Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater

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The use of carbon materials as catalytic support or direct catalyst in catalytic wet air oxidation (WAO) of organic pollutants is reviewed. The discussion covers important engineering aspects including the characterisation, activity and stability of carbon catalysts, process performance, reaction kinetics and reactor modelling. Recommendations for further research in catalytic WAO are outlined.

KEY WORDS: activated carbon; characterisation; CWAO; kinetics; modelling; organic pollutants; review; trickle bed reactor

1. Introduction

Currently half of the available freshwater is appropriated for human uses [1] indicating a high level of exploitation and contamination of the existing water resources. Large quantities of aqueous effluents arise from diverse industrial (petrochemical, chemical, pharmaceutical and agro-alimentary) or domestic activities and have to be treated before returning to the aquatic environment. The presence of highly bio-toxic and refractory organic pollutants in these effluents is challenging the traditional treatments including physical separation, incineration or biological abatement. At the same time, new regulations for the disposal and treatment of multicomponent toxic and potentially hazardous wastes are imposing lower discharge limits that are difficult to meet with the current technologies.

Significantly less contamination of water resources can be achieved in situ by the prevention of end-stream pollution in the specific production processes. Concepts of green chemistry and process sustainability have become issues of global importance for industrial companies. Nevertheless, the implantation of new production strategies is slowly developing in the competitively orientated industrial environment. Meanwhile, more efficient and economic solutions for end-stream treatment, avoiding high-energy input technologies [2], are imperative to produce reusable process water and environmentally friendly effluents.

A first step towards improved remediation of wastewater was the development and successful application of the Wet Air Oxidation technique (WAO) to treat sewage and other industrial effluents [3,4]. Investment and operation costs of WAO plants, however, are not favourable as WAO employs excessive temperatures between 150 and 300 °C and air pressures up to 200 bar. The effective treatment of effluents containing new highly refractory organic pollutants would make this method even more expensive.

WAO performance can be improved by the addition of homogeneous [5,6] or heterogeneous [4] catalysts at subcritical conditions or at severe ‘supercritical’ operating conditions [7,8]. Alternatively, low temperature oxidation processes replace oxygen by stronger oxidants such as O3 [9,10] or H2O2 [9,11,12] in combination with an energy input to form reactive OH-radicals [13,14]. Several reviews on catalytic and non-catalytic WAO [4,5,15–19], supercritical water oxidation (SCWO) [7,8,20–22] and advanced oxidation processes (AOP) [23–25] are now available in literature.

Moreover, the intensification or integration of wastewater treatments provides superior cleaning effectiveness compared to single step oxidation processes. Examples of such new concepts are the simultaneous adsorption and oxidation [26–29] or sequential adsorption–oxidation [30] of pollutants as well as adsorption-regeneration cycles in the same reactor unit [31–34]. Better performance of a continuous trickle bed reactor (TBR) for the phenol CWAO was also achieved by applying forced periodic operation of liquid flow [35]. The integration of a chemical oxidation/reduction pretreatment step takes advantage of the partial contaminant mineralisation reducing the effluent toxicity to levels acceptable for biological end-treatment plants [36–38]. Finally, abatement techniques that appear more appropriate than CWAO should be considered for specific pollutant groups including catalytic hydrotreatment for polyphenols [39], chlorophenols [40–44] and nitrites or nitrates [42,45–48].

Over the last 10–15 years, continuous SCWO technology proved to be an extremely powerful treatment for all kinds and concentration range of toxic organic wastewater [7,8,20–22]. Related problems with

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corrosion and plant plugging due to salt precipitation were solved on laboratory scale leading to new reactor configurations termed hydrothermal burner [49] and Transpiring Wall Reactor [50]. Long-term tests to check for the suitability of these reactors have not yet been performed [21]. The drastic operating conditions used make this technology rather expensive. Future industrial applications of SCWAO will be most probably restricted to effluents that contain highly concentrated and/or extremely refractory or hazardous organic pollutants [51]. On the other hand, emerging AOPs can perform well in drinking water purification and wastewater treatment with low concentration of pollutants, corresponding to the most efficient use of the highly active oxidation species [23–25]. Ambient operating conditions result in attractive process economics, although these benefits are partially offset by the use of expensive oxidants (O$_3$ or H$_2$O$_2$) and the energy source required.

For wastewater containing low to medium organic concentration, batch and continuous CWAO yielded satisfactory results in laboratory studies [4,5,15–19]. Relatively mild operating conditions of temperature and pressure lead to substantially lower investment and operation cost. CWAO becomes especially attractive when coupled with a biological or physical–chemical treatment avoiding the need for a complete mineralisation of the organic pollutants often difficult to achieve under CWAO reaction conditions. The lack of stable catalysts has prevented CWAO from being widely employed as industrial wastewater treatment. The most prominent supported catalysts prone to metal leaching in the hot acidic reaction environment are Cu based metal oxides [52–56] and mixed metal oxides (CuO, ZnO, CoO) [57,58]. Expensive supported noble metal catalysts (Pt, Pd, Ru, Rh, Ir, Ag) appear much more stable, although leaching was occasionally observed, e.g., during the CWAO of pulp mill effluents over Pd and Pt supported catalysts [59,60].

A frequently overlooked catalyst deactivation was the formation and strong adsorption of carbonaceous deposits on the catalyst surface. Such catalyst fouling was detected during CWAO of phenol over Ceria, CuO/ZnO and activated carbon (AC) [61–64]. Theses studies showed that the ability of catalysts to form carbonaceous deposits strongly depends on the reactor type used. Slurry reactors with a characteristic high liquid to catalyst ratio exhibited enhanced homogeneous side reactions and thereby the build-up of such deposits [62,64] while these side-reactions were significantly reduced in TBRs [61,65,66]. During the last years considerable research efforts were focused on reducing unwanted catalyst deactivation. Stable supported catalysts with high activity towards oxidation of organic pollutants have been successfully synthesised and tested in the oxidation of phenol [66–78]. These new catalysts remain, however, relatively expensive materials and the search for cheap, active and stable CWAO catalysts continues.

Recently, activated carbon was proved to render encouraging conversions in the oxidation of phenol [26–29, 79–82]. ACs are versatile materials that entail not only excellent properties for numerous pollutant adsorption and catalyst support applications, but also catalytic activity for many reactions including hydrogenation, oxidation, halogenation, hydration isomerisation and polymerisation reactions [83–85]. A close review of the carbon and catalytic wet oxidation literature reveals that little attention has been paid to the use of carbon materials in catalytic WAO. A discussion of the recent developments in CWAO using carbon-based catalyst is required to update the current state of the art of this emerging application.

The scope of this paper is thus to review in detail the relevant literature dealing with wet oxidation studies using carbon as support or direct catalyst. Our research group has over 10 years experience in the field of CWAO of organic pollutants, pioneering the use of AC as CWAO catalyst. Main results obtained with several ACs will be presented and completed with findings of related studies. The discussion covers the most important aspects of CWAO such as catalyst performance, process operation, complex reaction kinetics and reactor modelling.

2. Application of carbon materials

Carbons are cheap materials because they can be manufactured from any carbonaceous source by physical or chemical activation and high temperature pyrolysis. The most commonly used raw materials are wood, coal, lignite and coconut shells, although synthetic polymers or petroleum processing residues serve as precursor [86] for ash free carbons. Exhaustive information on manufacture of ACs is given in literature [87–90].

A broad variety of carbons is commercially available as granulated activated carbon (GAC), carbon black powder (CB) or graphite (G). Depending on the preparation, they have specific surface areas of 10–300 m$^2$/g for GS and 100–2500 m$^2$/g for CBs and ACs and pore size distribution including micro (<2 nm), meso (>2–50 nm) and macro pores (>50 nm). These textural properties give rise to remarkable and tuneable capacities for adsorbing many chemical species from gases and liquids. Excellent degrees of dispersion and stability were also achieved when depositing a catalytic active phase on carbon carrier. In addition, the performance of ACs as adsorbent or catalytic support is strongly affected by the presence of metal oxides in form of ashes and acidic, basic or neutral functional surface group that can interact with adsorbed species and the catalytic active phase deposited [83–85]. The surface groups mainly involve oxygen (up to 15 mol%) and hydrogen (up to 30 mol%) atoms as well as small...