

EFFECT OF TiO₂ LOADING ON POWDER-ACTIVATED CARBON IN ADVANCED DRINKING-WATER TREATMENT

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ABSTRACT

The viability of TiO₂ effect under UV irradiation for the advanced drinking-water treatment through sorption and photocatalysis processes using powdered activated carbon was evaluated in this work. Three types of TiO₂-modified powder-activated carbon materials characterized by three degrees of TiO₂ loading were tested as sorbent/photocatalyst for the removal of humic acids (HA) from water, which represents the important component of natural organic matter (NOM) considered as trihalomethans precursor for the stage of drinking water disinfection with chlorine. The materials were synthesised by sol-gel method, characterized morphologically by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and tested as sorbent/photocatalyst for HA removal. The sorption/photocatalysis process was assessed in terms of humic removal efficiency. The kinetics studies based on the pseudo-second-order equation related to sorption/photocatalysis were performed and the role of TiO₂ was evidenced in both processes. The great sorption characteristics of powdered activated carbon for humic acid were not enhanced by TiO₂ presence. However, TiO₂ presence favoured the photocatalysis process and diminished the fouling effect on the material surface during photocatalysis process, assuring the self-cleaning characteristics of the powdered activated carbon and as a consequence, the longer lifetime of the material.

Keywords: water treatment, sorption, photocatalysis, TiO₂, activated carbon.

1 INTRODUCTION

Up to date, titanium dioxide (TiO₂) is the most widely used photocatalyst in the water treatment field mainly because of its nontoxicity, low cost, chemical stability, and superior photoactivity over other semiconductors that have been investigated. The main drawbacks of the TiO₂ nanostructures, when used in a practical application, come from their easy loss during the process of water treatment and the tendency of suspended particles to aggregate. Therefore, great efforts have been made to improve the reuse efficiency of TiO₂, for example, the immobilization of TiO₂ nanoparticles onto some supports such as silica [1], zeolite [2], carbon nanotube [3], glass [4], ceramic [5], and activated carbon [6], [7].

In the past decade, titanium dioxide-activated carbon composite materials were prepared by various techniques, such as: mechanical mixture [8], hydrothermal synthesis [9], solvothermal synthesis [10], microwave synthesis [11], chemical vapor deposition [12], and sol-gel method [13]–[15].

Composite materials based on titanium dioxide and powder activated carbon are receiving increasing attention for the degradation of humic, phenolic compounds, pesticides, chlorinated compounds and dyes [16]–[18] because activated carbon possess high surface area, suitable pore structure and as a consequence, high adsorption capacity and nano-sized TiO₂ facilitates photocatalysis.

The removal of humic acids (HA) from water can be a difficult process, and conventional methods used for water treatment, such as coagulation, precipitation and filtration, can be insufficient to achieve desired degree of HA. Currently, there are several reports about



combined adsorption-photocatalysis processes for organics removal and as alternatives in removing humic substances from water characterized by better results than classical treatment methods [19], [20].

In this study, the powdered activated carbon was modified with three TiO_2 loadings using sol-gel method, characterized morphologically and tested for removal and degradation of HA from water in order to improve activated carbon performance.

2 MATERIALS AND PREPARATION OF TiO_2/AC COMPOSITE MATERIALS

All the chemicals were of analytical purity grade and used as received. Titanium dioxide-activated carbon composites ($\text{TiO}_2\text{-AC}$) were prepared using 5 mL titanium tetraisopropoxide with a purity of 97 % (TTIP, Aldrich) as titanium precursor, powder activated carbon (Flochem Industries) 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 value 2 of pH solution was adjusted with HNO_3 . Different composites characterized by various TiO_2 loading were obtained based on the ratio between mass (g) of activated carbon (AC) and volume (mL) of titanium tetraisopropoxide (TTIP), and are gathered in Table 1. After three hours of continuous stirring the composite materials were filtered, washed, and dried at 60°C for 6 hours. The thermal treatment was realized at 400°C for 3 hours. The humic acid (HA) was purchased 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.

2.1 Characterization methods of the composite materials

The composite material was characterized by instrumental analysis methods, i.e., X-ray diffraction (XRD) and scanning electron microscopy (SEM/EDX).

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

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.

2.2 Adsorption and photocatalytic experiments

The three types of the composite materials were tested as adsorbents and photocatalysts in advanced water treatment processes for the removal of humic acids (HAs) from water.

To study HAs sorption and photocatalytic activity, an accurate weight of 0.3 g of composite materials were shaken with 300 mL of 25 and 50 mgL^{-1} HA solutions for 180 min. The experimental solution was prepared by diluting the HA stock solution with distilled water.

Table 1: Code of composite materials.

Mass of PAC (g)	TTIP volume (mL)	Code
3	5	CT1.33
5	5	CT1
10	5	CT0.5



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. 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 0.4 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.

For both studied processes, the HA removal efficiency was calculated using the following equation:

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \quad (\%), \quad (1)$$

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}).

The kinetics of the sorption and photocatalytic processes of humic acid on TiO_2 -activated carbon were analysed using pseudo second-order Lagergren model equations. The linear forms of pseudo second-order equations are expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}, \quad (2)$$

where k_2 is the constant rate of the pseudo-second-order kinetics ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) and q_e is the equilibrium adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$).

3 RESULTS AND DISCUSSION

3.1 X-Ray diffraction

Fig. 1 presents the XRD patterns of TiO_2 -AC composites materials prepared by sol-gel method in comparison with TiO_2 anatase. The diffraction analysis indicates that all the samples contain anatase TiO_2 as predominant phase, identified by diffraction lines at 2Theta 25.3°, 38.6°, 48°, 54° [21] and diffraction lines intensity decreased with TiO_2 content decreasing as it was expected.

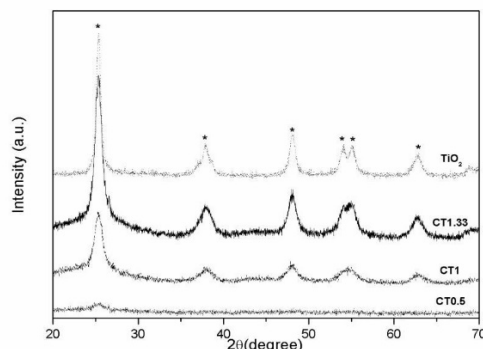


Figure 1: XRD pattern for TiO_2 , CT1.33, CT1 and CT0.5.

3.2 Scanning electron microscopy (SEM/EDX)

Scanning electron microscopy (SEM) gives valuable information regarding the shape and distribution of the TiO_2 nano-particles on the surface of the powdered activated carbon. It is obviously TiO_2 particles with a non-uniformly distribution have crystallized like spherical agglomerates on the activated carbon surface. The Ti content is evidenced also by EDX microprobe and it is in according with XRD results.

3.3 Performance of composite materials for HA removal and degradation from water

The performance of the TiO_2 modified powdered activated carbon is tested for HA removal and degradation by the sorption and the photocatalysis process.

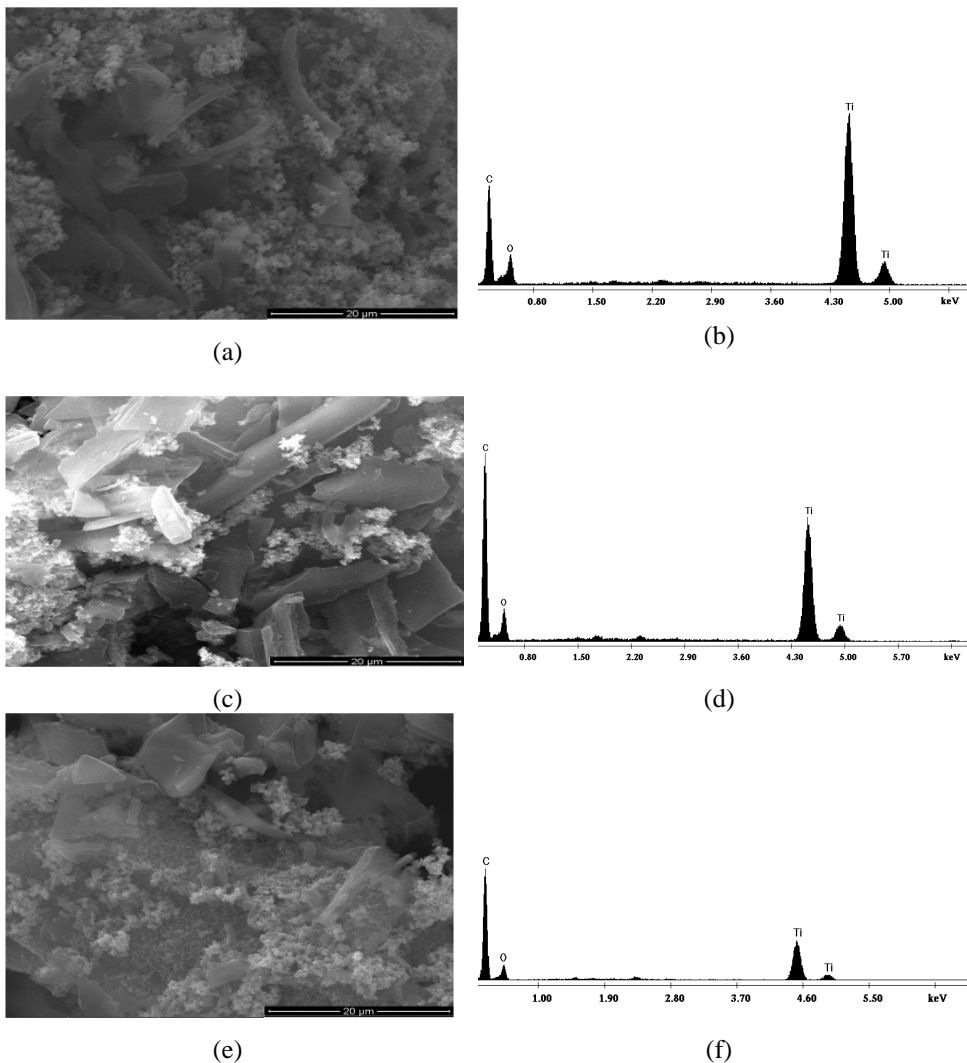


Figure 2: SEM/EDX images for (a), (b) CT1.3; (c), (d) CT1; (e), (f) CT0.5.

Due to the adsorption is prerequisite step in photocatalytic process and activated carbon is a very well-known treatment sorbent for organics removal from water, the comparative batch sorption studies are achieved. Fig. 3 shows the results regarding HA removal efficiency using the powdered activated carbon modified with different degrees of TiO_2 loading.

The best sorption results were achieved for simple powdered activated carbon, as we expected taking into account the higher active surface area of powdered activated carbon versus TiO_2 . The increased TiO_2 loading the decreased sorption capacity for HA. However, the fouling effect is expected to appear after certain HA concentration adsorbed onto sorbent. In this context, the question regarding possibility for in-situ cleaning of AC surface raised and the photocatalytic activity of the material should be the solution. Because AC does not possess the photocatalytic activity its surface was modified with certain TiO_2 loadings.

The results of photocatalysis application using TiO_2 -modified activated carbon in HA degradation are presented in Fig. 4. The best and similar results regarding the evolution of HA degradation was achieved for CT1.33 and the CT1. Due to the economic consideration CT1 was found as optimum composition.

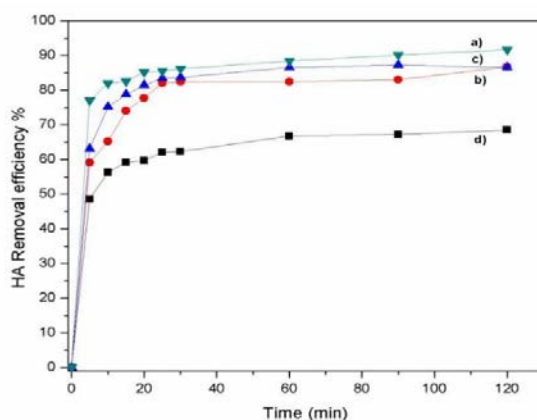


Figure 3: Evolution of removal efficiency of 25 mg/L HA by sorption onto: (a) AC; (b) CT0.5; (c) CT1; (d) CT1.33.

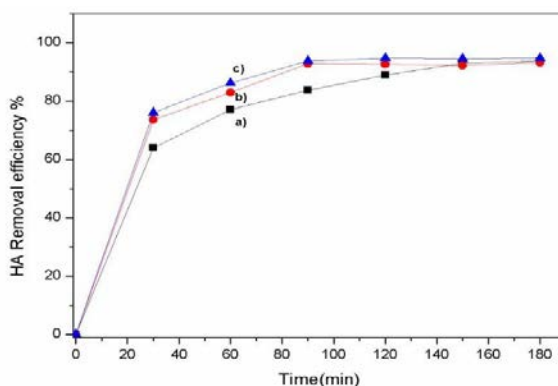


Figure 4: Evolution of removal efficiency of 25 mg/L HA by photocatalysis using: (a) CT0.5; (b) CT1; (c) CT1.33.



3.4 Kinetics studies for sorption and photodegradation of HA on composite materials

The kinetics of HA removal by adsorption and photocatalysis were fitted well by the second-order Lagergren model (eqn (2)) and the results of kinetics parameters are presented in Table 2. Taking into account that the pseudo-first order kinetic model is the most common for the sorption process, also this model was checked but the correlation coefficient was very bad that denotes that this model is not appropriate to describe sorption and photocatalysis process. For the second-order Lagergren model, the plot of t/q_t versus t showed a linear relationship, and k_2 rate constant and q_e equilibrium adsorption and photocatalytic capacity were determined, which were significantly close to the experimental ones for each tested material. Also, the kinetics results confirm the selection of CT1 as the most appropriate for HA degradation.

3.5 Testing the reuse of the catalyst

Two cycles of HA degradation by photocatalysis using comparative CT1 and AC were performed to evaluate the in-situ self-cleaning activity. The results are presented in Fig. 5, and it can be seen that after 180 minutes during the second cycle the HA degradation efficiency decreased from 91% to 49% using AC and no significant decreasing from 93% to 88% for CT1. This behaviour evidenced clearly the role of TiO_2 in the composition of AC as photocatalyst for HA mineralization and as consequence, the self-cleaning is assured.

Table 2: Results of fitting experimental data to pseudo-second-order kinetic model for 25 mgL^{-1} HA concentration.

Catalyst	Parameters	Adsorption	Photocatalysis
CT1.33	$q_t(\text{mg/g})$	15.3876	19.2445
	$q_e(\text{mg} \cdot \text{g}^{-1})$	16.0616	20.300
	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	0.0291	0.04967
	R^2	0.99986	0.99889
CT1	$q_t(\text{mg/g})$	12.2862	19.0457
	$q_e(\text{mg} \cdot \text{g}^{-1})$	11.8413	20.1369
	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	0.0469	0.0517
	R^2	0.99909	0.99815
CT0.5	$q_t(\text{mg/g})$	16.8588	17.4155
	$q_e(\text{mg} \cdot \text{g}^{-1})$	17.8507	19.4287
	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	0.0164	0.0556
	R^2	0.99408	0.9992
AC	$q_t(\text{mg/g})$	19.2047	18.5288
	$q_e(\text{mg} \cdot \text{g}^{-1})$	18.5185	18.8964
	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	0.0658	0.0549
	R^2	0.99973	0.9994



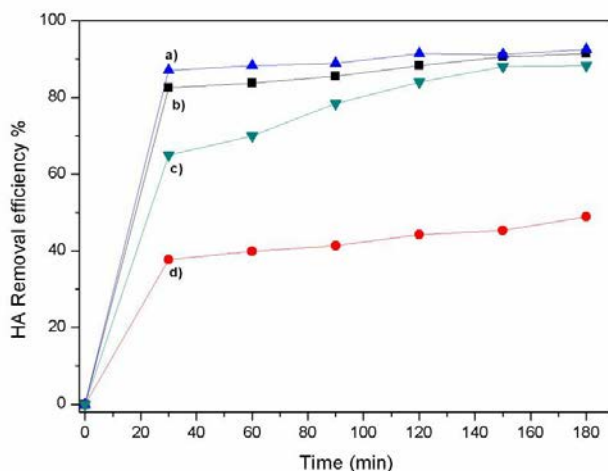


Figure 5: Evolution of HA degradation efficiency after first cycle of photocatalysis using CT1 (a) and AC (b) and after the second cycle of photocatalysis using CT1 (c) and AC (d).

4 CONCLUSIONS

Three types of TiO₂-modified activated carbon characterized by different TiO₂ loading were studied for sorption and degradation of humic acid (HA) from water. The highest sorption capacity for humic acid was found for activated carbon, which decreased with TiO₂ loading increasing. However, the fouling effect of activated carbon was found to lead to a decrease of the activated carbon surface activity, and as consequence, the sorbent lifetime and stability. TiO₂ incorporation within activated surface composition allowed in-situ self-cleaning during HA degradation under UV irradiation. An optimum TiO₂ loading obtained from mass (g) of activated carbon: volume (mL) of TiO₂ precursor ratio of 1:1 was determined based on technical-economic aspects. A slight decreasing of HA degradation efficiency after the second cycle of utilization was found from 93% to 88% for TiO₂-modified activated carbon in comparison with activated carbon that showed significant decreasing from 91% to 49%. The viability of TiO₂ effect under UV irradiation on powdered activated carbon surface to assure the self-cleaning activity was demonstrated making it suitable for the advanced drinking water treatment through photocatalysis processes.

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