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Titanium dioxide-modified activated carbon for advanced drinking water treatment

Corina Orha[a], Rodica Pode[b], Florica Manea[b,*], Carmen Lazau[a], Cornelia Bandas[a]

[a] National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Condensed Matter Department, 1 P. Andronescu Street, 300254, Timisoara, Romania
[b] "Politehnica" University of Timisoara, P-ta Victoriei no. 2, 300006 Timisoara, Romania

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ABSTRACT

This study reported a new anatase TiO_2-modified granular activated carbon (GAC-TiO_2) synthesized by microwave-assisted hydrothermal method. The composite was characterized morpho-structurally by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectra and Brunauer–Emmett–Teller (BET) measurement. GAC-TiO_2 composite was used for the removal of humic acids (HA) rom water by the photocatalysis under UV irradiation in comparison with the sorption process. Kinetics results correlated with Zeta potential results allowed elucidating some mechanistic aspects. GAC-TiO_2 composite revealed high photoactivity for HA degradation and mineralization. A self-cleaning activity of the composite proved in this study makes it very remarkable in developing next generation of filtering system avoiding its fouling in the drinking water treatment technology.

1. Introduction

Humic acids are the main constituent of the dissolved natural organic matter (NOM) and represents 90% of the dissolved organic carbon (DOC) in all natural waters. In the last decades, removal of humic substances has long been of concern in water treatment due to their diverse reactivity and abundance in natural waters. The presence of humic substances in water is dangerous because they are considered as the main precursors of disinfection by-products (DBP's), especially of trihalomethanes (THM's) during chlorination step. The presence of humic acids in the distribution system favors the bacterial growth in the network, which may lead to serious sanitary problems in drinking water quality (Kerc et al., 2003).

The usual drinking water treatment processes that involve sand filtration, settling and coagulation, generally are able to remove between 20 and 50% of the humic substances from water, involving high operating costs and toxic secondary pollution (Gaya and Abdullah, 2008). Humic acids are generally preferentially removed, in comparison with tannic and fulvic acids in solution (Ferro-Garcıa et al., 1998)

Nowadays, adsorption is considered a simple, promising and effective technique for water and wastewater treatment, and the key for the sorption performance is given by developing an efficient adsorbent. Usually, the most used adsorbents for ions and organics in water and treatment are clay minerals (De Aguiar et al., 2002; Crini, 2006), zeolites (Babel and Kurniawan, 2003; Hedstrom, 2001), activated carbon (Pollard et al., 1992) and so on.

Granular Activated Carbon (GAC) is a highly porous material, used in drinking and wastewater treatment for the removal of organic and inorganic compounds. It is used in both a powdered form (PAC) for periodic control of tastes and odors and in a granular form (GAC) when continuous

* Corresponding author.
E-mail addresses: haiduccorina@yahoo.com (C. Orha), rodica.pode@upt.ro (R. Pode), florica.manea@upt.ro (F. Manea), carmen.lazau@gmail.com (C. Lazau), elena_ratiu@yahoo.com (C. Bandas).
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treatment for trace organics is necessary (Yener et al., 2008). Granular activated carbon (GAC) is generally used for removing compounds (algae toxins, pesticides, tastes and odors, and industrial micropollutants) that are not always present in the water at high concentrations. Also, it is appropriate for the removal of dissolved humic acids. The surface and adsorption properties of the activated carbon are related to the different species that are adsorbed. In general, charged species by type of humic acids, can mainly change the surface properties of activated carbon during filtering porous, leading to the filter fouling (Ferro-Garcıa et al., 1998).

An alternative to carbon-based filtering system should be photocatalytic semiconductor modified carbon-based sorbent envisaging to avoid filtering fouling under UV irradiation by the self-cleaning.

Among various semiconductors that have been investigated in the last decade, in photocatalysis application, titanium dioxide (TiO_2) has attracted much attention because of many advantages, *e.g.*, nontoxicity, low cost, chemical stability, and superior photoactivity (Inagaki et al., 2001; Zhou et al., 2012; Baek et al., 2013).

The TiO_2 nanoparticle attachment to carbon-based structures, *e.g.*, single-walled carbon nanotubes (SWCNTs) (Zhou et al., 2010; Clemens et al., 2013), multi-walled carbon nanotubes (MWCNT) (Vatanpour et al., 2012; Zhao et al., 2013), graphene (Min et al., 2012; Zhao et al., 2012) or activated carbon (Asiltürk and Sener, 2012; Jung et al., 2010) can be prepared using different methods, *e.g.*, hydrothermal (Li et al., 2011), sol–gel (Zhao et al., 2013) or electrochemical (Wang et al., 2008) methods.

The synthesis of composite materials via microwave irradiation has been reported to be an effective technique (He et al., 2009; Caddick and Fitzmaurice, 2009) because it offers several advantages, *e.g.*, simple and fast synthesis procedures, improved reaction kinetics, uniform heat distribution and minimal structural damage (Cui et al., 2012).

There are several reports about combined adsorption-photocatalysis processes as alternatives in removing humic substances from water characterized by better results than classical treatment methods (Qourzal et al., 2004; Takeda et al., 1998; Yuan et al., 2005; Carpio et al., 2005; Fu et al., 2004; Zainal et al., 2008; Wang et al., 2009a, b).

In this work, a microwave-assisted hydrothermal method was applied for the synthesis of a new TiO_2-covered granular activated carbon (GAC-TiO_2) composite material characterized by advanced sorption and photocatalytically properties with greater adsorption and photocatalytic activities. This new composite material was morphologically and structurally characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), FTIR spectroscopy and BET analysis. GAC-TiO_2 composite was tested for humic acid removal from water by sorption and photocalysis processes. Some mechanistic aspects were discussed based on Zeta potential measurements results.

2. Experimental

2.1. *Materials and composite materials synthesis*

Commercial granular activated carbon was purchased from Flochem Industries SRL Bucharest with the dimension of 0.6–2.38 mm. The composite material based on the granular activated carbon covered with TiO_2 (GAC-TiO_2) was synthesized through microwave-assisted hydrothermal method from precursors. The hydrothermal method was carried out by mixing 1 g granular activated carbon with 5 mL of titanium tetraisopropoxide (TTIP) and 45 mL distilled water under continuous stirring for 2 h. Then, the solutions were introduced in a Teflon autoclave with a 50% degree of fullness, for 30 min to 200 °C, under the microwave radiations. After autoclaving, the composite materials (GAC-TiO_2) were washed with distilled water and dried at 60 °C for 5 h.

The humic acid (HA) was obtained from Sigma Aldrich, Switzerland, and 100 mg L^{-1} stock solution of HA was prepared by dissolving 0.1 g of HA in 1000 mL of distilled water.

2.2. *Characterization methods of the composite materials*

The composite material was characterized by instrumental analysis methods, *i.e.*, X-ray diffraction (XRD), scanning electron microscopy (SEM), FTIR spectroscopy and BET analysis. Also, the surface charge was determined by the electrokinetics Zeta potential (ς) measurements.

In order to determine the crystal phase composition, X-ray diffraction measurements were carried out at room temperature using a PANalytical X'PertPRO MPD Difractometer with Cu tube in the region $2\theta = 20–80°$.

A scanning electron microscopy (SEM) using Inspect S PANalytical model coupled with the energy dispersive X-Ray analysis detector (EDX) was used to characterize the morphology of the composite material using catalyst powder supported on carbon tape.

FTIR analysis was conducted on a Bruker Vertex 70 spectrophotometer using KBr pellets for sample preparation.

BET surface area determination was made by measuring N_2 adsorption at 167 K using a Micromeritics ASAP 2020 model instrument.

Zeta potential measurements were carried out by a Zeta Meter 3.0+ for suspensions of 1 g L^{-1} composite material in distilled water at pH of 7.

2.3. *Adsorption and photocatalytic experiments*

Composite material was tested as adsorbents and photocatalysts in advanced water treatment processes for the removal of humic acids (HA) from water.

To study HA removal and degradation by the sorption and photocatalytic activity, an accurate weight of 0.2 g of composite materials were shaken with 200 mL of 10, 15, 20 and 25 mg L^{-1} HA solutions for 180 min at different value of pH. The experimental solution was prepared by diluting the HA stock solution with distilled water.

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. Mercury medium pressure lamp characterized by the capacity of 150 W with additional radiation intensity 280–360 nm was used to generate UV irradiations. The adsorption of HA on composite materials were studied using batch method in the same photocatalytic reactor without UV irradiation to achieve the same hydrodynamic conditions. At certain running time, the suspension was sampled and filtered through a 0.2 mm membrane filter. The concentration of humic acid was measured in terms of absorbance at 254 nm (A_{254}) with a Carry 100 Varian spectrophotometer.