porosity, and charged functional groups. Performances of AERs for NOM removal are influenced by the inner characteristics of the resins (strong- or weak-base AER), the water quality (pH, ionic strength, hardness, etc.), and the nature of organic compounds (molecular weight, charge density, and polarity). The composition of most resins is either polystyrene or polyacrylic. Polystyrene resins are more hydrophobic than polyacrylic resins; as a result, polyacrylic resins tend to have more open structure and higher water content. The porosity of resins is defined as either macroporous or gel. Macroporous resins are highly porous solids, while gel resins do not contain any pores [30]. Strong-base resins typically contain either type I ($-N+(CH_3)_3$) or type II ($-N^+(CH_3)_2(C_2H_4OH)$) quaternary ammonium functional groups. Due to their ethanolic content, type II resins are more hydrophilic than type I resins [33]. Most strong-base anion exchange resins are used in the chloride form.

The advantages and disadvantages of NOM removal by using ion exchange treatment are presented in Table 2. As is evident this technology is very interesting since it has proven to be highly efficient, while exhibiting very low formation of DBP; only one disadvantage can be observed for this technology regarding the necessity of an additional treatment stage since the NOM removal is not complete.

3 NOM Removal from Water by Heterogeneous CWPO and Other Related AOPs

AOPs are gaining more and more interest as potential solutions in the field of water treatment; the use of appropriate catalysts can substantially decrease the energy consumption of oxidation processes, such as wet air and wet peroxide oxidation of refractory organic compounds. The main limitation of the conventional Fenton process is the dissolved homogeneous catalyst that cannot be easily recovered throughout the process, leading to additional pollution [34]. Besides, another outstanding issue that has deserved a number of works in the past few years regarding drawbacks of the homogeneously activated Fenton process has been the very narrow range of pH values (<~4.0) [35] under which it is operable as efficient catalytic process itself (Fig. 1); it associates high operating costs for industrial-scale

Table 2 Advantages and disadvantages of NOM using ion exchange treatment

Advantages	Disadvantages
Proven technology	Additional stage of treatment required
Potential highly efficient	
Very low formation of DBPs	
Efficient in treating the transphilic fraction of NOM	

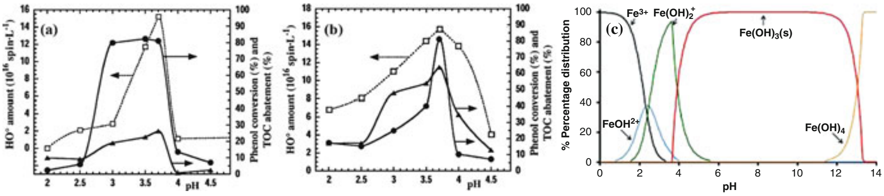

Fig. 1 Effect of pH on the catalytic performance of the Fenton process activated under either homogeneous or heterogeneous conditions: (**a**) homogeneous system ([Fe] = 5 mg/L) and (**b**) heterogeneous catalyst (Al/Fe-PILC FAZA, 5 g/L), amount of DMPO/HO adduct, phenol conversion (after 2 h of reaction), and TOC abatement (after 4 h of reaction) in function of the pH: (*open square*) DMPO/HO. Adduct amount (*dotted line*), phenol conversion (*filled circle*), TOC abatement (*filled triangle*) (reprinted from [35], with permission of Springer). (**c**) Speciation diagram of ferric hydroxyl species as a function of pH for a solution containing 1.0×10^{-5} M of Fe(III) at 25 °C obtained by MINEQL+ software (reprinted from [34], with permission of Elsevier)

applications of other variants of the Fenton process, including photo-Fenton. As it can be seen, although hydroxyl radical concentration becomes significantly affected in both Fenton systems over pH = 4.0, the homogeneous one seems much more susceptible (Fig. 1a, b), according to the speciation undergone by Fe(III) as a function of pH (Fig. 1c). In this sense, several works have been recently revised by Clarizia et al. [34], examining and comparing the most relevant papers dealing with photo-Fenton processes at neutral pH available in the literature. The main strategy to overcome this practical disadvantage so far (most or the real contaminated waters do not match such a range of pH values, including surface waters as common supply sources to produce drinking water) has been to adopt different types of chelating agents. Each iron(III)-ligand complex features a particular mechanism of photolysis, speciation pattern, light absorption properties, quantum yield, biodegradation, and toxicity that must be considered for choosing proper chelating agent and operating conditions in the photo-Fenton degradation under circumneutral pH values.

Therefore, one of the AOPs lately attracting more attention has been the so-called CWPO; it employs hydrogen peroxide as oxidizing agent in the presence of a solid Fenton or Fenton-like catalyst. The redox properties of the transition metals immobilized in solid catalysts (usually either Fe^{2+}/Fe^{3+} or Cu^{2+}) allow the generation of hydroxyl radicals in the presence of hydrogen peroxide under very mild conditions of temperature and pressure [36]. In addition, it enables easy recovery of the catalytic species, so available for use through a long-term, extended number of catalytic cycles. Hence, important efforts have been focused on finding heterogeneous catalysts with adequate catalytic activity and convenient stability even at pHs of reaction exceeding 4.0, taking into account the acidic conditions under which the reaction takes place more efficiently. Another important advantage linked to the Fenton process activated in heterogeneous phase is to avoid expensive extra steps to recover both the excess of dissolved metals and the sludge formed upon application under near-neutral pH conditions, typical of most water streams [37].

Several teams have reported different materials as possible carriers of active sites catalyzing CWPO: alumina-supported Fe [38], Fe-containing zeolites [39, 40], activated and other functionalized carbonaceous supports [37, 41], and pillared clays [42, 43] are the most common reported catalysts for the CWPO of NOM and other organics. The main limitations of the most suggested materials could be summarized as either low effectiveness under near-neutral pH, low stability against active metal leaching, and/or high cost. The first approach still thoroughly investigated by several groups has been the use of supported catalysts of the Fenton-active transition metals on typical hosts like alumina [44, 45] or silica [46, 47]. However, the most significant drawback of this kind of materials has been definitely poor chemical stability to leaching of the active metal in the reaction mixture in comparison to other solid, functional materials. After the pillared and other modified clay materials, activated carbons and synthetic zeolites have been perhaps the most studied heterogeneous carriers in the past few years because of their high effectiveness, and then these are more specifically analyzed hereafter.

3.1 CWPO by Pillared and Other Related Clay Catalysts

The catalytic potential of the clay-modified materials activating the CWPO reaction has been widely investigated along the past two decades, mainly emphasizing on Al/Fe-, Al/Cu-, and Al/Fe-Cu-pillared clays [48–53]. The high performance displayed by Fe, Cu-modified pillared clays in this reaction mainly relies on the high rates of elimination of several model toxic compounds in terms of both contaminant's depletion and both TOC and COD elimination. Besides, this type of catalysts can be obtained from inexpensive raw materials, increasing the cost-effective potential scaling-up in order to solve real problems in water treatment. Several studies have pointed out that smectites once pillared with mixed Al-based polycations containing iron or copper are materials displaying pretty high performance catalyzing the CWPO reaction [51, 52]. Timofeeva et al. [51] reported the effect of some synthesis variables like hydrolysis ratio of the pillaring solution (OH/(Al + Fe)), temperature of calcination in the preparation of Al/Fe-PILCs, as well as the atomic ratio Fe/Cu in Fe, Cu, Al-clays on the catalytic properties of the resulting materials in the CWPO reaction. Presence of Cu or Fe in isolated sites within alumina pillars, that is, truly mixed interlayering Al/M-polycations, has been believed from a time ago [54] to be closely related to the high catalytic response displayed by this kind of layered materials in the CWPO degradation of several types of compounds, as more recently strongly supported also by H_2-TPR measurements in the case of the Al/Fe-PILCs [52]. In this sense, this and other studies have evidenced that higher loadings of Fe in Al/Fe-pillaring solutions lead to higher fractions of the transition metal fixed in the inorganic host, but not necessarily improving the degradation of organics by a purely catalytic pathway of response in heterogeneous phase [52, 55]. Although higher fractions of Fe in the interlayering solutions clearly promote increased amounts of iron incorporated into the PILCs as isolated octahedrally coordinated Fe^{3+} cations (the most active in the CWPO reaction), together there is bigger incidence of Fe aggregates, less active but also less stable against leaching under the strongly oxidizing environment of the catalytic reaction [52, 55, 56]. Thus, leaching of the active metal(s) usually makes more difficult to interpret the contaminant removals along this type of reaction, since it implicitly leads to higher contribution of the homogeneously activated Fenton oxidation to the overall activity [52]. In addition, elimination of the contaminants should always account for the fraction adsorbed on the catalyst's surface in order to rule out a significant contribution, avoiding reporting it as a purely catalytic degradation. Of course, it must be more carefully assessed in the case of high-surface solid carriers as, for instance, metal-functionalized activated carbons.

Another important issue of the Fenton solid catalysts useful in the CWPO reaction is the presence, in most of cases, of an induction period before observing faster degradation of the contaminants. It is typical of the Fenton-like variant of reaction and must be mainly ascribed in the case of the iron-functionalized materials, to the balance (Fe^{3+}/Fe^{2+}) in the accessible, active sites of reaction; as higher ratio in this couple of oxidation states, as more prolonged must be expected such induction period. Zhou et al. [57] recently modeled the apparent induction period followed by a rapid oxidation observed during the catalytic wet peroxide oxidation of 4-chlorophenol (4-CP) by using Fermi's kinetic equation ($R^2 = 0.9938$–0.9993). 4-CP oxidation proceeded via 4-chlorocatechol (major) and hydroquinone (minor) pathways, along the formation of main intermediate (5-chloro-1,2,4-benzenetriol). Besides CO_2, H_2O, and Cl^-, two main compounds (I and II) formed, the former identified as 2,4-dioxopentanedioic acid, whereas the latter as ferric-oxalate complex. Finally, it has reported marked structural and active differences between Al/Fe-PILC and Al/Cu-PILC in which compared to the latter, the former possessed higher specific surface area and catalytic activity, but its optimal calcination temperature was lower. The induction period also resulted longer in the case of the Al/Fe-PILC. In addition, compound II accounted for a considerable proportion in Al/Fe-PILC system, whereas compound I was almost only component in Al/Cu-PILC system. Overwhelming advantage of the Al/Fe-PILC on the Al/Cu-PILC system catalyzing CWPO had been also clearly evidenced earlier dealing on degradation of the azo-dye methyl orange [52]. On the basis of elemental analyses, it was found that within the range of 0–10% of atomic metal ratio (AMR), Fe gets incorporated around 15 times more efficiently in Al/M-PILCs than copper, whereas the patterns of compensation of the starting CEC showed that increasing values of $AMR_{(Fe\ and/or\ Cu)}$ led to less and less efficient compensation of the aluminosilicate's layer charge. AMR is then a key and useful parameter to be considered in preparation of Al-mixed PILCs with Fe and/or Cu for CWPO, since different as could be believed by default, higher fractions of these active metals in the mixed interlayering solutions do not necessarily conduce to more efficient clay catalysts. However, in other reports published a little bit later [55, 56], adsorption of tartrazine showed slight rise with increasing content of Fe^{3+} in Al/Fe-PILCs ($AMR_{(Fe)}$ in the range of 1.0–20.0%) [55], probably related to the well-known high external surface featured by iron oxides, inferring that higher loadings of this active metal are necessarily forced to form iron oxide aggregates, not very useful for this particular application. However, apparently this increased incidence of non-pillaring iron aggregates as a function of $AMR_{(Fe)}$ did not lead to lower stability against leaching in the CWPO reaction, since pretty low concentration of Fe was reported for all samples evaluated. According to Mössbauer analyses, the structure of the incorporated iron-containing oxides resembled those of naturally occurring minerals akaganeite (β-FeOOH) or lepidocrocite (γ-FeOOH) [56]. AMR can be calculated as follows [52]:

$$\mathrm{AMR}_{(\mathrm{Fe\ and/or\ Cu})} = \frac{(\mathrm{Fe\ and/or\ Cu})}{(\mathrm{Al} + (\mathrm{Fe\ and/or\ Cu}))} \times 100$$

In related address, Timofeeva et al. [51] focused in studying the effect of the Fe/Cu ratio in the Al/Fe-Cu-containing pillaring solution on structural and catalytic properties, CWPO degradation of phenol, of final catalysts. The increase in copper loading led to decreased total surface area, micropore volume, and interlayer distance, whereas the decrease in Fe/Cu ratio favored the formation of oligomeric iron species. However, according to the authors, the introduction of copper ions also increased the rate of the catalytic reaction, an effect that was interpreted in terms of higher rate of radical generation. Moreover, a little bit later in other study [52], no cooperative effect in the CWPO degradation of methyl orange by the presence of both active metals in the same Al/M-pillared clay catalyst was found, which was explained by a possible competition between both active metals for octahedral sites into the framework of Al_{13} polycations in this three-metal system.

An important issue that has remained still controversial regarding Al/Fe-PILCs is whether there is or no formation of truly mixed pillars of both metals. In spite that several works have suggested the outstanding activity of this kind of materials in the CWPO reaction as being strongly related to the mixed Al/Fe pillars [52, 54], some others have ruled it out while proposing that only iron oxides either decorating the Al_2O_3 pillars or as external aggregates are stabilized in this type of materials [58, 59]. In this sense, Bankovic et al. [56] based on DR UV–Vis spectra, Mössbauer, and FTIR analyses proposed that in the AlFe1–15 PILCs (AMR_{Fe} values from 1.0 to 15.0%), the Fe^{3+} ion probably partially substituted Al^{3+} ions in Keggin ion, thus forming $Al_{13\text{-}x}Fe_x$ oxide pillars, whereas in the case of the AlFe20 PILC, other types of pillars might have been formed including those containing separate Al or Fe oxide pillars. Besides, it was shown that increasing iron content of the PILCs resulted in the increasing presence of species with greater clusters of octahedrally coordinated Fe^{3+} ions. The structure of the incorporated iron-containing oxides resembled those of naturally occurring minerals akaganeite (β-FeOOH) or lepidocrocite (γ-FeOOH) (Fig. 2a). It was in similar address to the trend already found as a function of the increased content of Fe in final materials, based in H_2-TPR analyses (Fig. 2b) [52]. Finally, same authors reported interesting behavior of the textural properties in Al/Fe-PILCs as a function of the increasing content in Fe. Particularly, pillaring with Keggin-like ions led to almost monomodal distribution of mesopore diameters. The addition of Fe^{3+} into the

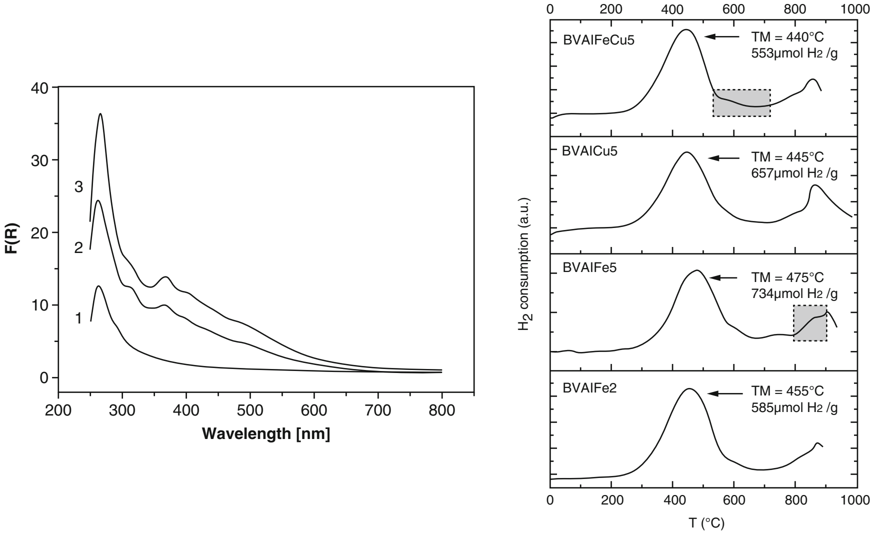

Fig. 2 Physicochemical properties of different Al/Fe- and Al/Cu-PILCs as a function of the AMR_{Fe}: (**a**) DR UV–Vis spectra of (1) Al PILC, (2) AlFe10 PILC (AMR_{Fe} = 10%), and (3) AlFe20 PILC (AMR_{Fe} = 20%) (reprinted from [56], with permission of Elsevier). (**b**) H_2-TPR diagrams of BVAlFe2 (AMR_{Fe} = 2.0%), BVAlFe5 (AMR_{Fe} = 5.0%), BVAlCu5 (AMR_{Cu} = 5.0%), and BVAlFeCu5 ($AMR_{Fe + Cu}$ = 5.0%) (reprinted from [52], with permission of Elsevier)

pillaring solution resulted in changes in the mesopore diameter distribution. Increasing Fe content led to the broadening of the distribution of mesopore diameters in the sequence Al PILC < AlFe1 PILC < AlFe5 PILC < AlFe10 PILC, which got inverted for increasing AMR_{Fe} values from 10 to 20%. This phenomenon was proposed to be further investigated.

Later, Khankhasaeva et al. [53] studied the degradation of sulfanilamide in water by H_2O_2 in the presence of Fe, Al/M-pillared clays from various cationic forms of the starting layered aluminosilicate (Fe, Al/M-MM, M = Na^+, Ca^{2+}, and Ba^{2+}). The montmorillonitic materials were exchanged with bulky Fe, Al-polyoxocations prepared at Al/Fe = 10/1 (AMR_{Fe} ~9.0%) and OH/(Al + Fe) = 2.0 and then calcinated at 500 °C and from XRD, and chemical analyses found that the rate of crystalline swelling was dependent on the nature of the starting interlayer cations in the clay mineral (Fe, Al−/Na-MM > Fe, Al/Ca-MM > Fe, Al/Ba-MM). In addition, the catalytic properties of Fe, Al/M-MMs depended on the type of exchangeable cations, although only slightly the textural properties. These differences were mainly ascribed to higher iron uptake in the Na-MM cationic form.

Gao et al. [60] recently studied the introduction of nickel in Fe-Al-pillared montmorillonite and its effect in the CWPO degradation of the azo-dye Orange II. The effects of active metal molar loading ($AMR_{Fe\text{-}Ni}$), Fe/Ni molar ratio, and calcination temperature on the pillared clays were measured and discussed. It was proposed the introduction of nickel to the pillaring solution may contribute to better active iron stability and catalytic performance. Iron was found in the clays in the form of FeOOH when nickel was introduced, whose integrity was more easily maintained when a moderate calcination temperature was used. Solid modified with 4/6 Fe/Ni molar ratio and $AMR_{Fe\text{-}Ni} = 6\%$, finally heated at 273 °C, displayed better catalytic behavior. Thus, Acid Orange II solution got 72.32% of COD removal after 3 h of reaction: pH = 3.0, $T = 60$ °C, and H_2O_2 dosing = 100% of the theoretical stoichiometric amount. Fe/Ni ratios above 4/6 led to declined catalytic behavior of pillared clays, which was attributed to formation of large iron aggregates.

Some other studies have also attempted combination of properties of Al-, Al/Fe-PILCs with other either transition or precious metals to improve catalytic properties of this kind of materials in water decontamination. For instance, recently a two-step treatment of p-chloro-m-cresol (PCMC) in water by catalytic hydrodechlorination (HDC) followed by CWPO under ambient-like conditions (25 °C, 1 atm) in the presence of catalysts supported on Al-PILCs using Fe and Pd or Rh as active phases was reported [61]. The bimetallic Pd-Fe catalyst showed the best performance, allowing complete dechlorination in less than 1 h reaction time (25 °C, 1 atm, $pH_0 = 6$, $QH_2 = 50$ N mL/min, $[\text{catalyst}]_0 = 1$ g/L, $[\text{PCMC}]_0 = 0.7$ mmol/L). Meanwhile, CWPO of PCMC with a monometallic Fe catalyst allowed complete conversion of that pollutant but with only about 33% reduction of TOC after 4 h. Then, a two-step approach consisting in HDC of PCMC followed by CWPO has been tested for the first time in two different ways. The first one used a Pd-Fe bimetallic catalyst in both steps, while in the second approach, monometallic Pd-Fe catalysts were used for HDC and CWPO, respectively. The HDC step extended for 30 min was enough to achieve complete dechlorination, the main reaction product being m-cresol (selectivity >85%). After the HDC step, the pH of the reaction medium was adjusted to 3.5, and the stoichiometric H_2O_2 dose was added to start the CWPO step. It allowed complete conversion of m-cresol in 15 min, with 60% TOC reduction after 4 h of reaction time. However, the stability of the catalysts against Fe leaching was more rather poor; the Fe leached from the catalyst in this combined treatment reached 2.5 mg/L in the HDC step and 4.9 mg/L at the end of the experiment. Although it represents only 6.6% of the initial Fe load reported, the recorded CWPO activity was undoubtedly influenced by the typical homogeneous Fenton process. It is a promising combined application of the CWPO process in order to contribute giving overall response to contamination by halogenated organics, but strong efforts should be made in order to significantly increase stability of the active metal in the step of the heterogeneous Fenton process.

Thanks to the highly promising potential exhibited by the Al/Fe-PILCs in the CWPO treatment of a variety of polluted aqueous systems, several efforts have been taking place along the past decade in order to make possible its preparation in both higher to lab scales and starting from concentrated precursors. Some studies have focused on the reduction of the synthesis time, involving the use of either microwaves [59, 62] or ultrasound [63] in the preparation of the metal interlayering precursor but increasing consumption of energy as a drawback. Other approaches have tried to increase concentration of the pillaring precursors, either interlayering polycationic solution or the clay suspension itself [43], where typical concentration of the oligomerized metal precursor was close to tenfold increased from around 0.06 to 0.63 mol/L. It implied the use of lower hydrolysis ratio (OH/(Al + Fe) = 1.6) in comparison to typical lab-scale preparations (~2.0–2.4). In addition, the use of ethanol as suspension medium demonstrated to be advantageous in order to perform the interlayering step (contact of the interlayering, oligomeric metal solution with the clay mineral) on concentrated clay suspensions (up to around 50% w/w). Another important step forward in the same address has been achieved by some researchers [64, 65] by means of the straightforward addition of the raw clays on the interlayering Al or Al/Fe solutions. It has allowed to save time and resources (extra added solvent-free suspension) by working on not previously swollen mineral, but attaining Al- or Al/Fe-pillared materials with basal spacings around 1.8 nm, significant increase in specific surface and pore volume. Moreover, as far as we know right now, there is no complete solution to this issue, and hence in general, reports about the application of this type of clay catalysts at industrial level are not still available. Regarding this issue, as a comparison reference, CWPO treatment in continuous reactors has started to be studied in the presence of other solid catalysts, like for instance zeolites. The CWPO degradation of phenol by a Fe-ZSM-5 catalyst in a fixed bed reactor was recently investigated [66]. The effects of feed flow rate and catalyst bed height were determined by following conversion of phenol, H_2O_2, and TOC concentrations. The Fe-ZSM-5 catalyst achieved the highest activity (99.2% phenol conversion and 77.7% of TOC conversion) at 80 °C, 2 mL/min feed flow rate and 3.8 cm as catalyst bed height. In spite that the authors claim remarkable low iron leaching concentration, since it was around 1.0 mg/L, it may anticipate sustained rapid deactivation of the catalyst under real conditions of treatment. In addition, such a level of concentration has demonstrated to be not negligible catalyzing the CWPO reaction based on a close to purely homogeneous Fenton mechanism. As it was stressed by the authors, further research should be focused on the deactivated mechanism and regeneration strategies of the catalyst. It is big evidence promoting the rapid development of scaled-up preparation of Al/Fe-pillared clays, since the concentrations of iron leached in the CWPO reaction mixture typically do not exceed 0.3 mg/L. The HPLC patterns of the solution at different catalyst bed heights demonstrated that low concentration of quinone was generated and then transformed into low molecular weight organic acids and finally changed into carbon dioxide and water with the increase of residence time. This pattern of degradation has been observed in the presence of other efficient CWPO catalysts.

Finally, some emerging materials attracting interest as CWPO-active clay catalysts along the past 5 years have been some naturally occurring or synthetic clay minerals, whose either structural or added content of Fe or Cu has been investigated as active sites of the catalytic reaction [67–69]. First of all, allophane clay materials with SiO_2/Al_2O_3 ratios between 1.0 and 2.2 were synthesized by a coprecipitation route and further impregnated with iron or copper species, in targeted loadings surrounding 2.0–6.0 w/w % [68]. The lower ratio resembled typical Al-rich soil allophane (AlSi1; BET surface <1.0 m^2/g), whereas the higher one looked like more as a hydrous feldspathoid with a large interspherule surface, thereby exhibiting a high surface area ($AlSi_2$; BET surface ~191 m^2/g; up to 287 c for 8.5 Fe_2O_3 wt.%). The iron-based $AlSi_2$ catalysts with taillike structure and high surface area proved to be far more active in the CWPO elimination of phenol (pH = 3.7, $[phenol]_0 = 5 \times 10^{-4}$ mol/L, [catalyst] = 0.4 g/L, $[H_2O_2]_{added} = 0.1$ mol/L under constant flow rate of 2.0 mL/h along 4 h for the Fe catalysts and 8 h for the Cu catalysts). The highest catalytic efficiency (94%/1 h of reaction; total organic carbon abatement 63%/4 h of reaction) was obtained at 40 °C for the calcined iron oxide-supported $AlSi_2$ allophane sample (300 °C/1 h), for which very low leaching level of iron species was noticed (0.37 mg/L). By contrast, large differences in terms of catalytic efficiency (conversion rates) and stability were observed for the copper-based counterparts.

Munoz et al. [67] recently explored the potential application of naturally occurring minerals as inexpensive catalysts in heterogeneous Fenton, namely, catalytic wet peroxide oxidation (CWPO). Performance of magnetite, hematite, and ilmenite as CWPO catalysts was tested under different working conditions (25–90 °C, $[H_2O_2]$ = 250–1,000 mg/L, [catalyst] = 1–4 g/L). In general terms, the use of naturally occurring Fe minerals is attractive because of pretty low cost of this kind of minerals. However, CWPO activated by this kind of materials proceed in fairly longer times of reaction and/or demands for increased temperatures. As expected, in this study the operating temperature showed to play a key role on the rate of H_2O_2 decomposition, so that in the presence of magnetite, the H_2O_2 conversion after 4 h increased from 8 to 99% by increasing the temperature from 25 to 90 °C ($[phenol]_0$ = 100 mg/L). Here it is noteworthy that every Celsius degree of higher reaction temperature of course also supposes increased cost of operation of the catalytic system, and then it may rapidly offset the benefit related to the use of a cheaper catalyst. Conversely, as a clear advantage, leaching is not a big deal in the case of the treatment of wastewaters given the very low cost featuring this kind of ferrous minerals. A significant metal leaching may also become not practical in the use of the catalyst in an extended range of pH values, a crucial difference of the CWPO process against the conventional Fenton process. Complete phenol conversion and almost 80% TOC reduction were claimed at 75 °C with a catalyst loading of 2 g/L in the presence of theoretical stoichiometric amount of H_2O_2 required for complete mineralization of a phenol sample solution (500 mg/L). Among the minerals compared, magnetite (Fe_3O_4) was particularly attractive, since it showed the highest activity and can be easily separated from the liquid phase given its magnetic properties. Moreover, it must be stressed that such a promising mineral was also the one leaching a higher Fe concentration along three consecutive runs; of course it decreased steadily with the cycles of reuse (over 12 mg/L in the first run, around 4 mg/L after the third run), but it allows to infer quite significant contribution of homogeneous Fenton reaction.

In summary, Fe-containing naturally occurring minerals could be devised as interesting CWPO catalysts in the field of wastewater treatment, mainly on those with significant carbon loadings in order for the exothermal enthalpies of oxidation to contribute decreasing the costs of heating of the catalytic system over around

70 °C. Such a kind of materials, together with other types of synthetic-based supported catalysts, mainly Fe and/or Cu oxides as active sites, has demonstrated as a general drawback the low stability against metal leaching in the oxidizing reaction mixture. Outstanding, worth mentioning exception has been the case of modified allophane clay synthetic materials functionalized by impregnation with Fe, which recently showed proper activity and chemical stability ($Fe_{leached}$ <0.4 mg/L) in phenol oxidation under still middle temperature of reaction (40 °C). Al/M-mixed pillared clays in general have exhibited lower contents of the active metals (Cu and/or mainly Fe) incorporated in final materials. They usually display high performance in contaminant depletion even at room temperatures, with output concentrations of active metals typically below 0.3 mg/L, thanks to the specific location of them in very active sites at the interlayer space of the starting aluminosilicates. Moreover, in order to ensure such a set of desirable properties in the CWPO application, cumbersome steps and parameters of preparation must be carefully followed, which definitely have delayed the scaled-up preparation of this kind of materials and, in turn, their more widely spread use in the treatment of a variety of contaminated waters at industrial scale. Therefore, further work in the short term in these still exciting materials should focus in the development of Al/Fe-PILC preparation from concentrated precursors (significantly intensified process), exhibiting physicochemical properties comparable with products obtained in conventional preparations from diluted precursors as well as under reproducible conditions at higher to lab scales (let's say bench followed by pilot scale).

3.2 NOM Removal by CWPO and Other AOPs

AOPs have been intensively studied about the treatment of wide variety of contaminated waters but predominantly wastewaters. NOM removal by such a set of powerful technologies has attracted interest from more rather short time ago, strongly focused in the improvement of drinking water treatment systems. In this context, effect of the NOM removal to decrease the potential of formation of disinfection by-products, more particularly THMs, has been studied. The presence of NOM causes many problems in drinking water treatment processes, including (1) negative effect on water quality by color, taste, and odor problems, (2) increased coagulant and disinfectant dose requirements (which in turn results in increased sludge and potential harmful disinfection by-product formation), (3) promoted biological growth in distribution system, and (4) increased levels of complexed heavy metals and adsorbed organic pollutants [4, 70]. Among the assessed AOPs have been O_3/H_2O_2, O_3/UV, UV/H_2O_2, TiO_2/UV, H_2O_2/catalyst, Fenton, and photo-Fenton processes as well as ultrasound so far, as reviewed in 2010 by Matilainen et al. [4]. Thus, in this section we focus in reviewing the heterogeneous Fenton-like applications reported on the past few years together with the most strongly related others.

First of all, within this recent period, several efforts have been made in order to more confidently and in depth characterize NOM. This is because NOM is a very complex matrix, with widely distributed compositions, chemical functionalities, polar properties, and molecular weight distributions. In addition, there is a high variability of their properties as a function of the source (surface water, groundwater, place, etc.) and even season of the year. For instance, dissolved organic matter (~6.0–15.0 mg/L as dissolved organic carbon) present in two secondary effluents was recently characterized and monitored through UV/H_2O_2 and ozonation treatments by using LC-OCD technique [71]. Biopolymers, humic substances, building blocks, low molar mass neutrals, and low molar mass acids were the fractions resolved. Monitoring of the organic matter fractions with LC-OCD demonstrated that the reduction of effluent's aromaticity (decreasing in specific UV absorbance – SUVA) was not strictly correlated with the complete depletion of humic substances in the effluents for both advanced treatments. However, the UV/H_2O_2 process led to an effluent with lower biopolymer content together with important increase in low molecular mass fractions, although significant amounts of humic acids still remained after extended oxidation treatments. In spite that both AOPs efficiently removed different fractions of the dissolved organic matter, the final composition of the treated effluents was significantly different between the two processes.

During the treatment of natural sources of water by AOPs to remove micropollutants, NOM gets broken down into smaller species, potentially affecting biostability by increasing AOC and BDOC. Bazri et al. [72] found that by means of the UV/H_2O_2 treatment, both AOC and BDOC increased by about three to four times over the course of treatment, indicating the reduction of biological stability. Although a wide range of organic molecular weights were found responsible for AOC increase, low molecular weight organics seemed to contribute more, which could be a serious drawback in order to apply in general AOPs in drinking water facilities. Accordingly, it can be easily anticipated that higher fraction of the TOC represented in low molecular weight organic compounds in this kind of effluents may lead to either higher incidence of microbiological growth in distribution pipes or higher demand of residual chlorine in the effluents of typical disinfection units. Another very important issue in this field is the pH and alkalinity at which a given AOP can operate efficiently. Typical range of pH values for surface waters is close to neutral, sometimes slightly basic. This condition, together with variable alkalinity, may significantly compete with NOM scavenging $HO^{\bullet}$. A little bit later, Black et al. [73] compared UV/H_2O_2 and ozonation of surface water focused on the performance exhibited by a biofiltration unit (acclimatized biological activated carbon) before and after the AOP treatment, finding significantly different results regarding biodegradability of the final oxidized products. Straight oxidation on source water investigated in this case did not preferentially react with the biodegradable or nonbiodegradable NOM. In addition, the type or dose of oxidation applied did not affect the observed rate of biodegradation. Although the oxidation prior to biofiltration increased the overall removal of organic matter, it did not affect the rate of NOM biodegradation. Moreover, most outstanding conclusions reached in this study regarding NOM and NOM intermediaries recording could be summarized as follows: (1) Ozonation preferentially reacted with higher molecular weight chromophoric NOM. However, the reduction in high molecular weight NOM did not appear to increase the biodegradability of the raw water. (2) Advanced oxidation processes reacted with all molecular weight chromophoric NOM fractions equally. (3) Neither ozonation nor AOP treatment with UV/H_2O_2 preferentially reacted with either the biodegradable or the nonbiodegradable fractions of organic matter. (4) Regardless of the oxidation condition applied, the rate of biodegradation did not change. Therefore, and also according to the same authors, such a set of final statements are very source-depending and contradicted results reported by others, who suggested that AOP oxidation increases biodegradability of NOM.

One of the main aspects speeding up research in NOM removal by advanced oxidation technologies has been certainly to decrease occurrence of DBPs, especially THMs. THM generation can be limited by reducing the levels of NOM prior to the chlorination step. It was recently reported that a solar photo-Fenton system (total intensity of Suntest solar simulator, 600 W/m^2; UV intensity 20–30 W/m^2; experiments performed at room temperature around 25 °C, increased up to 30 °C during irradiation) degraded either humic acid solutions (as NOM model compounds) or NOM contained in a river water, dramatically reducing THM formation during the subsequent chlorination step under close to neutral pH of reaction [74]. Whereas in non-pretreated river water, 100–160 μg/L of THMs was formed upon chlorination, values of 20–60 μg/L were reported for water previously treated through 4 h by neutral photo-Fenton under solar simulator in the presence of 1.0 mg Fe/L as initial concentration. Undoubtedly, such a very low concentration of dissolved iron could be one outstanding advantage of this solar photo-Fenton system, since apparently it would not be too much susceptible against metal precipitation in the strongly chelating environment provided by dissolved NOM. It is noteworthy the peroxide concentration used in this study was around four times the stoichiometric dosage required for full oxidation (calculated on the basis of 2.12 mg H_2O_2/L consumed per 1.0 mg COD/L as theoretical mass ratio reported by Deng et al. for NOM dissolved in leachates of landfills when treated by the Fenton process [75]; together, it must be assumed a ratio 3.33 mg COD/mg TOC corresponding to own experimental results [76] obtained from a synthetic standard resembling NOM composition in most surface and underground waters[1]). Although highly source dependent, the use of a standard theoretical mass ratio COD/TOC for NOM could be very useful in the purpose of unbiased comparison between results

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[1] Distribution of synthetic fractions in the NOM standard model solution (mass %):

1. Polyacrylic acid (PAA) (transphilic fraction; average MW, 130,000 Da), 20
2. Polystyrene sulfonate (PSS1) (hydrophobic fraction; average MW, 200,000 Da), 12.5
3. Polystyrene sulfonate (PSS2) (hydrophobic fraction; average MW, 1,000,000 Da), 12.5
4. Polygalacturonic acid (PGUA) (hydrophilic fraction; MW, 25,000–50,000 Da), 30
5. Humic acid (HA) (hydrophobic fraction; average MW, 1,000,000 Da), 25

of NOM degradation reported by several Fenton and AOP treatments, in the presence of widely variable concentrations of H_2O_2.

From very different focus, some studies have stressed the role played by dissolved NOM hindering targeted reactions and removal efficiency exhibited by photocatalytic AOPs. Brame et al. [77] recently claimed the development of an analytical model to account for various inhibition mechanisms in catalytic AOPs, including competitive adsorption of inhibitors, scavenging of produced ROS at the catalyst's surface and in solution, and the inner filtering of the excitation illumination, which combine to decrease ROS-mediated degradation, in the case of the photocatalytic processes. Competitive adsorption by NOM and ROS scavenging were found to be the most influential inhibitory mechanisms and should be carefully taken into account in forthcoming studies mainly in heterogeneously activated photocatalytic AOPs. Among this kind of technologies, it was very recently reported the removal of the NOM present in raw drinking water (around 30 mg TOC/L) by coupling an optimized conventional coagulation-flocculation process with heterogeneous photocatalysis (either TiO_2-P25 suspended catalyst or TiO_2-P25/β-SiC foam-supported material). It was claimed that 80% of mineralization of humic substances was achieved after 220 min of irradiation on the clarified water (7.8 mg TOC/L), effluent of the coagulation-flocculation unit. According to the authors, the fraction remaining after the photocatalytic tests was only the hydrophilic fraction of humic acids. The stability tests of the supported catalyst with clarified water collected in treatment plant showed a progressive deactivation due to adsorption of different ions coexisting with humic substances, resulting in the decrease in catalyst efficiency.

Another interesting family of techniques recently reviewed as promising for NOM removal from surface waters has been that of the electrochemical methods like EC and EO [11]. Whereas in EC systems significant increase of NOM removal rates can be achieved when combined with membrane filtration hybrid systems, in EO technology electrolysis efficiency is strongly linked to electrode composition. Efficiency could be increased by changing the reactor design, using commercial electrodes and exploring the semiconducting properties of oxide mixtures. In this purpose, particularly Boron-doped diamond (BDD) anodes have proved to be effective in humic acid removal from aqueous solutions and potentially their total mineralization.

Kasprzyk et al. [38] studied the NOM removal from water using catalytic ozonation in the presence of Al_2O_3. The main purpose of the paper was to show the potential of alumina for longer-term usage. Alumina found application in water treatment technology mainly as an ion exchanger for the removal of inorganic anions such as As, Se, and F. The usage of alumina as a support for active species, mainly metal or metal oxides in the process of catalytic ozonation of several organic compounds was also studied.

As so far showed, the assessment of the Fenton systems activated by either homogeneous or heterogeneous catalysts has been more rather scarcely studied in NOM removal. The Al/Fe-PILC-catalyzed CWPO removal of NOM from a raw surface water employed as supply source in a drinking water treatment plant (pH around 7.5) was investigated in semi-batch lab-scale experiments [37]. It has achieved full color removal in less than 45 min of reaction and 96% of COD removal in 4 h of reaction for the best clay catalyst (5.0 g/L) under room temperature (18 ± 2 °C) and atmospheric pressure (72 kPa). The clay catalyst displayed high chemical stability against iron leaching even under a very high humic/catalyst ratio, around 28 times more concentrated than surface water studied, and longtime reaction (24 h). This kind of clay catalysts is very promising for this application at real scale given their pretty low cost, since more than 90% in weight is constituted by natural, widely available layered clay minerals. However, only one additional study has been published in the past few years regarding the interaction between humic substances and clay minerals [78]. The aim of the research was to investigate the influence of montmorillonite as a representative clay mineral on the TiO_2 photocatalytic removal of humic acids as model compound of NOM. The effect of Mt was found to be proceeding through a dose-independent trend mainly resulting in the humic structural changes rather than an efficient degree of mineralization. The molecular size distribution profiles displayed the formation of lower molecular size fractions through oxidative degradation of higher molecular size fractions. In comparison to the regular decreasing scheme attained for the specific UV–Vis parameters of HA, the presence of Mt significantly altered the spectroscopic properties of the molecular size subfractions of HA. Therefore, in the field of the Al/Fe-pillared clay-catalyzed CWPO degradation of NOM, an interesting chapter in the short term should account for the degree of adsorption as well as to realize if there is any molecular size and/or polar selectivity displayed by this type of functional materials to adsorb typical fractions of NOM.

3.3 Other Solid Catalysts Used for NOM Removal

3.3.1 Zeolites

Zeolite-based materials are extremely versatile, and their main applications include ion exchange resins, catalytic applications in the petroleum industry, separation process, and as an adsorbent for water, carbon dioxide, and hydrogen sulfide. Zeolites are the compounds of aluminosilicates and can be artificially synthesized by reacting sodium aluminate with sodium silicate. The ratio of silica to the alumina determines the type (X or Y) of the synthetic zeolite. The Y type of synthetic zeolite is the most commonly applied type in preparation of heterogeneous catalysts [79]. One way of producing heterogeneous catalyst from synthetic zeolite is by impregnation of ferric ions followed by calcinations [80]. Another process is by the ion exchange, for example, where the sodium in zeolite containing high sodium content is replaced with ferric ions [79].

The synthetic zeolites have been used as heterogeneous catalytic materials for CWPO treatment of wastewater, where high effectiveness was reported. For instance, Arimi M. [39] studied the treatment of recalcitrants in industrial effluent using a modified natural zeolite as heterogeneous Fenton catalyst. In this case the effects of pH and temperature on heterogeneous Fenton were studied using the modified catalysts. The catalysts showed the highest affectivity which achieved removal of 90% of color and 60% of total organic carbon at 150 g/L pellet catalyst dosage, 2,000 mg/L H_2O_2, and 25 °C. The catalyst was also applied to pretreat the raw molasses distillery wastewater and increased its biodegradability by 4%. Probably even more remarkable was that heterogeneous Fenton with the same catalyst improved biodegradability (BOD_5/COD) of the anaerobic effluent from 0.07 to 0.55, making more feasible the reuse of the treated stream at least as dilution fresh water for the input raw wastewater before conventional microbiological treatment. The color of the resultant anaerobic effluent was also reduced. The kinetics of total TOC removal was found to depend on operation temperature [39].

3.3.2 Fe-Functionalized Activated Carbon

Definitely one type of functional materials more investigated along the past decade as active solids of the CWPO reaction has been that of the carbon-based ones. Several motivations have prompted the scientific community toward the application of hybrid magnetic carbon nanocomposites as catalytic materials for this still emerging technology. The most relevant literature on this topic has been recently reviewed by Ribeiro et al. [37], with a special focus on the synergies that can arise from the combination of highly active and magnetically separable iron species with the easily tuned properties of carbon-based materials. These are mainly ascribed to increased adsorptive interactions, together with good structural stability and low leaching levels of the metal species, as well as to increased regeneration and dispersion of the active sites, which are promoted by the presence of the carbon-based materials in the composites. According to the authors, the presence of stable metal impurities, basic active sites, and sulfur-containing functionalities, as well as high specific surface area, adequate porous texture, adsorptive interactions, and structural defects, was shown to increase the CWPO activity of carbon materials, while the presence of acidic oxygen-containing functionalities had the opposite effect.

Some efforts in the purpose of giving added value to waste raw materials in preparation of this kind of carbonaceous catalyst must be remarked. Sewage sludge was in recent times used as precursor to prepare catalysts for CWPO by both simple drying and pyrolysis [81]. Iron-functionalized biosolids (Fe/ABS) were obtained from the dried biosolids, upon contact with aqueous solution of $FeCl_3$ at several concentrations followed by thermal treatment at 750 °C for 30 min. The materials displayed narrow developed microporosity, with total iron contents up to 9.3% w/w. The catalysts showed a relatively high activity in the CWPO oxidation (80 °C, $pH = 3.0$) of three target pollutants (phenol, bromophenol blue, and dimethoate), allowing a high mineralization (65% TOC reduction for phenol and dimethoate). A fairly good stability was observed in long-term continuous experiments where the Fe leaching remained below 11% of the initial loading after 170 h on stream. More recently, highly stable iron on activated carbon catalysts was prepared by chemical activation of dry sewage sludge with iron chloride at different mass ratios [82]. The iron content of the resulting catalysts varied between 5.2 and 7.3%, and there was developed porosity (BET specific surfaces above 800 m^2/g). The catalysts were tested batchwise in the CWPO of antipyrine (50 °C), a recognized emergent pollutant. Working with 500 mg/L of the best catalyst prepared, complete conversion of antipyrine (20 mg/L) and almost 70% of TOC reduction were achieved in 1 h with the stoichiometric theoretical amount of H_2O_2. In spite that very soundly results have been claimed in this area so far, metal stability remains being one of the main drawbacks. In addition, the best results were reported under high temperatures, pH or reaction very low and close to the Fenton's optimal value (3.0), and conditions easily reproduced at lab scale but still far for application on a real-scale process where environmental conditions of reaction are mandatory (RT; natural pH, being in general a circumneutral one).

3.3.3 Biologically Activated Carbon

The BAC treatment is one of the most promising, environmentally friendly, and economically feasible processes. The BAC can overcome several limitations of AC treatment and other conventional water treatment processes. The BAC uses the highly porous AC as a medium to immobilize microorganisms and remove organic matters present in water.

It is possible to substantially reduce the GAC replacement costs by implementing a biofiltration process, where microbial activity on activated carbon possibly extends GAC adsorption capacity via in situ regeneration of adsorption sites on the external surface or in inner pores through the biodegradation of previously adsorbed organic matter [83]. The BAC process combines both biosorption/sorption and biodegradation functions, providing many benefits for the water treatment. In this work [84], DOC content in the influent and effluent ranged between 1.1–5.5 and 0.5–2.5 mg/L, respectively, showing a good DOC removal (see Fig. 3).

3.3.4 Carbon Nanotubes

NA possesses a series of unique physical and chemical properties. A very important one is that most of the atoms that have high chemical activity and adsorption capacity are on the surface of the nanomaterials. CNTs have been at the center of nanoscience and nanotechnology research for a variety of applications such as adsorbents. The adsorption capacity and strength strongly depend on the type of NOM and the type of CNT. Factors affecting adsorption have been reported to include (1) size and chemical characteristics of NOM and (2) pore structure and surface chemistry of CNT. Due to the polydisperse nature of NOM, various fractions of NOM tend to have a different degree of adsorptive interactions with the adsorbent. This preferential adsorption is reflected by the occurrence of dose-

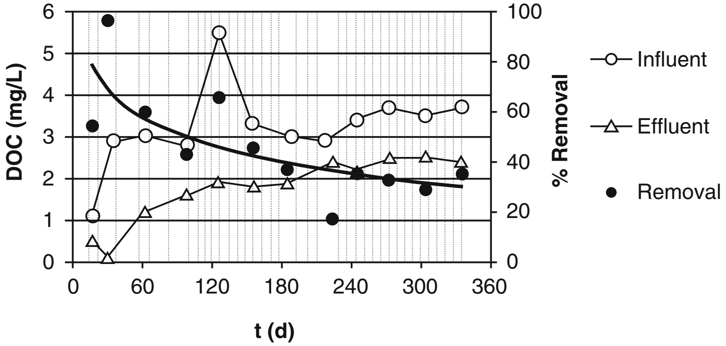

Fig. 3 Evolution of DOC concentration (mg/L) in the influent and effluent of the column and removal percentage over the whole experiment. *Vertical lines* indicate dates of backwashing events (reprinted from Gibert et al. [84], with permission of Elsevier)

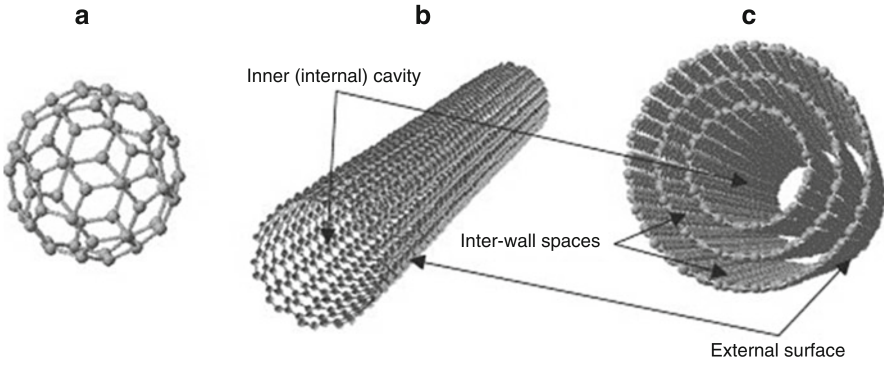

Fig. 4 Schematic structures of fullerene (**a**), single-walled carbon nanotubes (**b**), and multiwalled carbon nanotubes (**c**), showing inner cavity, inter-wall spaces, and external surface. Fullerene (C60) has only external surface (reprinted from Yang et al. [87], with permission of Elsevier)

dependent isotherm relationship. For example, the strongly adsorbable fraction of NOM exhibits a more favorable adsorption at lower CNT dose.

Finally, NOM adsorption is affected by water quality parameters such as ionic strength and pH which influence the charge and configuration of NOM. Specifically, the adsorption of negatively charged NOM to the activated carbon surface generally increases as ionic strength increases and pH decreases [85].

NOM generally carries a negative charge in the natural environment, due to the carboxylic and phenolic moieties distributed throughout the entire molecule [86]. These physical and chemical characteristics of NOM are likely to be closely related to the mechanism of NOM interaction with CNT. Compared to NOM adsorption onto CNT, the mechanism of NOM adsorption onto activated carbon is relatively well-known. A few characteristics of NOM interaction with activated carbon are noteworthy and might be helpful for interpretation of CNT-NOM interaction.

Differences between activated carbon and CNT also need to be recognized for the proper interpretation of CNT-NOM adsorption phenomena. The activated carbon consists of micropores with different sizes which provide sites for NOM adsorption. CNT in contrast provides adsorption sites only along the surface of a cylindrical structure; see Fig. 4 [87].

4 Conclusions

Removal of NOM and other synthetic surrogates by several AOPs, focused in the Fenton-like, heterogeneous CWPO, has been critically reviewed. Main advances achieved along the past few years by these still emerging technologies have mainly focused on increasing the removal efficiency, not only in terms of color and TOC but also in the aromatic content, under the lower possible temperature. Moreover, several efforts are still to be made in order to unify the information about the amount of H_2O_2 as oxidizing agent employed per unit of concentration of NOM, preferably in terms of stoichiometric loading against some widely accepted reference; a standard model synthetic solution is proposed for. In addition, recording of molecular weight distribution is also strongly advised in order to get better correlation between mineralization and changes in polar and size of NOM intermediaries and by-products.

Several types of solid materials have been studied in order to more efficiently catalyze the heterogeneous activation of the oxidizing agent (higher removal of organics through as low as possible either H_2O_2 consumption or temperature of reaction, under real-water pH values, typically circumneutral): being prepared from low-cost, widely available clay minerals, Al/Cu- but mainly Al/Fe-pillared clays have shown to gather in a great extent such a challenging set of features, but their preparation process must be first seriously intensified before getting proper applications in real-scale water treatment. Some naturally occurring minerals have lately shown good rates of reaction but under still high temperatures (e.g., >50 °C). Regarding this type of materials, Fe-functionalized allophane showed interesting activity in phenol degradation at 40 °C with outstanding stability of the active metal against leaching in comparison to many other supported catalysts reported so far in the literature for this reaction.

Some zeolites and carbon-based materials are extremely versatile and have been used as heterogeneous catalytic materials for CWPO treatment of wastewater. In particular, functional materials, biologically activated carbon, and carbon nanotubes were used as active solids of the CWPO reaction with a special focus on NOM removal showing higher efficiencies of reaction.

Finally, in the future several integrated technologies will be used to remove NOM from supply water, including nanofiltration membranes, coagulation with subsequent floc separation, and CWPO followed by biofiltration and sorption processes (chemisorption and physical adsorption). The evolution of water-related normativity and progressively more restrictive standards for drinking water, however, will seek the research of advanced, more efficient, and cost-effective water treatment processes.

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