

ASSOCIATION OF ACTIVATED CARBONS OF DIFFERENT ORIGINS WITH TITANIA IN THE PHOTOCATALYTIC PURIFICATION OF WATER. USE OF SOLAR ENERGY

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Introduction

Heterogeneous photocatalysis has recently emerged as a new Advanced Oxidation Technology (AOT), able to remove (in-)organic pollutants from water and/or from air [1]. More than 1700 references have been recently collected in this discipline [2]. Titania under the form of anatase is the most active photocatalyst because of its peculiar aptitude of combining good adsorptive properties with respect to diluted pollutants with good absorptive properties with respect to near UV photons.

Several attempts based on metal deposits or on ion-doping failed in improving the photoefficiency of titania. A composite photocatalyst associating titania and activated carbon (AC) was synthesized to combine the adsorptive properties of the latter with the photocatalytic properties of the former [3]. Recently, we could put into evidence a synergy effect between titania and AC used in a mixed suspension for degrading phenol in water [4]. In the present study, we want to extend this phenomenon to others AC either of different industrial origin or home-made from different biomass precursors, or resultin from various activating methods.

Experimental

In all experiments performed, titania Degussa P-25 was used (50 m²/g, 70 % anatase, non-porous particles of ca. 30 nm). Different AC of industrial origing (Merck, Purocarbon) were used as received as well as after various pretreatments. Home-made AC were prepared from soft (Apamate) or hard (Algarrobo) woods employing "physical" or "chemical" activation methods. Other forms of carbon, carbon black (CB) and catalytic filamentous carbon (CFC), were also employed.

The photocatalytic degradation of phenol chosen as a test reaction was performed as described previously [4]. Other model pollutants (4-chlorophenol, and the herbicide 2,4-D) were also employed in the laboratory microreactor as well as in a solar pilot plant at the Plataforma Solar de Almeria (Spain).

Results and Discussion

The photocatalytic degradation of phenol into CO₂+H₂O on UV-illuminated titania followed an apparent first order kinetics with a rate constant $k = 5.6 \times 10^{-3} \text{ min}^{-1}$. The addition of AC to titania induced a large adsorption in the dark which decreased the initial concentration for the photoreaction, thus decreasing the initial reaction rate. However, the main kinetic parameter: the rate constant, which is independent of concentration, has been taken into account for comparison. A synergy factor (R) has been defined as the ratio of the rate constants with and without AC:

$$R = k(\text{AC-TiO}_2) / k(\text{TiO}_2)$$

It can be seen (Table 1) that commercial AC-Merck used as received induced a strong synergy effect equal to 2.5, whereas comercial AC-Purocarbon induced an inhibition ($R < 1$). In general, physical treatments (CO₂ and steam at high temperature, vacumm) were found to be beneficial for a synergy between TiO₂ and AC. By contrast, the chemical treatment was found detrimental (excepting the AC-Purocarbon washed with KOH).

Temperature-programmed reduction (TPR) spectra of activated carbon samples [5], as well as measurements of the solid pH (8 for AC-Merck and 5 for AC-Purocarbon) and the Horwatt-Kawazoe (HK) median micropore width (8 Å for AC-Merck and 19 Å for AC-Purocarbon) suggested that the AC-Merck is an H-type activated carbon (i.e., prepared by high temperature physical activation), and that the AC-Purocarbon ia an L-type activated carbon (i.e., prepared by low temperature chemical activation). Therefore, physical activation appears to be a preparation method better than chemical activation for the present synergy effect.

The synergy has been ascribed to an enhanced adsorption of the pollutants on AC followed by a transfer, through an interphase, to titania where it is photodegraded.

Table 1. Data from the adsorption and the photodegradation of phenol in a suspended mixture of TiO₂ and AC (10⁻³ mol/lit, TiO₂/AC=50/10).

Type of carbon	Treatment	BET surface area (m ² /g)	Micromols of phenol adsorbed in the dark	k (min ⁻¹) x10 ³	Synergy factor R
no AC	TiO ₂ as received	50	1.7	5.6	-
AC-Merck	as received	780	13.4	13.9	2.5
AC-Purocarbon	as received	1240	6.2	4.6	0.8
AC-Merck*	HNO ₃ wash	1170	10.3	7.2	1.3
	KOH wash	830	12.8	8.8	1.6
AC Purocarbon*	vacuum 250 C	1010	4.7	8.3	1.5
	KOH wash	1330	5.8	7.4	1.3
AC-Apamate	H ₃ PO ₄ 450 C	1300	2.4	4.5	0.8
	CO ₂ 800 C	640	10.1	7.6	1.4
	H ₂ O 800 C	420	5.9	8.0	1.4
AC-Algarrobo	H ₃ PO ₄ 450 C	1000	3.5	4.3	0.8
	CO ₂ 800 C	520	5.7	6.7	1.2
	H ₂ O 800 C	450	4.2	6.6	1.2
BC	as received	70	1.6	4.9	0.9
CFC	as received	590	2.7	2.4	0.4

*modified

The absence of synergy effect (i.e., $R < 1$) in the cases of samples CB and CFC is probably due to the relatively low surface area of the former and to doping by the presence of the catalyst (probably Fe or Ni) used for preparing the second.

The most favourable mixture TiO₂/AC-Merck was successfully extended to the other pollutants: 4-chlorophenol, and the herbicide 2,4-D [6], as well as to a large solar pilot plant. In this last case, besides a volume extrapolation factor of 12500, a synergy factor was found identical to that obtained in the laboratory experiments [7].

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References

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