



Efficient reduction of bromates using carbon nanofibre supported catalysts: Experimental and a comparative life cycle assessment study



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HIGHLIGHTS

- Highly efficient Pd/CNF catalyst for bromates reduction in water is presented.
- Production of carbon nanofibre support scaled to 10 g.
- LCA study of carbon nanofibrous catalyst was developed.

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ABSTRACT

Structured hierarchical catalysts were developed for efficient reduction of bromates in water. In the catalysts a small amount of active metal, 0.3 wt.% Pd, is supported onto carbon nanofibres grown either on sintered metal fibres or on a carbon cloth. In both cases high rates of reaction and high selectivity were achieved, allowing a significant reduction in the amount of catalyst required for the treatment of a set volumetric flow of polluted water, compared to a conventional Pd/Al₂O₃ catalyst. Manufacture of carbon nanofibres grown on a hierarchical structured support was scaled to 10 g batches. Cradle-to-gate life cycle assessment (LCA) study was performed to compare potential water treatment processes based on two catalyst types, and to identify the areas for future optimisation of the novel technology based on structured hierarchical catalysts.

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1. Introduction

Bromate (BrO₃⁻) in drinking water is considered as a potential carcinogen to humans by World Health Organization (WHO) and United States Environmental Protection Agency (USEPA). In 1998 its maximum contaminant level in drinking water was set to 10 µg L⁻¹ [1]. Bromate could form during ozonation of water containing bromides. As ozonation is increasingly used for the treatment of emergent pollutants, especially pharmaceutical residues and pesticides, it is anticipated that the problem of bromate contamination of such aqueous streams will become more potent. It

is therefore an important task to develop an efficient water treatment technology allowing reduction in the level of contamination by BrO₃⁻ complementing the efforts in reducing the source bromide contamination.

Several methods of reducing aqueous bromate contamination have already been suggested. These include the use of bioreactors [2,3], reduction with iron Fe²⁺/Fe⁰ pair [4,5], electrochemical reduction [6,7] and a photochemical process [8]. However, most of these methods do not show the desirable level of efficiency in terms of the final bromate concentration and process throughput. For instance, it was shown that augmentation of filters with bacteria known to reduce bromate to bromide did not significantly improve bromate removal compared to the control, passive, filters [3]. Reduction of bromate with Fe²⁺/Fe⁰ pair proved to be rather

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effective [4]. But additional downstream purification of water from Fe^{2+} may be required. Electrochemical reduction of BrO_3^- was shown to be fast [7]. However, further development of electrode materials with high catalytic activity is needed to improve current efficiency and make this technology economically viable. Better results were obtained by Ding et al. who used polyaniline (PANI) as the electrode material, which reached its optimum catalytic efficiency around pH 7, producing a high removal efficiency of 99% for trace bromate in 0.10 M Na_2SO_4 solution [6].

Another possible technique of bromate reduction is the use of layered double hydroxides (LDH). Thus, the Fe(II)–Al(III)–LDH with SO_4^- counter anion, with the structural Fe(II) of the LDH being the active reductant in the system, were found to decrease bromate concentration in water to an acceptable level [9]. However, regeneration of the LDH could not be achieved after bromate reduction, due to the formation of $\alpha\text{-FeOOH}$ and amorphous aluminium hydroxide.

Catalytic reduction is not yet recognised as a technology of choice for water treatment at an industrial scale. Hitherto, if promising results have been collected, lab and pilot studies are still on going without industrial applications to date. Very limited information is available regarding the catalytic removal of bromate from aqueous solutions.

Chen et al. studied catalytic reduction of bromate with noble metal (Pd, Pt) catalysts, supported onto SiO_2 , Al_2O_3 and activated carbon [10]. Al_2O_3 was found to be a more suitable support than activated carbon due to its higher isoelectric point. Thakur et al. studied catalytic reduction of bromate in water and observed high catalytic activity of a carbon nanofibre-supported ruthenium catalyst (Ru/CNF), higher than Ru supported on an activated carbon [11]. The latter was attributed to greater accessibility to Ru active sites in the case of the open structure of carbon nanofibre support in comparison to microporous activated carbon. Unfortunately, gradual deactivation of the catalyst was observed. Comparison of the data reported in these two papers suggests that Pd/ Al_2O_3 is a more active catalyst, compared to Ru/CNF: the TOF of the former is 0.166 s^{-1} vs 0.032 s^{-1} for the latter (our calculations based on the reported experimental data). It is not clear from the available data if this is the effect of the metal or the effect of the support.

In summary, scant available literature suggests that catalytic reduction is potentially highly efficient for the removal of bromate from water. However, the catalysts reported for the reaction to date are not very stable or not very active. There is scope for further development of new active catalysts for this reaction. There is also a need for analysis of the competitive effects with other anions, and the effect of the initial bromate concentration.

Carbon nanofibres have already been shown to be effective as a catalytic support in this reaction in comparison to un-structured carbons [11]. To develop a catalytic system that could be used on a large scale and with high linear velocities of water, the active catalyst must be supported in such a way as to not generate significant pressure drop. Therefore, the concept of hierarchical catalysts could be adopted [12].

Here we report two catalysts showing good activity in reduction of aqueous bromates. We then demonstrate scale-up of the supported carbon nanofibres manufacture to a 10 g pilot scale. Life cycle assessment (LCA) was then used to analyse the relative impacts of different stages of manufacture of the novel catalysts compared to manufacture of a conventional alumina-based catalyst. The LCA analysis is intended to provide guidance towards further optimisation in the development of the carbon nanofibre-based catalysts, and not necessarily for the reported application only.

There are very few published LCA studies on carbon nanomaterials, e.g., an assessment of carbon nanotubes growth [13] and of carbon nanofibre growth [14]. The latter is the only readily available LCA study of the relevant process to the one used in the cur-

rent work. However, the reported LCA was based on an inventory of a lab-scale process and on literature data. Furthermore, the step of treatment of off-gases from the carbon growth process was not considered in constructing the LCA inventory, despite having a significant contribution to environmental impacts. In the present study the LCA is based on a pilot-scale growth of carbon nanofibres and a broader assessment boundary was used. The results show that the catalyst based on carbon nanofibres has a substantially less harmful overall environmental impact than the conventional catalyst.

2. Experimental

2.1. Preparation of Pd/CNF/SMF and Pd/CNF/CF catalysts

Commercially available Inconel sintered metal fibres (SMF) (Inconel 601, Bekipor ST20AL3, thickness 0.49 mm, elementary fibre diameter 8 μm , Bekaert Fibre Technology, Belgium) were used as a support for carbon nanofibres. Chemical composition of the material is as follows: Ni – 60.5%; Cr – 23.0%; Al – 1.25%; Cu – 1.0%; Mn – 1.0%; Si – 0.5%; C – 0.1%; S – 0.015%; Fe – balance. Before use, SMF panels were calcined at 650 °C for three hours in order to oxidise the fibre surface. The SMF panels were subsequently cut into disks ($d = 24 \text{ mm}$).

Carbon felt (CF) from the Carbon Lorraine Company with a surface area of approximately $1 \text{ m}^2 \text{ g}^{-1}$ was used as a host material. Disks of 22 mm diameter, 6 mm thickness were used.

Carbon nanofibres (CNF) were grown on both supports, metal fibres and carbon felt, by catalytic pyrolysis of ethane in the presence of hydrogen. The synthesis was carried out in a tubular quartz reactor with 24 mm internal diameter placed in a tubular oven. The SMF filters were first treated with hydrogen (625 °C, two hours, 120 mL min^{-1}) in order to create Ni nanoparticles as a catalyst of CNF growing on the fibre surface. Then, the reactor was heated to 675 °C, and a mixture $\text{Ar}:\text{C}_2\text{H}_6:\text{H}_2 = 80:3:17$ (600 mL min^{-1}) was introduced for two hours. The obtained 5%CNF/SMF composite supports were activated in a boiling 30% H_2O_2 aqueous solution during one hour. The samples were then treated ultrasonically in ethanol using an ultrasonic cleaner (HF-output nominal power 30 W, Branson Ultrasonics Corp., USA) over three hours. The weight loss after the H_2O_2 and ultrasonic treatments was less than 0.5% of the initial weight of 5%CNF/SMF samples.

Monometallic Pd-containing catalysts based on the activated 5%CNF/SMF were prepared by incipient wetness impregnation using palladium acetate dissolved in acetonitrile as a precursor for Pd-deposition. Concentration of the impregnation solution was set to have the final Pd^0 loading equal to 0.3 wt.%. After impregnation the material was dried at room temperature and reduced by H_2 at 300 °C for two hours.

In the case of CF support preparation of Ni catalyst for CNF grow was described elsewhere [15]. Briefly, CF pieces were oxidised for one hour in nitric acid under reflux (100 °C, 65% HNO_3). The samples were filtered and washed in distilled water until the pH of the filtrate levelled out at 6, and then dried for 12 h at 100 °C. Due to the hydrophobic character of the material, ethanol was used as a solvent when the carbon felt was impregnated to achieve 2 wt.% Ni with a nickel nitrate solution ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and dried at room temperature for 12 h. The material was calcined in static air at 300 °C for two hours to form the corresponding nickel oxide.

The catalyst was heated from room temperature to 650 °C at a temperature ramp of $20 \text{ }^\circ\text{C min}^{-1}$ in 300 mL min^{-1} flow of Ar. The nickel oxide was then reduced in situ at 650 °C for two hours in 100 mL min^{-1} flow of H_2 and 300 mL min^{-1} flow of Ar.

CNF synthesis was performed in a tubular flow reactor at 650 °C for 5 h, using a reactant mixture of ethane and hydrogen (25/

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