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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

A Study of the Photocatalytic Activity of Titanium Dioxide Nanopowders

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Abstract—Photodestruction and adsorption of dyes in aqueous suspensions of nanopowders of titanium dioxide of anatase modification was studied. The photocatalytic activity of titanium dioxide nanopowders was examined in relation to the dispersity of particles and pH of the medium.

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Development of new optically active nanocrystalline materials and technologies of their effective application has become particularly important in recent years. This is due both to the need to search for new power sources (solar light convertes in the case in question) and to the ecological safety of the technologies employed.

Of particular scientific and applied interest in this context are studies in the field of synthesis and analysis of properties of semiconducting nanopowders, oxides of transition metals, including titanium dioxide. Owing to the excellent combination of physicochemical, optical, and catalytic properties, fields of its application are rather extensive. In particular, use of TiO_2 in heterogeneous catalytic oxidation processes for destruction of chlorine- and nitrogen-containing compounds, acids, dyes, surfactants, pesticides, and herbicides was described in [1].

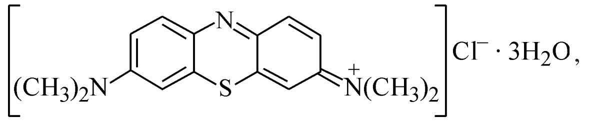
However, certain aspects of heterogeneous processes of this kind are insufficiently understood because of their multifactor and multistage nature. This is largely due to very complex chemical and structural features of the surface of TiO_2 powders, which includes basic and acidic centers, hydroxy groups, and hydroxy and oxygen radicals generated by photocatalytic processes [2]. The situation is made even more complicated in the case of nanosize TiO_2 particles having large specific surface area, mesoporous structure, and high interparticle interaction energy. Of particular interest in this case are TiO_2–dye systems with varied chemical composition and structure, which, in addition, can exhibit sensitizing properties [3].

EXPERIMENTAL

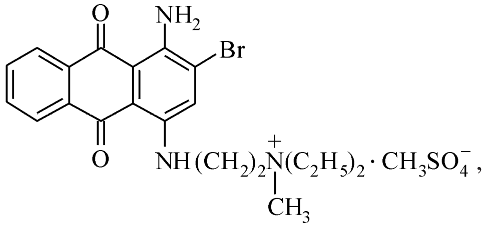
The communication reports on a study of the photocatalytic activity of TiO_2 nanopowders with different particle sizes in photodestruction of dyes of varied chemical nature and structure in aqueous solutions under UV irradiation.

As objects of study were chosen the following TiO_2 powders: of anatase crystalline modification with a particle size of 5 nm and specific surface area of 140 $m^2 g^{-1}$ (Aldrich) (TiO_2-I); of rutile modification with a particle size of <5 nm and specific surface area of 2.7 $m^2 g^{-1}$ (TiO_2-II); of anatase modification with a particle size of 20–25 nm and specific surface area of 108 $m^2 g^{-1}$, synthesized at the Institute of Material Science Problems, National Academy of Sciences of Ukraine (TiO_2-III); and a powder of AV-01-SF brand (Precheza) with a particle size of 100–120 nm and specific surface area of 15.5 $m^2 g^{-1}$ (TiO_2-IV).

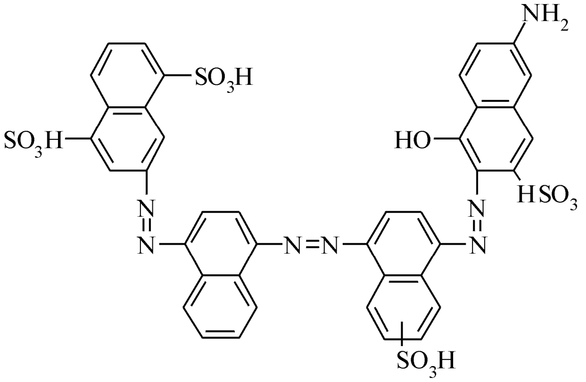
The interaction of titanium dioxide with the following dyes was studied: Methylene Blue (MB) of the thiazine series {analytically pure grade, TU (Technical Specification) 6-09-29–76 [4]}



Cationic Violet 4S (CV) of the anthraquinone series (TU 6-00-49222775-07–2001 [5])



and Direct Blue 2S polyazo dye (DB), GOST (State Standard) 22849–77 [5]



The photocatalytic activity of the TiO_2 powders was determined in 40 mg l^{-1} aqueous solutions of the dyes. The manner in which the optical density and the residual concentration of a dye in solutions vary with the type of TiO_2, pH of the medium (3.2–9.2), and duration of contact between the components (5–60 min) with and without UV irradiation was analyzed. The pH value of dye solutions was adjusted by addition of hydrochloric acid and sodium tetraborate. The optical density of the dye solutions was measured with a KFK-2MP photoelectric colorimeter at wavelengths of 540 (for CV and DB solutions) and 590 nm (for MB solutions) and solution layer thickness of 0.5 cm. The wavelengths corresponded to the absorption peaks. After being brought in contact with TiO_2 powders, the dye solutions were subjected to centrifugation at 8000 rpm for 15 min and their optical density was measured. The residual dye concentrations were found using optical density–dye concentration calibration plots obtained at the corresponding wavelengths. The UV irradiation of dye solutions and suspensions was performed using an SVD-120A high-pressure mercury lamp at an intensity of 18.9 W m^{-2} in the wavelength range 200–400 nm.

The photocatalytic activity of TiO_2 powders is mostly due to the presence of oxygen vacancies and Ti^{3+} ions in the crystal lattice and is manifested upon irradiation with photons with energies of no less than 3.0 and 3.2 eV for the rutile and anatase TiO_2 modifications, respectively. The anatase form of TiO_2 exhibits a higher activity in photoreactions [6–9]. In heterogeneous photocatalytic processes in aqueous media, electron–hole pairs are generated in TiO_2 crystals in the presence of oxygen under the action of UV light, with the subsequent formation of $O_2^{\cdot}$, $O_3^{\cdot}$, $HO^{\cdot}$, and $HO_2^{\cdot}$ radicals [1] having a strong oxidizing effect. In this case, changes in the pH of the medium can strongly affect the concentration of $HO^{\cdot}$ radicals and destruction of organic substances and, in particular, synthetic dyes.

The UV irradiation of TiO_2 suspensions in MB solutions at pH 9.2 is accompanied by an initially, during the first 5–10 min, steep and then insignificant decrease in the residual concentration of the dye (Fig. 1). The discoloration process has the highest intensity in systems containing photocatalyst nanopowders with the smallest particle size, TiO_2-I and TiO_2-III. As the particle size increases, the rate of the discoloration process becomes substantially lower. For example, for powders with particle sizes of 5 and 100–120 nm, the residual dye concentration reaches in 5 and 60 min values of 9 and 2, and 35 and 22 mg l^{-1}, respectively. The process of MB discoloration by TiO_2 nanopowders in the first 5–10 min can be attributed, in accordance with the data of [3], to zeroth-order photoreaction. A similar kinetic dependence of the residual con-

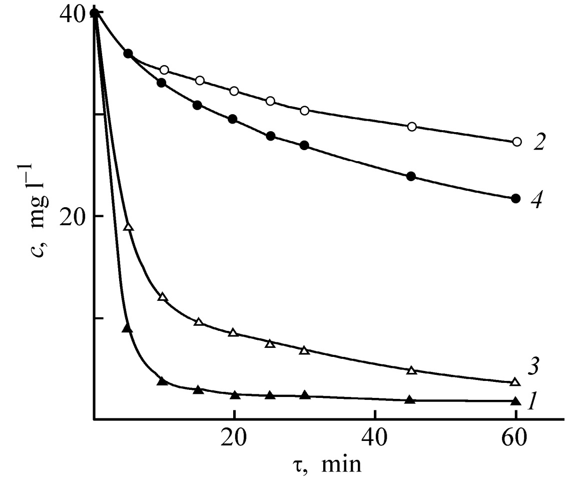


Fig. 1. Kinetics of discoloration of Methylene Blue dye solutions at pH 9.20 in suspensions containing TiO_2 powders. (*c*) Residual dye concentration in the suspensions and (τ) duration of UV irradiation; the same for Fig. 3. Sample: (*1*) TiO_2-I, (*2*) TiO_2-II, (*3*) TiO_2-III, and (*4*) TiO_2-IV; the same for Figs. 2–4.

Table 1. Residual dye concentration *c* and the degree *G* of adsorption of MB dye in TiO_2 suspensions at pH 6.1 upon UV irradiation for 10 and 60 min

Sample	*c*, mg l^{-1}		*G*, %	
	10 min	60 min	10 min	60 min
TiO_2-I	38	35	2.5	6.3
TiO_2-II	38	23	2.5	2.5
TiO_2-III	40	29	0	6.3
TiO_2-IV	35	32	12.5	15.0

centration of a fungicide, fanarimol, has been observed when the role of a photocatalyst was played by TiO_2 of P-25 brand (Degussa) with a specific surface area of 50 m^2 g^{-1}, which is a mixture of the anatase (70–85%) and rutile (15–30%) modifications of TiO_2 [7].

As the pH value of the MB solution is lowered to 6.1, the degree of discoloration dramatically decreases (Table 1), with this effect being characteristic of all TiO_2 powders; the relative positions of the kinetic curves is preserved, as also for dye suspensions with pH 9.2.

Because the optical density of MB solutions remains almost unchanged as pH is lowered from 9.2 to 6.1 and upon UV irradiation for 1 h, the steep decrease in the photocatalytic activity of TiO_2 powders can be attributed to changes in the properties of the photocatalyst itself, whose isoelectric point is 6.7 [10]. The adsorption of OH^- ions on the surface of TiO_2 particles makes larger their negative charge. As a result, the concentration of highly reactive $HO^{\cdot}$ radicals generated by the reaction OH^- + electron vacancy → $HO^{\cdot}$ increases, too. As the pH of TiO_2 suspensions decreases, these factors become less important and the aggregation of TiO_2 particles increases, primarily for the nanosize catalyst, which makes lower the degree of discoloration of the dye solution.

Undoubtedly, an important role is played in the mechanism of photocatalytic discoloration and destruction of a dye by adsorption of its molecules on the surface of TiO_2 particles, which is the initial event of this process. The dynamic nature of the adsorption–desorption of dye molecules and products of their destruction has the key importance for the effective course of the whole photocatalytic process.

As follows from Fig. 2, the run of the kinetic curves in the case of a dark contact of TiO_2 particles with dye solutions is similar to that for irradiated suspensions. As the size of particles decreases and their specific surface area becomes larger, the degree of dye adsorption grows. For example, for TiO_2-I, TiO_2-II, and TiO_2-IV powders brought in contact with MB solutions with pH 9.20 for 1 h, the degree of adsorption reaches values of 70, 50, and 18%, respectively, relative to the initial dye concentration. These values are substantially lower than the residual concentrations of the dye in its photocatalytic discoloration. Substantially lower degrees of MB adsorption on TiO_2 powders were observed for the suspensions at pH 6.10 (Table 1). The interaction of dye molecules with the surface of TiO_2 particles may occur as a result of electrostatic attraction between positively charged cations

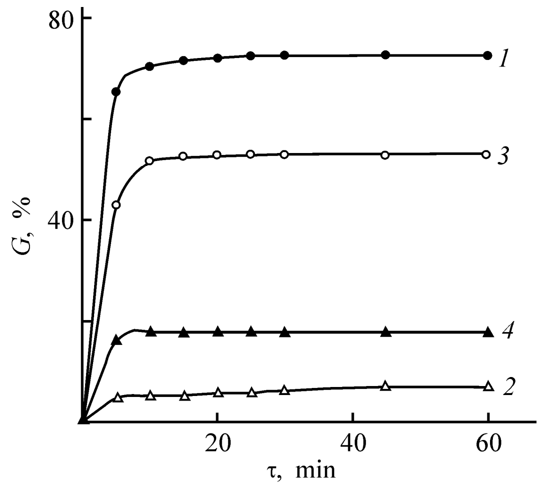


Fig. 2. Kinetics of Methylene Blue dye adsorption in suspensions containing TiO_2 powders at pH 9.20. (*G*) Degree of dye adsorption and (τ) adsorption duration; the same for Fig. 4.

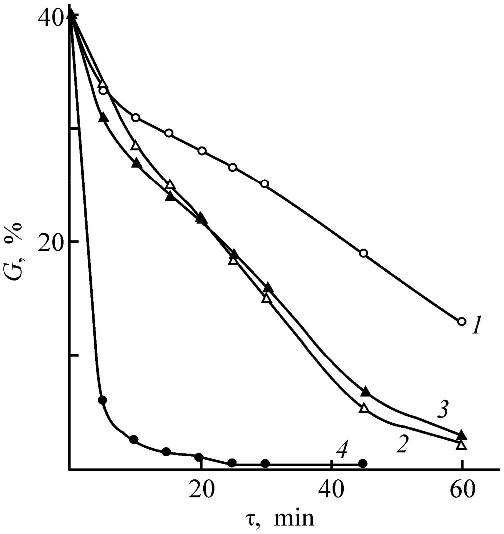


Fig. 3. Kinetics of discoloration of Cationic Violet 4S dye solutions in suspensions containing TiO_2 powders at pH 6.10.

of the dye and negatively charged TiO_2 particles and formation of π-bonds involving electrons of the conjugated system of bonds of the dye, hydrogen bonds, and van der Waals bonds [11].

Thus, there exists a direct relationship between the photocatalytic activity of TiO_2 powders, their dispersity, and adsorption of a dye on the surface of photocatalyst particles, which is noticeably manifested in the difference between the kinetic curves of discoloration of MB and carbonyl-containing CV (Table 1, Fig. 3). It should also be kept in mind that, being a comparatively strong oxidizing agent, CV itself exhibits a certain photosensitivity in the spectral range of the UV irradiation, which is expressed in a decrease in its residual concentration to 32 mg l^{-1} upon exposure for 60 min. As the solution pH increases, the coloration intensity noticeably decreases and almost completely disappears at pH 9.2.

As follows from Fig. 3, the rate of CV discoloration and destruction in TiO_2 suspensions markedly exceeds that for the thiazine dye. Noteworthy is the very high photocatalytic activity of the TiO_2-IV powder, which has the coarsest particles (100–120 nm) among TiO_2 nanopowders. This may be due to the minimum particle aggregation of this photocatalyst and to the maximum degree of adsorption of CV dye on its particles (Fig. 4). All the other TiO_2 powders also exhibit a rather high catalytic activity, compared with that in MB solutions at pH 6.1. This should be particularly emphasized for the TiO_2 powder of the rutile modification, with a particle size of less than 5 μm, for which the particle aggregation effect is the least pronounced. For example, the residual concentration of the dye in CV solutions reaches for TiO_2-I and TiO_2-II, upon 5 and 60 min of UV irradiation, values of 31 and 13 mg l^{-1} and 33 and 2.5 mg l^{-1}, respectively. In most cases, the degree of CV adsorption is smaller than that for MB, especially for the TiO_2-IV powder. Thus, the anthraquinone dye is less stable against UV irradiation as compared with the thiazine Methylene Blue.

The pH of the medium strongly affects the photocatalytic activity of TiO_2 powders. Rather important in the interaction of a dye with surface OH groups of TiO_2 is the formation of hydrogen bonds [12] involving carbonyl groups of the dye, which is accompanied by its discoloration. The nature of kinetic dependences and the absolute values of the residual concentration of the dye under UV irradiation in the course of interaction between CV and TiO_2 powder suggest the following. In given case, there is a favorable combination of the spectral sensitivity of the photoreaction of discoloration and destruction of the anthraquinone dye and the spectral excitation of the photocatalyst, which promotes high-intensity generation of electron–hole pairs and leads to an increase in their lifetime before recombination and thereby enables their involvement in the photochemical reaction.

Table 2. Residual DB dye concentration *c* in TiO_2 suspensions upon UV irradiation for 60 min

Sample	*c*, mg l^{-1}, at indicated pH		
	3.2	6.7	9.2
TiO_2-I	0.6	5/0*	35
TiO_2-II	32	29/23*	32.5
TiO_2-III	22	20/3*	34
TiO_2-IV	24	30/18*	32

* After contact in the dark between the dye solution and TiO_2 powder for 10 min and subsequent UV irradiation for 30 min.

The key role in evaluation of the catalytic activity of TiO_2 particles is played by the intrinsic photoactivity of the dye used for this purpose. As shown by studies of the photostability of the acid polyazo dye, Direct Blue 2S, its aqueous solutions are stable in the pH range studied, and only at pH 3.2 and UV irradiation, the residual concentration decreases by 10%. The nature of kinetic dependences of the residual concentration of DB in TiO_2 suspension is nearly the same as that for cationic dyes. As in the case of MB, the highest catalytic activity is exhibited by the TiO_2-I powder at any of the pH values studied (Table 2). For example, at pH 3.2 and UV irradiation duration of 60 min, the re-

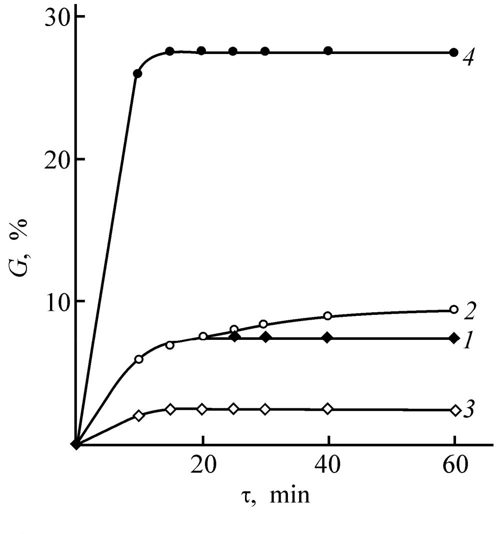


Fig. 4. Kinetics of Cationic Violet 4S dye adsorption in suspensions containing TiO_2 powders at pH 6.10.

Table 3. Residual dye concentration c and total carbon content [C] of MB and DB solutions upon UV irradiation of TiO_2-I suspensions

Suspension no.	Dye	pH	Duration of UV irradiation, min	c, mg l^{-1}	[C], mg l^{-1}
1	MB	9.2	10	4.0	6.3
2			60	2.5	7.9
3^*			60 + 60	10.0	16.5
4^{**}			60 + 60 + 60	17.5	18.6
5	DB	3.2	20	0.6	5.2
6		6.7	60	5.0	8.7

* Suspension no. 3 was produced from suspension no. 2 after a UV irradiation for 60 min, centrifugation, dispersion of the sediment in the same volume of a fresh dye solution, and UV irradiation for 60 min.

** Suspension no. 4 was produced from suspension no. 3 on performing the same procedures as those with suspension no. 2.

sidual concentration of DB reaches a value of 0.6 mg l^{-1}. In this case, the higher the dispersity of a TiO_2 powder, the stronger its catalytic activity, with this tendency becoming weaker at higher pH values and the dye discoloration being only slightly manifested at pH 9.2. In contrast to the cationic dyes, the TiO_2–DB system is characterized by a smaller difference between the residual concentrations of the dye in its discoloration via adsorption of photocatalyst particles and UV irradiation, with the correlation between these concentrations for different TiO_2 powders preserved. The degree of adsorption after a dark contact of the components for 60 min at pH 9.2 reaches a value of 70% for the TiO_2-I powder and 51% for TiO_2-III, whereas the residual concentrations of DB are 5 and 20 mg l^{-1}, respectively. This points to a considerable contribution of the adsorption of the dye to its discoloration under UV irradiation in the presence of TiO_2 powders. At the same time, the results of experiments with preliminary contact (adsorption) of the components for 10 min and subsequent UV irradiation and those with continuous UV irradiation of the suspensions for 60 min demonstrate that the residual concentration of the dye is substantially lower in the first case. These data suggest that the discoloration of the dye under UV irradiation of the suspensions studied is of dynamic nature.

A specific feature of the discoloration and destruction of DB under UV irradiation in the presence of TiO_2 powders is that this process can occur by the mechanism of photoreduction or photooxidation, as it has been observed for other azo dyes [3]. Presumably, one or the other mechanism will be observed, depending of the pH value of TiO_2 suspensions. In an aqueous medium in the presence of oxygen and low pH values, it is possible that the nitrogen atoms of nitro groups are protonated and the dye is discolored to give amines as a result of destruction of the backbone of dye molecules and oxidation by atmospheric oxygen and by ozone formed in its ionization. As the pH of the medium increases, the concentration of hydrogen ions decreases and the intensity of complexation of azo groups, dye discoloration, and destruction of dye molecules to give products with various degrees of oxidation becomes higher. Simultaneously, the negative charge of the surface of TiO_2 particles increases, the degree of ionization of acid-dye molecules grows, the electrostatic repulsion between TiO_2 particles and dye molecules becomes stronger, the adsorption decreases, and the catalytic activity of TiO_2 powders declines.

Analysis of dye solutions after the UV irradiation in the presence of TiO_2-I powder (Table 3) shows that their total carbon content markedly exceeds that corresponding to the residual concentration of a dye. This may indicate that, together with the disruption of the system of conjugated bonds, there occurs chemical destruction of the dyes to give low-molecular-weight compounds with various degrees of oxidation.

It should be kept in mind, when analyzing the results obtained, that the total carbon concentrations in the starting solutions of MB and DB are 20.6 and 20.2 mg l^{-1}, respectively. Comparison of the absolute values of the residual concentrations of the dyes and the total carbon content of solutions subjected to UV irradiation in the first 10–60 min shows that a considerable amount of volatile products is formed in photodestruction of MB and DB.

A repeated use of the TiO_2 nanopowder as a photocatalyst (suspension nos. 3 and 4) demonstrated that, in this case, the residual concentration of the dye and the total carbon content in solution increase. The decrease in the photocatalytic activity of the TiO_2 powder in its repeated use may be due not only to "poisoning" of the catalyst, associated with blocking of active centers on the surface of its particles as a result of chemisorption of products formed in dye destruction, but also to impossibility of restoring the initial dispersity of particles of the photocatalyst in its redispersion.

Thus, the photocatalytic activity of highly dispersed TiO_2 powders in dye-containing aqueous suspensions strongly depends not only on the physicochemical properties of photocatalyst particles, but also on the chemical composition and structure of dye molecules and their mutual influence on the process of discoloration and destruction of an organic substance under UV irradiation of the system constituted by TiO_2 and an aqueous solution of a dye.

CONCLUSIONS

(1) A correlation was revealed between the kinetics of discoloration, destruction, and adsorption of a polyazo dye and thiazine and anthraquinone dyes in aqueous suspensions of titanium dioxide powders of anatase modification, with particle size of 5–120 nm.

(2) It was demonstrated that the kinetics of photodiscoloration and adsorption of aqueous solutions of the dyes studied shows the highest rate in the first 5–10 min and is largely determined by the type of interaction of their molecules with the surface of titanium dioxide particles.

(3) It was shown that the photocatalytic activity of titanium dioxide nanopowders increases with the dispersity of their particles and strongly depends on the pH of the medium, which markedly affects both the stability of synthetic dyes and the activity of titanium oxide photocatalysts.

REFERENCES

1. *Ekologicheskie aspekty sovremennykh tekhnologii okhrany vodnoi sredy* (Ecological Aspects of Modern Technologies for Protection of Water Basins), Goncharuk, V.V., Ed., Kiev: Naukova Dumka, 2005.
2. Solomon, D.H. and Howchorne, D.G., *Chemistry of Pigments and Fillers*, New York: John Wiley Sons, 1983.
3. *Khimiya sinteticheskikh krasitelei* (Chemistry of Synthetic Dye), Venkataramana, K., Ed., Leningrad: Khimiya, 1975, vol. 4.
4. Froinshtadt, D.M., *Reagenty i preparaty dlya mikroskopii* (Reagents and Preparations for Microscopy), Leningrad: Khimiya, 1980.
5. Stepanov, B.I., *Vvedenie v khimiyu i tekhnologiyu organicheskikh krasitelei* (Introduction to Chemistry and Technology of Organic Dyes), Moscow: Khimiya, 1984.
6. Sopajaree, K., Qasim, S.A., Basak, S., and Rajeshwar, K., *J. Appl. Electrochem.*, 1999, vol. 29, pp. 533–539.
7. Balansbramanian, G., Dionjsion, D., Suidan, M.T., et al., *Appl. Catal. B: Environmental*, 2004, vol. 47, pp. 73–84.
8. Bessergenev, V.G., Peretra, R.J.F., Mateus, M.C., et al., *Thin Solid Films*, 2006, vol. 503, pp. 29–39.
9. Sheng, Q., Yuan, S., Zhang, J., and Chen, F., *Microporous Mesoporous Mater.*, 2006, vol. 87, pp. 177–184.
10. Fernandez-Ibañez, P., Blanco, J., Malato, S., and de las Nieves, F.J., *Water Research*, 2003, vol. 37, pp. 3180–3188.
11. *Adsorption from Solution at the Solid/Liquid Interface*, Parfitt, G.D., Rochester, C.H., Eds., London: Academic, 1983.
12. Pimentel, G.C., *The Hydrogen Bond*, McClellan, A.L. and Pauling, L., Eds., San Francisco: Freeman, 1960.