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Development of Glycerol-based Carbon Materials for Environmental Catalytic Applications in Advanced Oxidation Processes

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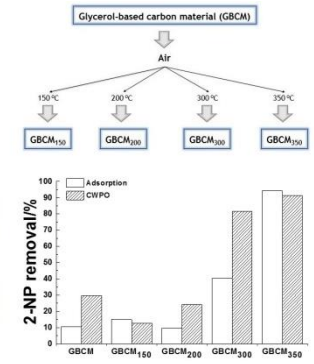

A glycerol-based carbon material was initially produced by partial carbonization of glycerol with sulphuric acid followed by calcination under inert atmosphere. This material, characterized by high thermal stability, low ash content, non-porous structure and basic character, was further activated in air atmosphere at different temperatures (from 150 to 350 °C), resulting in materials with less basic character, due to the incorporation of oxygenated surface groups, and to a notorious evolution of the porosity. These metal-free carbon materials are highly active catalysts for environmental applications, more specifically for the catalytic wet peroxide oxidation process, when the surface chemistry and textural properties are properly tuned. Effective catalytic degradation of 2-nitrophenol was achieved with the material treated under air atmosphere at 300 ºC, opening a window of opportunity for the valorisation of crude glycerol by-products and the production of value-added materials.

Introduction

The complexity of industrial wastewaters is always increasing, following industry's demand towards the development of new products and needs, while conventional biological wastewater treatment processes are often not suitable treatment solutions, due to the presence of toxic compounds, which are inhibitory to the microorganisms employed in such biological plants. In this context, treatment options based on advanced oxidation processes (AOP) are the most adequate. The catalytic wet peroxide oxidation process (CWPO), an AOP characterized by the use of a suitable catalyst (typically an iron-based catalyst) for the decomposition of hydrogen peroxide (H_2O_2) through the formation of hydroxyl radicals ($HO^{\bullet}$), is included in this set of technologies. These radicals, exhibiting high oxidizing potential, serve as effective and non-selective species for the degradation of several organic pollutants in liquid phase, including those with a negative impact on conventional biological wastewater treatment plants. CWPO is also especially attractive due to the environmental safety of H_2O_2, mild operating conditions and simplicity of the equipment required. Homogeneous and heterogeneous catalysts have been extensively used in this process for the degradation and mineralization of organic pollutants in water (e.g., iron species used directly in solution or supported on different types of materials) [1-4]. However, a final chemically-driven separation step for the removal of the catalyst from the treated water is required when using homogeneous catalysts, while the leaching of the active phase from the solid to the liquid phase is often observed when heterogeneous catalysts are employed, thus resulting in catalyst deactivation. Taking these drawbacks into consideration, the use of metal-free catalysts in CWPO would bring considerable advantages to the process.

Previous works dealing with the use of carbon materials (namely activated carbons, activated carbon xerogels and carbon nanotubes), without any supported phase, already proved to be active catalysts for CWPO [5-7]. On the other hand, crude glycerol, such as that resulting from the biodiesel transesterification production process, is being offered as an abundant and low cost feedstock calling for valorisation [8]. New markets for crude glycerol are nowadays a focus of attention [9], and the development of metal-free catalysts for CWPO is currently of great interest in order to avoid leaching, deactivation and the use of high-cost metals. Thus, in the present work, glycerol-based carbon materials (GBCMs) with distinct properties were produced, characterized and tested for CWPO. 2-nitrophenol (2-NP) was used as a model pollutant, since it is often found in industrial wastewaters, such as those from pharmaceutical, petrochemical, metallurgical, textile, rubber and plastic industries, refineries, fungicides and even from municipal landfill leachate.

Materials and methods

A non-calcined glycerol-based carbon material was initially prepared by adapting the procedure described elsewhere [10], which involves the in situ partial carbonization and sulfonation of glycerol with concentrated sulphuric acid at 180 °C. This starting material was then ground to obtain particle sizes in the range 0.106-0.250 mm and later calcined under a N_2 flow at 800 °C, the resultant material named GBCM. The so obtained GBCM was further thermally activated in air flow at 150, 200, 300 and 350 °C, producing distinct materials ($GBCM_{150}$,

$GBCM_{200}$, $GBCM_{300}$ and $GBCM_{350}$, respectively). In this temperature range, the weight loss (burn-off) due to the thermal activation in air atmosphere ranges from 9 wt.% to 20 wt.%.

The produced materials were thoroughly characterized: textural characterization was performed in a Quantachrome NOVA 4200e adsorption analyser, thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC equipment and the surface chemistry was characterized by (i) the pH of point of zero charge (pH_{PZC}), determined by pH drift tests, (ii) the concentration of acidic and basic sites, using titration techniques, and (iii) the amount of CO and CO_2 released from the materials surface by temperature programmed desorption (TPD).

In order to assess the suitability of the developed GBCMs for CWPO, batch experiments (adsorption and reaction) were performed in a 500 mL well-stirred (500 rpm) glass reactor, charged with 250 mL of a 2-NP solution (100 mg L^{-1}), considering as reaction conditions T = 50 ^{o}C, pH = 3 and GBCMs load = 1.0 g L^{-1}. In the reaction runs, a calculated volume of H_2O_2 (6 wt. %) was injected into the system after catalyst addition, in order to reach the desired concentration of 34.6 mmol L^{-1}. Periodically, sample aliquots were collected from the reactor and an excess of sodium sulphite was immediately added to consume residual H_2O_2 and to instantaneously stop the reaction. The concentration of 2-NP was followed by HPLC.

Results and Discussion

Textural and surface chemistry characterization

The results obtained by TGA of GBCM are shown in Figure 1. The analysis carried in N_2 atmosphere allows the quantification (mass loss) of the functional groups present on the GBCM surface, which decompose upon heating, 3.1 wt.% of volatiles being determined, indicating that GBCM is thermally stable under inert atmosphere. On the other hand, the analysis in air atmosphere allows the determination of its fixed carbon and ash contents. A very low ash content (1.1 wt.%) was quantified, the GBCM sample showing stability up to 400 ºC under air atmosphere.

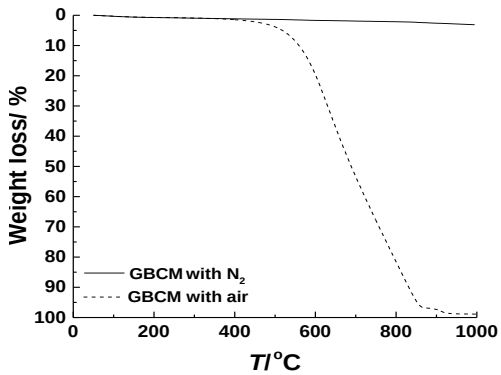

Figure 1. TGA of GBCM under N_2 and air atmospheres.

The textural parameters of the carbon materials were obtained from the N_2 adsorption isotherms and are gathered in Table 1. As observed, the thermal activation in air atmosphere has a significant impact on the textural properties, with a considerable generation of porosity being noticed. The original GBCM is a non-porous material (S_{BET} = 10 m^2 g^{-1}) and the thermal activation of GBCM in air atmosphere resulted in materials with a S_{BET} increasing with the temperature (25, 399, 519 and 598 m^2 g^{-1} at 150, 200, 300 and 350 ºC, respectively), due to a significant development of microporosity (V_{Mic} of 0.00, 0.16, 0.19 and 0.24 cm^3 g^{-1}, respectively). In fact, thermal activation of GBCM in air atmosphere at 350 ^{o}C leads to a tremendous evolution of porosity (about 60-fold in S_{BET}), resulting a material whose microporosity fraction (V_{Mic}/V_{Total} = 0.90) is close to that of some activated carbons and carbon xerogels.

Table 1. Specific surface area (S_{BET}), non-microporous surface area ($S_{Non\text{-}mic}$), micropore volume (V_{Mic}) and microporosity fraction (V_{Mic}/V_{Total}) of the carbon materials.

Material	S_{BET}/ m^2 g^{-1}	$S_{Non\text{-}mic}$/ m^2 g^{-1}	V_{Mic}/ cm^3 g^{-1}	V_{Mic}/ V_{Total}
GBCM	10	10	0.00	0.00
$GBCM_{150}$	25	34	0.00	0.00
$GBCM_{200}$	399	69	0.16	0.71
$GBCM_{300}$	519	61	0.19	0.79
$GBCM_{350}$	598	27	0.24	0.90

The surface chemical properties of the materials were also determined, the corresponding values being summarized in Table 2. It can be seen that the original GBCM possesses an evident basic character, with a concentration of basic functionalities higher than the concentration of acidic functionalities and a pH_{PZC} above 7. As the temperature of the thermal treatment of the original GBCM in air atmosphere increases, the amount of acidic functionalities of the resulting materials also increases, with a markedly acidic material being obtained at 350 ^{o}C. As expected, this evolution is followed by the increase of oxygen-containing groups released during TPD analysis, suggesting that the increase of acid functionalities is due to the incorporation of surface oxygen groups during thermal activation in air atmosphere.

CWPO experiments

The ability of the developed carbon materials to act as metal-free catalysts in the CWPO of 2-NP was evaluated. Comparisons between removal of 2-NP by pure adsorption over GBCM and CWPO in the presence of GBCM (may include adsorption), obtained after 240 min, are given in Figure 2.

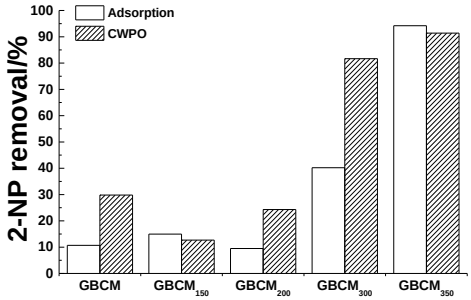

Figure 2. 2-NP removal in adsorption and CWPO runs after 240 min.

Catalytic activity is unequivocally obtained for carbon materials produced from glycerol, after the appropriate activation conditions. A marked increase in the removal of 2-NP is observed when H_2O_2 is added in the presence of some of the produced GBCM materials and, in particular, for the material treated under air atmosphere at 300 ºC ($GBCM_{300}$), the performance observed is markedly superior when compared to that of the original GBCM.

It should also be noted that the highest removal of 2-NP is observed when using $GBCM_{350}$, but in this case there is a significant adsorption of 2-NP on the carbon material surface. In either case, the thermal activation of GBCM in air atmosphere at and above 300 ^{o}C results in carbon materials with high activity for CWPO of 2-NP.

Lower GBCM activation temperatures have a negative impact on the catalytic activity.

Conclusions

Glycerol-based carbon materials thermally activated under oxidative conditions (air atmosphere) at specific temperature (300 °C) produced very active catalysts for oxidative degradation of 2-nitrophenol.

The temperature of activation influences both the textural and the surface chemical properties: lower temperatures (up to 200 °C) lead to basic materials (pH_{PZC} > 7.6) with poorly developed porous structure; higher temperatures (≥ 300 ^{o}C) produce acid materials (2.6 < pH_{PZC} < 6.2) with a significant porous structure.

Metal-free glycerol-based catalysts for CWPO can thus open a window of opportunity for added-value crude glycerol products.

Table 2. Physical-chemical characterization of the carbon materials: pH_{PZC}, acid-base properties, and concentration of CO and CO_2, and percent of oxygen, obtained from the TPD spectra.

Material	pH_{PZC}	Acidity/ µmol g^{-1}	Basicity/ µmol g^{-1}	CO_2/ µmol g^{-1}	CO/ µmol g^{-1}	O/ %
GBCM	9.5	380	590	352	464	1.9
$GBCM_{150}$	9.2	270	450	211	893	2.1
$GBCM_{200}$	7.6	310	500	399	887	2.7
$GBCM_{300}$	6.2	520	400	663	2843	6.7
$GBCM_{350}$	2.6	1250	250	955	3482	8.6

Acknowledgements

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