Removal of benzene and toluene by carbonized bamboo materials modified with TiO₂

Chih Shen Chuang^a, Ming-Kuang Wang^b, Chun-Han Ko^{a,*},
Chia-Chih Ou^c, Chien-Hou Wu^d

^a School of Forestry and Resource Conservation, National Taiwan University, Taipei 106, Taiwan

^b Department of Agricultural Chemistry, National Taiwan University, Taipei 106, Taiwan

^c Department of Material and Chemicals Engineering, National University of Kaohsiung, Kaohsiung 811, Taiwan

^d Department of Biomedical Engineering and Environmental Sciences, National Tsing-Hua University, Hsin-Chu 300, Taiwan

Received 5 November 2006; received in revised form 8 March 2007; accepted 8 March 2007

Available online 24 April 2007

Abstract

Carbonized moso bamboo (*Phyllostachys pubescens*) was coated with TiO₂ nanoparticles to enhance its removal efficiency of harmful gases. Carbonized bamboo–TiO₂ composite (CBC) was prepared by heating mixtures of carbonized bamboo powder (CB) and TiO₂ nanoparticles, denoted as CBM, under nitrogen condition. TiO₂ nanoparticle and carbonized bamboo powder were mixed with the mass ratios of 1/1 and 2/1, respectively. At the same mass ratio of TiO₂ to CB, the benzene and toluene removal efficiencies follow the trend: CBC > CBM > CB, which is consistent with the amount of TiO₂ validated by elemental analysis. Sorption mechanism of benzene and toluene by CB, CBM and CBC might belong to hydrophobic–hydrophobic interaction, observed by depletion of untreated bamboo (UB) carbohydrates during carbonization. Sorption kinetics was further analyzed, and optimal correlation was found by fitting with the Elovich kinetic equation.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Benzene; Toluene; Carbonized moso bamboo; Elovich equation; TiO₂ nanoparticles

1. Introduction

Charcoals from biomass are popular adsorbents for air and water purification (Mor et al., 2006; Sarin and Pant, 2006). Recently, bamboo charcoal has been widely applied as well (Mizuta et al., 2004) with moso bamboo (*Phyllostachys pubescens*) being recognized as one of the most popular biomaterials for air purification (Asada et al., 2002). UV/TiO₂ systems are also widely employed for removing volatile organic compounds (Wang et al., 2003; Dagaonkar et al., 2003). UV/TiO₂ combined with wood charcoal (Doi et al., 2000) and commercial activated carbon (Ao and Lee, 2004) possess greater efficiencies in removal of gaseous organics than those of unmodified materials. Similar find-

ings were widely reported for aqueous organics (Qourzal et al., 2004). However, the modification of TiO₂ on carbonized moso bamboo and its enhanced air purification capabilities has not been reported yet.

In this study, TiO₂ nanoparticles were firstly synthesized by the sol–gel process, then coated on carbonized moso bamboo powder (CB) surface to produce the composites (CBC). To investigate the synergetic effects, mixtures of TiO₂ nanoparticles and carbonized bamboo powder (CBM) were prepared under mass ratios of 1/1 and 2/1, respectively. Benzene and toluene removal efficiencies for CB, CBM and CBC were compared. Removal kinetics was further analyzed by fitting with zero, first, second-order models, as well as the Elovich equation. Coupled magic angle ¹³C nuclear magnetic resonance (CPMAS ¹³C NMR) and energy dispersive elemental analyses were also conducted to further clarify removal mechanisms.

* Corresponding author. Tel.: +886 2 3366 4615; fax: +886 2 2365 4520.
E-mail address: chunhank@ntu.edu.tw (C.-H. Ko).

2. Methods

2.1. Carbonized bamboo (CB) preparations

Chips (100 mm × 50 mm × 5 mm) of moso bamboo were oven-dried at 105 °C for 24 h. They were carbonized up to 600 °C isothermally for 60 min under nitrogen gas flow (500 mL min⁻¹). The heating rate was increased at 10 °C min⁻¹. The carbonized bamboo was then heated again up to 800 °C at a heating rate of 10 °C min⁻¹ to obtain bamboo charcoal under carbon dioxide flow (500 mL min⁻¹). The cooled bamboo charcoal was ground and passed through 140 mesh (i.e., 0.105 mm). Carbonized bamboo powder was oven-dried at 120 °C for 24 h under vacuum. The carbonized bamboo is denoted as CB.

2.2. Preparation of TiO₂ nanoparticles

TiO₂ nanoparticles were prepared with 200 mL of 1 M TiCl₄ solution placed into a 500-mL beaker, with pH adjusted by 4 M ammonia solution to 1.5 until TiO₂ was precipitated. TiO₂ precipitates were separated by 11-μm cellulose filters (Whatman Qualitative filter papers grade #1). The TiO₂ precipitates thus obtained were washed five times by double deionized water (DDW) and directly dried on the cellulose filter. Then 3 g of TiO₂ dry powder was suspended into 300 mL of DDW, with 2 mL of concentrated HCl added to dissolve TiO₂ gel with suspension pH maintained at 1.5. The solution was stirred at 50 °C for 6 h. These conditions are able to transform TiO₂ gel into anatase of nanoparticle size (Bruckner et al., 1997). To stabilize TiO₂ nanoparticles, citric acid was added to adjust to neutral pH at the ratio citric acid/Ti of 0.3% (w/w) (Hidber et al., 1997). The pH of suspension was adjusted by 1 M NaOH to get suspension in neutral pH of TiO₂ nanoparticles. The solid content of TiO₂ in suspension was 1%.

2.3. Preparation of carbonized bamboo (CB), mixture (CBM), composite (CBC) with TiO₂ nanoparticles

First, 10 g of carbonized bamboo (CB) powder were mixed with different amounts of TiO₂ nanoparticles, stirred overnight at 25 °C and stirring rate of 400 rpm, and then diluted to 1 L by DDW. The weight ratios of CB to TiO₂ were 1:1 and 1:2, respectively. The suspension was centrifuged at 21,400 × g for 20 min to separate the mixed materials. After removal of the supernatant, the mixed materials were then oven-dried at 120 °C for 24 h under vacuum. The carbonized bamboo mixed with different amounts of TiO₂ was named as CBM1 (Ti/CB = 1:1) and CBM2 (Ti/CB = 2:1).

The CMB prepared as above-mentioned was reheated to 600 °C isothermally for 100 min under nitrogen gas flow (500 mL min⁻¹). The calcined bamboo charcoal was then oven-dried at 120 °C for 24 h under vacuum. Then, the CB/nanoparticles of TiO₂ composite materials were named as CBC. The CBC containing different amounts of TiO₂

was also denoted as CBC1 and CBC2. The capabilities and efficiencies of carbonized bamboo (CB), mixture (CBM) and composite (CBC) for removal of benzene and toluene were compared.

2.4. Characteristic and morphology of CB, CBM and CBC materials

The particle size of TiO₂ precipitates was determined using Malvern Zeta-Sizer 3000 and identified by X-ray diffraction (XRD) using Rigaku Geigerflex X-ray diffractometer. The CB, CBM and CBC materials were examined by a JOEL scanning electron microscope coupled with energy dispersive X-ray spectrometer (EDS) (JSM-6500F). Organic functional groups of untreated bamboo (UB) (<0.105 mm in size) and carbonized bamboo (CB) were examined by coupling magic angle ¹³C nuclear magnetic resonance spectroscopy (CPMAS ¹³C NMR), using a Bruker DSX 400WB NMR instrument. Samples were spun at the magic angle in the boron nitride rotor with a Kel-F cap. The NMR spectra were divided into the following chemical shift regions: alkyl-C (0–45 ppm), *N*-alkyl-C (46–65 ppm), *O*-alkyl-C (65–90 ppm), acetal-C (90–110 ppm), aromatic-C (110–140 ppm), phenolic-C (140–160 ppm) and carboxyl-C (16–200 ppm) (Oades, 2006). The phenolic C contents were calculated from *O*-substituted aromatic C (Baldock et al., 1992). The contents of different organic carbon functional groups were measured by cutting and weighing the areas in different chemical shift regions and expressed as percentages (relative intensities) (Preston et al., 1990).

Brunauer–Emmett–Teller (BET) surface areas of all samples at 77 K were obtained using Carlo Erba Sorptometer (Model 1990) instrument. All the samples were degassed at 400 K for 12 h. The instrument used for nitrogen adsorption analysis was NOVA 2200 from Quantachrome Corporation. Infrared studies in the range of 4000–400 cm⁻¹ for as synthesized manganese oxide samples were recorded on Nicolet 380 spectrophotometer. The samples were mixed well with KBr in 0.5:300 (mg) ratio and then pelletized. Elemental composition (C, H, N, O and S) of HAs was determined using dry combustion method by an elemental analyzer (EA, Heraeus VarioEL-III), with acetonitrile as standard.

2.5. Photo-catalytic activities of CB, CBM and CBC materials for benzene and toluene removal

In order to evaluate the synergistic effects of sorption and the subsequent photo-catalytic activities of the UB, CB, CBM and CBC materials, benzene and toluene removal experiments were conducted in a closed chamber with an ultraviolet (UV) irradiation source, internal recirculation and 0.03 m³ volume. The above setting was to emulate a possible scheme for indoor air pollutant removal. The UV light intensity was 0.5 mW cm⁻² at a wavelength of 365 nm. Benzene and toluene concentrations were detected by GC/FID (SRI 8610 C) with a Quadrex Methyl

Phenyl 5 column, 150 °C injector temperature and 250 °C detector temperature. A sorption experiment was operated for 180 min and sampled at 30 min interval for benzene, toluene and their decomposed products. All the sorption experiments were operated under UV irradiation.

Prior to sorption experiments, 5 g of oven-dried samples (i.e., UB, CB, CBM and CBC) were spread over the glass surface of a plate with an area of 100 cm² and placed into the chamber. Both benzene and toluene at 45 ppmv were injected and then circulated inside the apparatus at the flow of 1.5 L min^{−1} at room temperature. The carried gas of GC was nitrogen and the flow rate was 10 mL min^{−1}, while the ignition gas was hydrogen and the flow rate was 25 mL min^{−1}. All measurements were made in triplicates under same humidity.

2.6. Kinetic models for fitting toluene and benzene sorption

Triplicate kinetic runs were carried out for each treatment. Sorption data were fitted by the kinetic models, including zero-order, first-order, second-order, and Elovich equations. These four selected models were the differential forms of the general rate equation (Benson, 1960).

$$\text{Zero order: } [A] = [A]_0 - kt \quad (1)$$

$$\text{First order: } \ln[A] = \ln[A]_0 - kt \quad (2)$$

$$\text{Second order: } 1/[A] = 1/[A]_0 + kt \quad (3)$$

$$\text{Elovich: } q_t = (1/\beta) \ln(\alpha/\beta) + (1/\beta) \ln t \quad (4)$$

where q_t is amount of sorbate per unit mass of sorbent at time t . α and β are empirical constants. Slope and intercept are $1/\beta$ and $(1/\beta) \ln(\alpha/\beta)$, respectively.

2.7. Statistical analysis

The linear form of kinetic equations was applied to the sorption data and their goodness-of-fit was evaluated according to the R^2 , level of significance (P -value), and standard error (SE). The comparisons of the maximum monolayer sorption amounts and sorption rate constants were performed using the least significant difference (LSD). The LSD values were calculated using SE and t values at appropriate degrees of freedom at 95% confidence levels. The LSD values for the rate constants were obtained from the standard error of the slopes for rate equation.

3. Results and discussion

3.1. Characterization of TiO₂, UB, CB, CBM and CBC materials

The mean particle size of TiO₂ was 28.0 nm and the d -spacing of the TiO₂ nanoparticles was 0.352 nm of an intense anatase peak (JCPDS 21-1272) and the other weak X-ray reflection peaks. Specific surface areas of the CB, CBM2 and CBC2 were 250.7, 275.7 and 286.0 m² g^{−1}, respectively.

Table 1

Distribution (%) of organic carbon functional groups in UB and CB samples (¹³C NMR)

Sample code	Functional group (%)				
	<i>N</i> -Alkyl-C	<i>O</i> -Alkyl-C	Acetal-C	Aromatic-C	Phenolic-C
UB	31.9 ± 1.6	30.1 ± 2.7	14.2 ± 0.4	23.8 ± 0.4	–
CB	31.6 ± 1.2	–	–	46.3 ± 3.3	22.1 ± 1.3

From ¹³C NMR analysis, untreated bamboo (UB) contains mainly *N*-alkyl-C (31.9%), *O*-alkyl-C (30.1%), acetal-C (14.2%) and aromatic-C (23.8%) (Table 1), CB contains *N*-alkyl-C (31.6%), aromatic-C (46.3%) and phenolic-C (22.1%). Thus, UB contains more cellulose (*N*-alkyl-C and acetal-C) and hemicellulose (*O*-alkyl-C) than CB. However, CB contains more lignin (aromatic-C) and phenolic-C fractions than UB. On the other hand, both UB and CB samples have not presented any alkyl-C of microbial re-synthesis and carboxyl-C components. Thus, most long chain fatty groups were broken when UB was heated at 600 °C under nitrogen condition. The decomposition of cellulose and hemicellulose in UB was indicated by increased lignin (aromatic-C) and phenolic-C contents in the CB sample after 600 °C heating in a nitrogen gas flow. Thus, we attribute the sorption of benzene and toluene by CB, CBM and CBC to hydrophobic–hydrophobic interaction.

Infrared spectra (IR) of the UB samples show the absorption bands at 1000–700 cm^{−1} of the C–H bond. However, IR spectra of the CB samples show significantly the absorption bands at 1667–1640 cm^{−1} of C=C bond. It is indicated that the UB samples contain more alkyl-C functional groups than the CB samples. The bamboo samples contain higher aromatic-C after carbonization. These results show the similar trend to those by ¹³C NMR analysis. Infrared analysis of anatase showed a wide-range spectrometer giving spectra down to 300–200 cm^{−1} (Farmer, 1974). Infrared spectra of the CBM and CBC samples show a shoulder absorption band at 650 cm^{−1}.

The energy dispersive elemental analysis (EDS) shows that Ti content of the CBC2 sample is higher than that of the CBM2 in the mixed samples. The C contents show the trend of CB > CBM2 > CBC2 while the O contents show the trend of CBM2 ≈ CBC2 > CB. As can be seen, high Ti contents can coat on the surface of CBC2 and enhance the catalytic capability for high-efficiency removal of benzene and toluene.

Elemental analysis (EA) indicates that the N and C contents in the CB is higher than those in the UB samples, however, the H contents show the reversed trend. Due to carbonization, CB contains less H percentages of aromatic functional groups than the UB sample. These results show the similar trend to those by ¹³C NMR analysis.

3.2. Benzene and toluene removal by CB, CBM and CBC

Benzene sorption studies show the removal efficiencies of benzene in 180 min from CB, CBM1, and CBC1 were

Fig. 1. Benzene (a) and toluene (b) removal efficiencies by CB, CBM1, CBM2, CBC1 and CBC2.

30%, 45%, and 54%, respectively (Fig. 1a). This indicates that CBC removed more benzene than the CB and CBM. On the other hand, 55% and 72% of benzene were removed in 180 min from CBM2 and CBC2, respectively. In general, higher TiO_2 contents in bamboo (i.e., CBM2, CBC2) can sorb more benzene than those of the CB, CBM1 and CBC1 samples.

The CB, CBM1 and CBC1 samples remove in 180 min 37%, 41% and 48% of toluene, respectively (Fig. 1b). However, CBM2 and CBC2 can remove in 180 min 51% and 71% of toluene, respectively. This indicates that higher TiO_2 contents are responsible for removing more toluene. The removal efficiency of benzene is slightly higher than that of toluene. Thus, CBC sorb more benzene and toluene than CBM and CB, demonstrating that TiO_2 enhances benzene and toluene sorption with high catalytic capability. In general, composite materials (i.e., CBC1, CBC2) can remove more benzene and toluene than mixed TiO_2 and carbonized bamboo (i.e., CBM1, CBM2), and carbonized bamboo (CB) materials.

Under illumination of wavelength <370 nm, the valence band electron of TiO_2 can be excited to the conduction band, creating highly reactive electron–hole pairs. After

migration to the solid surface, it can be trapped at different sites. Doi et al. (2000) pointed out that the photo-adsorbed holes are trapped by hydroxyl ions or water on the surface, producing hydroxyl radicals. The mechanism of charge trapping is supported by the fact that the oxygen photo-adsorption increases surface hydroxyl concentration and does not take place on completely dry surface. The hole trapping by the hydroxyl species prevents electron–hole recombination at the surface, thus allowing oxygen chemisorption and electron transfer. In general, the removal efficiencies of benzene by CB, CBM and CBC are greater than those of toluene.

3.3. Kinetic models of toluene and benzene sorption

The kinetic and empirical equations, including the zero-, first-, and second-order rate equations, and Elovich

Table 2
Statistical analysis of benzene and toluene sorbed by CB, CBM1, CBM2, CBC1 and CBC2 and fitted by different kinetic models

	CB	CBM1	CBM2	CBC1	CBC2
Benzene					
R^2					
Zero order	0.9338	0.9330	0.9464	0.8701	0.9553
First order	0.8622	0.8537	0.8868	0.7768	0.8855
Second order	0.7764	0.7493	0.7997	0.6719	0.7911
Elovich	0.9971	0.9937	0.9856	0.9410	0.9890
P					
Zero order	1.7×10^{-2}	1.7×10^{-3}	1.1×10^{-3}	6.6×10^{-3}	7.6×10^{-4}
First order	7.5×10^{-3}	8.5×10^{-3}	5.0×10^{-3}	2.0×10^{-2}	5.1×10^{-3}
Second order	2.0×10^{-2}	2.6×10^{-3}	1.6×10^{-2}	4.6×10^{-2}	1.8×10^{-3}
Elovich	3.1×10^{-6}	1.5×10^{-5}	7.79×10^{-5}	1.3×10^{-3}	4.5×10^{-5}
SE					
Zero order	1.4×10^{-2}	2.7×10^{-2}	2.8×10^{-3}	3.8×10^{-2}	2.9×10^{-2}
First order	1.0×10^{-3}	1.4×10^{-3}	1.1×10^{-3}	1.5×10^{-3}	9.9×10^{-4}
Second order	6.35×10^{-5}	7.02×10^{-5}	4.8×10^{-5}	5.79×10^{-5}	3.05×10^{-5}
Elovich	2.4×10^{-1}	6.9×10^{-1}	1.2	2.2	1.3
Toluene					
R^2					
Zero order	0.9514	0.9776	0.9701	0.9721	0.9589
First order	0.8719	0.9085	0.9299	0.9213	0.9245
Second order	0.7565	0.8015	0.8625	0.8451	0.8672
Elovich	0.9863	0.9866	0.9710	0.9781	0.9651
P					
Zero order	8.9×10^{-4}	1.9×10^{-3}	3.0×10^{-4}	2.9×10^{-4}	6.4×10^{-4}
First order	6.4×10^{-3}	3.2×10^{-3}	1.9×10^{-3}	2.4×10^{-3}	2.2×10^{-3}
Second order	2.4×10^{-2}	1.6×10^{-2}	7.4×10^{-3}	9.5×10^{-3}	6.9×10^{-3}
Elovich	7.03×10^{-5}	6.7×10^{-5}	3.2×10^{-4}	1.8×10^{-4}	4.6×10^{-4}
SE					
Zero order	2.0×10^{-2}	1.4×10^{-2}	1.8×10^{-3}	1.8×10^{-2}	3.1×10^{-2}
First order	1.6×10^{-3}	1.1×10^{-2}	8.3×10^{-4}	9.7×10^{-4}	8.7×10^{-4}
Second order	1.2×10^{-4}	7.49×10^{-5}	3.7×10^{-5}	4.87×10^{-5}	2.6×10^{-5}
Elovich	9.1×10^{-1}	9.1×10^{-1}	1.5	1.3	2.4

Table 3
 α and β values of Elovich equation

	α (% benzene/min)	β (% benzene/1 g) ⁻¹	R^2
<i>Benzene</i>			
CB	59.83	0.111	0.9971
CBM1	106.82	0.077	0.9937
CBM2	238.23	0.049	0.9856
CBC1	147.55	0.058	0.9410
CBC2	212.03	0.042	0.9890
<i>Toluene</i>			
CB	258.114	0.064	0.9863
CBM1	215.201	0.064	0.9866
CBM2	184.530	0.057	0.9710
CBC1	276.305	0.056	0.9781
CBC2	276.407	0.039	0.9651

equations were applied to the benzene and toluene sorption data. The goodness-of-fit of the equation to the data was evaluated by the correlation coefficient (R^2), probability (P), and standard error (SE) of linear regression analysis. The values of these three parameters obtained by applying different models to the kinetic data obtained in the reactions of benzene and toluene adsorption for CB, CBM and CBC are given in Table 2. All the four rate equations fit satisfactorily the benzene and toluene adsorption data. Among the four models tested, the correlation coefficient (R^2) values normalized to the same unit were the lowest for the Elovich kinetic model. More emphasis should be given on the normalized R^2 value as a criterion for evaluating the model performance, since it is indeed related to the closeness of the model prediction with the observed untransformed data, especially the SE and P -values of four models are similar in these adsorption kinetic experiments.

Showing best correlations, the Elovich equation was chosen as the common model in this study to determine the rate constants. The Elovich kinetic plots for the data are shown in Table 3. The rate of reaction was evaluated by α and β values. A high α value and a low β value indicate fast reaction rate reaction. In this study, the fast reaction rates of benzene and toluene sorption were by CBM2 and CBC2, respectively.

4. Conclusions

Moso bamboo (UB) has been successfully modified to carbonized bamboo (CB), mixture (CBM) and composite (CBC) with TiO₂ nanoparticles. The synergetic effects have been demonstrated by higher removal efficiencies of benzene and toluene from CBM and CBC at the same ratio of Ti/CB. The kinetic data could be well described by the Elovich equation. The modified products demonstrated significantly higher capacity in removal of harmful gases than unmodified materials. This study suggests that the modified products possess high potential of economic values for removing indoor air pollutants and merit further studies.

Acknowledgments

This work was generously supported by Grant NSC 94-2313-M-007-039, 91-2313-B-002-361, 92-2313-B-002-090, and 93-2313-B-002-008 from the National Science Council, Taiwan and Grant 93AS-2.3.3-E-e2(2) from the Taiwan Forestry Bureau, Council of Agriculture, Taiwan.

References

- Ao, C.H., Lee, S.C., 2004. Combination effect of activated carbon with TiO₂ for the photodegradation of binary pollutants at typical indoor air level. *J. Photochem. Photobiol. A: Chem.* 161, 131–140.
- Asada, T., Ishihara, S., Yamane, T., Toba, A., Yamada, A., Oikawa, K., 2002. Science of bamboo charcoal: study on carbonizing temperature of bamboo charcoal and removal capability of harmful gases. *J. Health. Sci.* 48, 473–479.
- Baldock, J.A., Oades, J.M., Waters, A.G., Peng, X., Vassallo, A.M., Wilson, M.A., 1992. Aspects of the chemical structure of soil organic materials as released by solid-state ¹³C NMR spectroscopy. *Biogeochemistry* 16, 1–42.
- Benson, S.W., 1960. Experimental characterization of simple kinetic systems. *The Foundations of Chemical Kinetics*. McGraw-Hill Book Co. Inc., New York, pp. 10–83.
- Bruckner, H.D., Hamann U., Heyland A., 1997. Photostabilization of Titanium Dioxide Sols. US Patent 5,698,205.
- Dagaonkar, M.V., Heeres, H.J., Beenackers, A.A., Pangarkar, V.G., 2003. The application of fine TiO₂ particles for enhanced gas absorption. *Chem. Eng. J.* 92, 151–159.
- Doi, M., Saka, S., Miyafuji, H., Goring, D.A.I., 2000. Development of carbonized TiO₂ woody composites for environmental cleaning. *Mater. Sci. Res. Int.* 6, 15–21.
- Farmer, V.C., 1974. The anhydrous oxide minerals. In: Farmer, V.C. (Ed.), *The Infrared Spectra of Minerals*. Mineralogical Society, London, pp. 193–196.
- Hidber, P.C., Graule, T.J., Gauckler, L.J., 1997. Influence of the dispersant structure on properties of electrostatically stabilized aqueous alumina suspensions. *J. Eur. Ceram. Soc.* 17, 239–249.
- Mizuta, K., Matsumoto, T., Hatate, Y., Nishihara, K., Nakanishi, T., 2004. Removal of nitrate–nitrogen from drinking water using bamboo powder charcoal. *Bioresour. Technol.* 95, 255–257.
- Mor, S., Ravindra, K., Bishnoi, N.R., 2006. Adsorption of chromium from aqueous solution by activated alumina and activated charcoal. *Bioresour. Technol.* 98, 954–957.
- Oades, J.M., 2006. Recent advances in organominerals interactions: implication for carbon cycling and soil structure. In: Huang, P.M., Berthelin, J., Bollag, J.M., McGill, W.B., Pages, A.L. (Eds.), *Environmental Impact of Soil Component Interactions, Natural and Anthropogenic Organics*, vol. 1. CRC Press/Lewis Publishers, Boca Raton, FL, pp. 119–134.
- Preston, C.M., Sollins, P., Sayer, B.G., 1990. Changes in organic compounds for fallen logs in old-growth Douglas-fir forests monitored by ¹³C nuclear magnetic resonance spectroscopy. *Can. J. For. Res.* 20, 1382–1391.
- Qourzal, S., Assabbane, Y., Ichou, A., 2004. Synthesis of TiO₂ via hydrolysis of titanium tetraisopropoxide and its photocatalytic activity on a suspended mixture with activated carbon in the degradation of 2-naphthol. *J. Photochem. Photobiol. A: Chem.* 163, 317–321.
- Sarin, V., Pant, K.K., 2006. Removal of chromium from industrial waste by using eucalyptus bark. *Bioresour. Technol.* 97, 15–20.
- Wang, W., Chiang, L.W., Ku, Y., 2003. Decomposition of benzene in air streams by UV/TiO₂ process. *J. Hazard. Mater.* B101, 133–146.