EFFECT OF CARBON NANOFIBER ONTO TiO_2-MODIFIED POWDER/GRANULAR ACTIVATED CARBON FOR ADVANCED WATER TREATMENT

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Abstract
In this work, the influence of carbon nanofiber on the performance of TiO_2-modified activated carbon (TiO_2-AC) as photocatalyst for advanced water treatment was studied. TiO_2-modified carbon nanofiber/activated carbon in powder form (TiO_2-CNF/PAC) and in granular form (TiO_2-CNF/GAC) were prepared by sol-gel method. Comparative morphological characterization studies for TiO_2-CNF/PAC and TiO_2-CNF/GAC and their testing for 25 mgL^{-1} humic acid (HA) degradation showed a better performance of the overall sorption-involved photocatalysis using TiO_2-CNF/GAC.

Introduction
Natural organic matters presence in drinking water source is responsible for membrane fouling in ultra- or nano-filtration steps of the advanced drinking water treatment technology. For this reason, various approaches have been investigated for the development of cheaper and more effective materials characterized by advanced properties suitable for the adsorption and photocatalysis applications in the water treatment.

Photocatalysis, one of the advanced water treatment processes, has been extensively studied to eliminate natural pollutants from water in the presence of semiconductor catalyst and UV illumination [1]. It is obviously that semiconductor catalyst is responsible for photocatalysis performance and among various materials used as semiconductors, titanium dioxide (TiO_2) has been widely used for a broad range of applications because it is cheap, non-toxic, very active and stable in chemical reactions [2-4].

Various carbonaceous materials, e.g., activated carbon (AC), carbon nanotubes and carbon nanofibers (CNFs) have been intensively tested as sorbents, composite filters, antifouling membranes and support for photocatalysis processes. Composite materials based on titanium dioxide and activated carbon are receiving increasing attention for the degradation of humic, phenolic compounds, pesticides, chlorinated compounds and dyes because the activated carbon possesses high surface area, suitable pore structure and as consequence, high adsorption capacity and nano-sized TiO_2 facilitates photocatalysis [5-7]. However, the size of activated carbon influences the sorption charactersitics and its combination with a nanostructured carbon should improve its performance.

The aim of this paper is to explore the role of CNF as support for TiO_2 in conjunction with powder and granular activated carbon, in form of TiO_2-CNF/GAC and TiO_2-CNF/PAC synthesized by sol-gel method and tested for the removal and the degradation of humic acid, the main constituent of natural organic matters from water.

Experimental

All the chemicals were of analytical purity grade and used as received. Composite materials based on titanium dioxide-modified carbon nanofiber and activated carbon were prepared using 5 mL titanium tetraisopropoxide with a purity of 97 % (TTIP, Aldrich) as titanium precursor, 2 g of powder/granular activated carbon (Flochem Industries) and 1 g carbon nanofiber (Nanocyl, Belgium) as matrix. The mixture was vigorously magnetic stirring (700 rpm, IKA RCT basic stirrer) in the presence of 30 ml ethanol and 30 ml distilled water, and pH solution value of 2 was adjusted with HNO_3. After three hours of continuous stirring the composite materials were filtered, washed, and dried at 60ºC for 4 hours. The thermal treatment was realized at 400ºC for 3 hours.

The morphology of the TiO_2-CNF/PAC and TiO_2-CNF/GAC composites was studied by a scanning electronic microscope (SEM, Inspect S PANalytical Model) coupled with the energy dispersive X-Ray analysis detector (EDX).

The photocatalytic experiments were carried out under magnetic stirring at 20°C into a RS-1 photocatalytic reactor (Heraeus, Germany), which consisted of a submerged UV lamp surrounded by a quartz shield.

For each experiment, an adsorption step of 30 minutes was assured under the same hydrodynamic conditions without UV irradiation.

At certain running time, the suspension was sampled and filtered through a 0.4 µm membrane filter. The concentration of humic acid was measured in terms of absorbance at 254 nm (A_{254}) using a Carry 100 Varian spectrophotometer.

The HA removal efficiency was calculated using the following equation:

$$\text{Removal efficiency} = \frac{c_0 - c_t}{c_0} \times 100 \quad (\%) \qquad (1)$$

where: C_0 and C_t are the concentrations of HA in aqueous solution in term of A_{254} at initial time and at any time t, respectively (mgL^{-1}).

Results and discussion

Figure 1 a-d presents SEM images for TiO_2-PAC, TiO_2-GAC, TiO_2-CNF/PAC and TiO_2-CNF/GAC. From SEM images, it is clearly seen that PAC and GAC have a layered structure, CNF have covered complete and uniform the both forms of activated carbon, forming a mesh on which TiO_2 nanoparticles characterized by spherically shape are distrubuted more uniform in comparison with PAC and GAC modified with TiO_2.

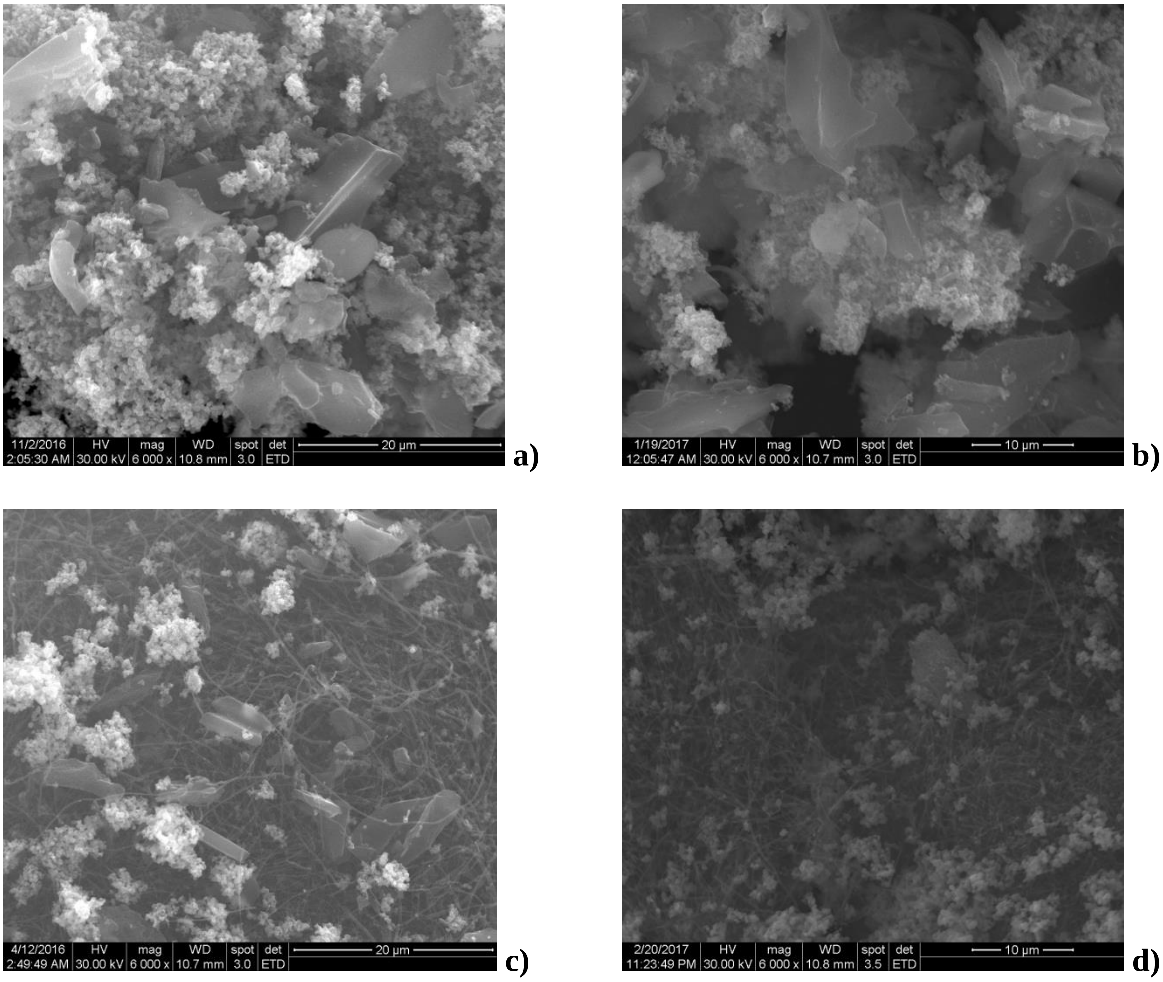


Fig.1. SEM/EDX images for a) TiO_2-PAC, b) TiO_2-GAC, c) TiO_2-CNF/PAC and d) TiO_2-CNF/GAC

The performance of the TiO_2 modified powdered activated carbon is tested for HA removal and degradation by the sorption and the photocatalysis process, with the mention that the sorption was considered as a prerequisite step of the photocatalysis process. The role of CNF in the composition of TiO_2 modified activated carbon was checked for the performance of the photocatalysis process. Figures 2 and 3 show the results of the photocatalysis involving sorption step applied for HA removal and degradation expressed as the HA removal efficiency, using TiO_2-CNF/PAC and TiO_2-CNF/GAC in comparison with TiO_2-PAC and TiO_2-GAC, respectively. It can be noticed that the presence of CNF as support for TiO_2 improved the sorption performance for TiO_2-GAC while no effect on the TiO_2-PAC is found.
Also, the overall performace of the sorption step-involved photocatalysis was better in the presence of CNF. A slight enhancement of TiO_2-PAC performance was found by introduction of CNF as support for TiO_2 that showed no necessity of CNF integration into TiO_2-PAC composition for the degradation of 25 mgL^{-1}HA.

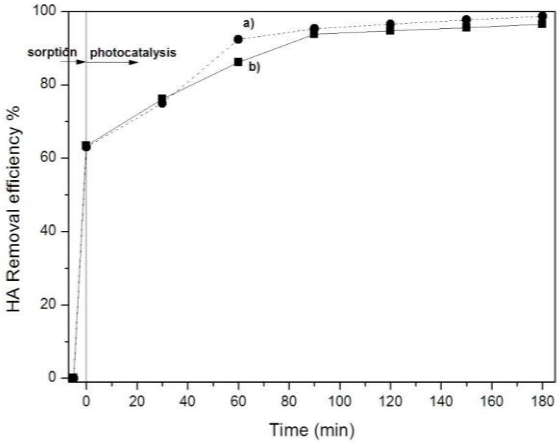


Fig. 2. Evolution of HA removal (25mgL^{-1}) efficiency versus time by sorption step-involved photocatalysis under UV irradiation using a)TiO$_2$-CNF/PAC and b) TiO$_2$-PAC

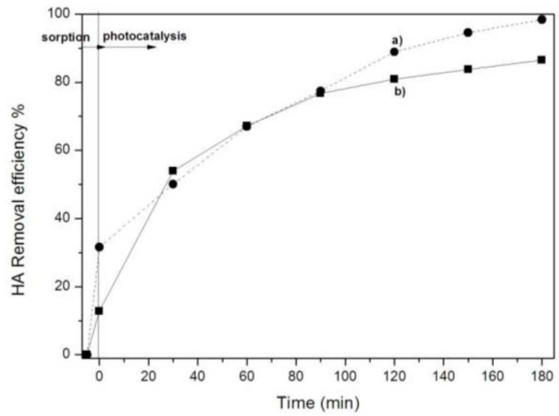


Fig.3. ***Evolution of HA removal (25mgL^{-1}) efficiency versus time by sorption step-involved photocatalysis under UV irradiation using*** **a)TiO$_2$-CNF/GAC and b) TiO$_2$-GAC**

Due to the overall photocatalysis contains sorption and photocatalysis component, an assessment of the photocatalysis component was done by subtracting sorption component from the overall performance and the comparative results are presented in Figure 4. It can be noticed that the highest performance of photocatalysis was obtained for TiO$_2$-GAC composite with the mention that these materials were tested only for 25 mgL^{-1} HA and the overall photocalaysis performance was higher than 90%, which imposes further studies for higher HA concentrations.

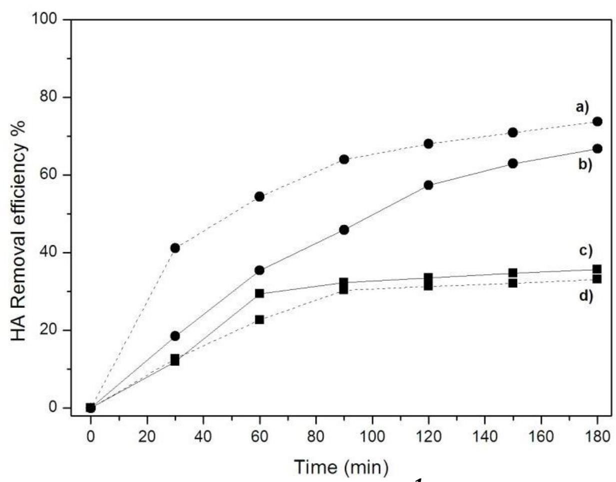
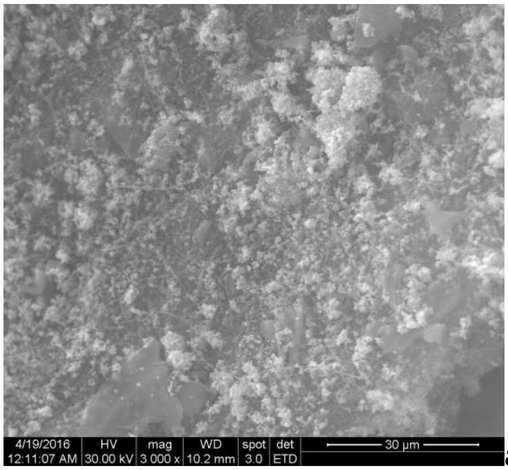
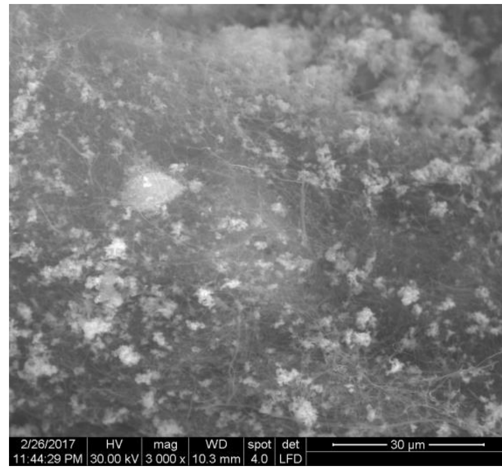


Fig. 4. Evolution of HA removal (25mgL^{-1}) efficiency versus time by photocatalysis under UV irradiation using a) TiO$_2$ –GAC; b) TiO$_2$ – CNF/GAC; c)TiO$_2$ – CNF/PAC and d) TiO$_2$ –PAC

A very important aspect is the stability of the material and their morphologies were tested also, after the photocatalysis application. The SEM images of TiO$_2$–CNF/PAC and TiO$_2$–CNF/GAC are gathered in Figure 5a and b, and it can be noticed the presence of TiO2 and CNF into catalyst composition, which denotes their good stability.



a)



b)

Fig.5. SEM/EDX images recorded after phototcalysis application of a) TiO_2-PAC, b) TiO_2-GAC

Conclusion

TiO_2-CNF/PAC and TiO_2-CNF/GAC composite materials were successfully synthesized by sol-gel method. CNF covered activated carbon forming a mesh layer that assured a better and more uniform distribution of TiO_2 onto carbanaceous support. TiO_2-CNF/PAC, TiO_2-CNF/GAC, TiO_2-PAC and TiO_2-GAC acted as photocatalyst towards humic acid degradation and allowed the removal of 25 mgL^{-1} HA with an overall photocatalysis performance higher than 90%. The presence of CNF into composite allowed a slight enhancement of sorption properties of granular activated carbon without any effect onto the powdered activated carbon for removal of 25 mgL^{-1} HA. The morphology characterization of the composite after their application in the photocatalysis proved a good stability of the material that reclaim their potential for the further studies, which will envisage more concentrated humic acid removal from water.

Acknowledgements

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