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High surface area microporous carbons as photoreactors for the catalytic photodegradation of methylene blue under UV–vis irradiation

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ABSTRACT

High surface area (*ca.* 1700–3400 $m^2\ g^{-1}$) activated carbons (ACs) were prepared from Chinese anthracite by chemical activation with KOH using KOH/Anthracite weight ratios ($W_{KOH}/W_{Anthracite}$) ranging from 1.6 to 5. The photocatalytic degradation of methylene blue (MB) at high concentration conditions up to 25 ppm under UV–vis irradiation was performed on AC and on TiO_2-AC mixtures prepared by slurry methodology. The highest values of both BET surface area and of micropore volume to total pore volume ratio were found with a $W_{KOH}/W_{Anthracite}$ ratio of 4. It was found that ACs developed photocatalytic activity and an important synergistic effect with TiO_2. TiO_2-AC mixtures showed enhancements in the photocatalytic activity up to 6 times higher than commercial TiO_2. The photocatalytic activity of ACs and binary materials was discussed with respect to textural properties and surface functional groups of carbons. The ratio of micropore volume to total pore volume and the surface pH of the ACs play important roles upon the photocatalytic activity of TiO_2-AC, and the combination of adsorption followed by photodegradation clearly contributed to the treatment of highly concentrated methylene blue. It was concluded that photochemical reactive microporous ACs have a beneficial influence upon the photocatalytic activity of TiO_2.

1. Introduction

An important fraction of the total world production of dyes and azo-dyes is released in textile effluents with concomitant environmental hazards [1]. Water is an economic good and the quality of potable water permit to promote equity, efficiency, and sustainability [2]. It has been reported [3] that 783 million people do not have access to clean water and almost 2.5 billion do not have access to adequate sanitation. Therefore, 6–8 million people die annually due to diseases related to the poor quality of water. Moreover, the global population growth projections of 2–3 billion people over the next 40 years indicate a worse panorama by 2050. In this sense, an important aim for science is to develop efficient processes to control and treat adequately polluted water. Classical technologies for the removal of inorganic and organic molecules are adsorption, bio- and chemical degradation methods. A novel approach deals with advanced oxidation processes (AOPs) such as direct photolysis by high-energy UV, peroxidation, ozonolysis, Fenton, photo-Fenton, and heterogeneous photocatalysis by using TiO_2. Because of important advantages such as high photoefficiency, photostability under UV irradiation, high resistance to strong acids or bases, bio-inertness and relatively low cost, TiO_2 has been reported as the best photocatalyst so far [4]. However, it has important disadvantages such as the high recombination rate of the photogenerated (e^-, h^+) pair, the low yield as it absorbs only around 6% of the solar spectrum (energy band-gap equal to 3.2 eV, photo-excited at 385 nm), and finally the low to moderate surface area and therefore its limitation for treating diluted pollution.

Operational constraints have been solved by using hybrid materials based on TiO_2 and carbon and the combination of adsorption and photocatalytic processes [4–16]. In previous works, our group

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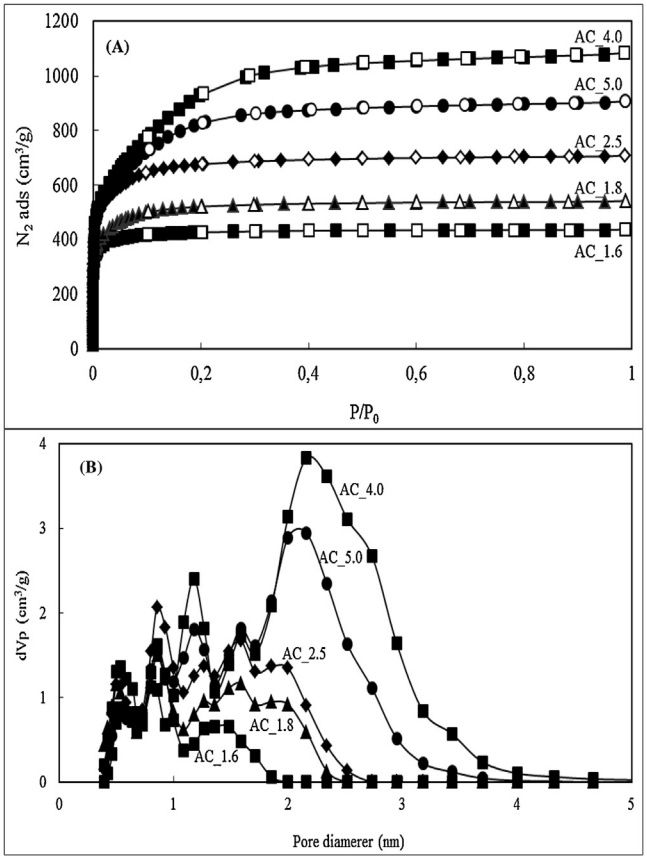

Fig. 1. (A): N_2 adsorption–desorption (full and empty symbols, respectively) isotherms at −196 °C of the ACs, and (B): corresponding pore-size distributions.

Table 1
Pore texture parameters determined by nitrogen adsorption at −196 °C.

ACs	S_{BET}[a] ($m^2\ g^{-1}$)	$V_{0.99}$[b] ($cm^3\ g^{-1}$)	V_{DR}[c] ($cm^3\ g^{-1}$)	E_a[d] ($kJ\ mol^{-1}$)	L_o[e] (nm)	$V_{DR}/V_{0.99}$	V_{me}[f] ($cm^3\ g^{-1}$)
AC_1.6	1688	0.68	0.64	22.1	1.0	0.94	0.04
AC_1.8	1973	0.84	0.71	23.0	0.9	0.85	0.13
AC_2.5	2493	1.10	0.90	20.3	1.2	0.82	0.20
AC_4.0	3438	1.68	1.04	21.8	1.0	0.62	0.64
AC_5.0	2978	1.40	0.96	21.4	1.1	0.69	0.44

[a] BET surface area (S_{BET}).
[b] Total pore volume ($V_{0.99}$).
[c] Micropore volume (V_{DR}).
[d] Adsorption energy (E_a).
[e] Average micropore diameter (L_0).
[f] Mesopore volume (V_{me}) calculated as the difference $V_{0.99}$–V_{DR}.

Table 2
pH at equilibrium of each solution at initial pH_0 = 3, 6 and 10. The pH_{PZC} given here was taken as the average of the three analyses.

Sample	pH at equilibrium			
	pH_0 = 3	pH_0 = 6	pH_0 = 10	pH_{PZC}
AC_1.6	4.70	5.53	4.98	5.07
AC_1.8	7.41	7.38	7.12	7.30
AC_2.5	7.99	7.91	7.83	7.91
AC_4.0	7.50	7.57	7.47	7.51
AC_5.0	7.79	7.81	7.87	7.82

showed that surface functionalization of activated carbon with oxygenated functional groups plays a photo-assisting role which enhances TiO_2 photoactivity in the degradation of phenol [4], 4-chlorophenol [5,6] and dyes [7,8], and in hydrogen photoproduction by water splitting [9] under solar irradiation. Recently, Ania et al. have shown that some activated carbons are photoactive under UV irradiation for phenol photodegradation [10], while Wang et al. showed that mesoporous graphitic carbon nitride is photoactive under visible light for the hydrogen evolution [11,12] and for the selective oxidation of benzene to phenol [13]. Former results from our group have already shown an important synergy effect [14–16] between microporous activated carbons and TiO_2 in the photocatalytic degradation of phenol [14], 4-chlorophenol [15] and a common herbicide such as 2,4-dichlorophenoxyacetic acid