

High adsorption capacity of MWCNTs for removal of anionic surfactant SDBS from aqueous solutions

Seyede Shima Mortazavi and Abbas Farmany

ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) are an effective adsorbent for removing various organic and inorganic contaminants because of their high surface area. In this study, MWCNTs were used to investigate the removal of sodium dodecyl benzene sulfonate (SDBS) in industrial wastewater. The effect of pH, adsorbent dosage, dispersion time and temperature on the kinetics and equilibrium of SDBS sorption on MWCNTs were examined. Consistent with an endothermic reaction, an increase in the temperature resulted in a decreasing SDBS adsorption rate. The adsorption kinetic was well fitted by the pseudo second-order kinetic model. The adsorption isotherm data could be well described by the Freundlich equations. The results suggest that MWCNT could be employed as an efficient adsorbent for the removal of SDBS from aqueous media.

Key words | aqueous media, multi-walled carbon nanotube, sodium dodecyl benzene sulfonate

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INTRODUCTION

Surfactants have specific physico-chemical properties, such as solubility in polar/non-polar liquids, the ability to form micelles and adsorption to phase boundaries. They are economically important due to specific properties that allow them to be used as washing, wetting, emulsifying and dispersing agents. Surfactants are widely used in industry and in the household. Huge volumes of surfactants are entering the environment, where these compounds and/or their degradation products may cause damage depending on their concentrations (Emmanuel *et al.* 2005; Murphy *et al.* 2005). Surfactants are *non-degradable* and toxic in nature, so their removal from aqueous solutions and industrial effluents is a matter of great concern (Eichhorn *et al.* 2002). Several treatment processes have been developed over the years to remove surfactants in water and wastewaters, such as chemical precipitation (Shiau *et al.* 1994), electrochemical treatment (Lissens *et al.* 2003), membrane filtration (Kowalska *et al.* 2004), and photocatalytic degradation (Zhang *et al.* 2003). However, these techniques have disadvantages including incomplete metal removal, high consumption of reagents and energy, low selectivity,

high capital and operational costs, and generation of secondary wastes that are difficult to dispose of. For these reasons, cost-effective alternative technologies for treatment of metal-contaminated waste streams are needed. Adsorption has proved to be an appropriate method, as it is a simple, selective and economical process for the removal of surfactants from aqueous solutions. Silica gel (Purakayastha *et al.* 2005), resins (Yang *et al.* 2006), bentonite (Gunister *et al.* 2004), zeolites (Savitsky *et al.* 1981), sand (Khan & Zareen 2006) and activated carbons (Wu & Pendleton 2001; Gonzalez-Garcia *et al.* 2004) have been used for removal of surfactants.

Among other adsorbents, carbon nanotubes, due to their large specific surface area (SSA), small size, highly porous, hollow structure and light mass density, have been used for the removal of organic and inorganic contaminants from water (Long & Yang 2001; Merkoci 2006). The aim of this study was to evaluate the adsorption capacity of surface-oxidized multi-walled carbon nanotubes (MWCNTs) for the removal of sodium dodecyl benzene sulfonate (SDBS) from industrial wastewater.

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MATERIALS AND METHODS

Chemicals

All chemicals used were of analytical reagent grade and were used without further purification. Double-distilled water was used throughout this study. An anionic surfactant, SDBS, used in adsorption studies, was purchased from Merck (Darmstadt, Germany). MWCNT (purity >95%; external and internal diameter: 10–20 nm and 5–10 nm) was purchased from Merck. To prepare oxidized MWCNT, 10 g of MWCNT was added to 100 mL concentrated HNO₃ solution, and the mixture was refluxed for 48 h at 120 °C. After cooling at room temperature, the suspension was filtered through a 0.45 μm filter membrane and then rinsed with deionized water until the pH reached neutral. Finally, the sample was dried in an oven for 2 h at 100 °C. Synthetic wastewater was prepared by dissolving SDBS. The synthetic wastewater was treated using H₂O₂ and ultraviolet to investigate the adsorption process.

Methods

Adsorbent characteristics

SSA may be obtained using the Brunauer, Emmett and Teller (BET) method. The SSA of the sample was determined by measuring the amount of adsorbed gas N₂ on the surface of MWCNT corresponding to a monomolecular layer on the surface. The pore size distribution of MWCNTs and oxidized MWCNTs was measured using the Barrett, Johner and Halenda method.

Adsorption experiments

Batch experiments were performed to evaluate the equilibrium studies. All experiments were conducted in 25 mL glass flasks. To make up the test solution, 0.01 g of MWCNTs was added to 20 mgL⁻¹ of SDBS, and HCl was used to adjust the pH to 5.6. The mixed solution was shaken at room temperature for 15 min and was filtered through 0.2 μm membrane filters, and the residual SDBS concentration was determined. The removal percentage

(%R) was determined as follows:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100$$

where C_0 and C_e are the initial and the final SDBS concentration (μg g⁻¹). All adsorption experiments were performed in triplicate.

The effects of pH, adsorbent dosage, dispersion time and temperature on the adsorption of SDBS were studied. To study the effect of pH, 0.1 mol L⁻¹ HCl or NaOH solution were used to vary pH in the range 1–9, at 15 min intervals and with 20 mgL⁻¹ SDBS as the initial surfactant concentration. The effect of varying the MWCNT mass (adsorbent dosage) was studied at room temperature with 20 mgL⁻¹ initial SDBS and a pH of 5.6. The adsorption percentage of SDBS onto oxidized MWCNTs was studied to obtain the dispersion time required to remove 20 mgL⁻¹ initial SDBS at pH 5.6 and 0.01 g of adsorbent.

Adsorption isotherms are used for the design of adsorption systems. Correlation of equilibrium data by either theoretical or empirical equations is important for practical operations. Langmuir and Freundlich equations were used for further interpretation of the adsorption data obtained.

The Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_m} \right) + \left(\frac{1}{K_L q_m} \right)$$

where K_L is the Langmuir adsorption equilibrium constant (L mg⁻¹) and C_e is the equilibrium SDBS concentration (mg L⁻¹), q_e is the amount of SDBS adsorbed per unit of adsorbent (μg g⁻¹) at equilibrium concentration C_e and q_m is the maximum adsorption capacity (μg g⁻¹), which depends on the number of adsorption sites. The Langmuir isotherm assumes that adsorption will increase with increasing metal concentration, but as soon as all of the sites are occupied, no further adsorption can take place at that site, as long as there is no interaction between the SDBS and the adsorbent, and the adsorption is localized in a monolayer (Langmuir 1916). The correlation coefficients of Langmuir plots (C_e/q_e vs. C_e) are shown in Table 1.

Table 1 | Isotherm model parameters for SDBS adsorption on MWCNTs

Langmuir model			Freundlich model		
q_{\max}	K_L	R^2	K_f	$1/n$	R^2
250	0.2	0.9166	35.8	0.569	0.9291

The Freundlich adsorption model takes the following form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

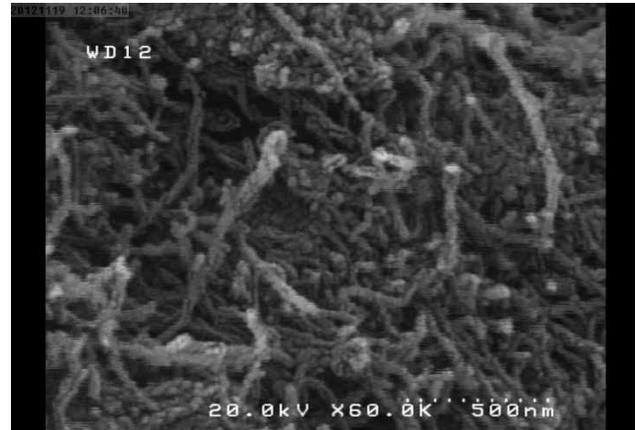
where K_f is the Freundlich isotherm constant ($L \text{ mg}^{-1}$), and n is the Freundlich constant depending on the intensity of adsorption. When $1/n$ is in the range $0.1 < 1/n < 1$, the adsorption process is favorable (Freundlich 1926; Vazquez *et al.* 2007). The Freundlich isotherm shows monolayer adsorption but not a saturation-type isotherm, and is suitable for adsorption over heterogeneous surfaces (Freundlich 1906).

RESULT AND DISCUSSION

Characterization of the adsorbent

To study the SSA of MWCNTs and oxidized MWCNTs, nitrogen adsorption/desorption isotherms on the adsorbent surfaces were obtained. The data were treated according to the BET theory (Brunauer *et al.* 1938; Walton & Snurr 2007). The results of the BET method showed that the SSAs of MWCNTs and oxidized MWCNTs were $115 \text{ m}^2 \text{ g}^{-1}$ and $158 \text{ m}^2 \text{ g}^{-1}$, respectively.

The average pore diameter and pore volume, respectively, were 29 nm and $0.17 \text{ cm}^3 \text{ g}^{-1}$ for MWCNTs and 36 nm, and $0.24 \text{ cm}^3 \text{ g}^{-1}$ for oxidized MWCNTs, respectively (Yavari *et al.* 2011), showing that the pore volume and average pore diameter of MWCNTs are less than oxidized MWCNTs. This can be explained by considering the structural change produced in oxidized MWCNTs with HNO_3 , which can easily break up the MWCNTs into smaller pieces with many surface defects and open ends, exposing the holes through the MWCNTs (see Figure 1) (Li *et al.* 2003).

**Figure 1** | The scanning electron micrograph of MWCNTs.

Effect of pH

Surfactant removal ratios increased when the pH of the solution increased from 1 to 5.6, and remained constant at higher pH values. This may be due to a chemical reaction between SDBS and the adsorbent. At low pH values, the H^+ ion concentration in the system increased so the surface of the MWCNTs could acquire a positive charge by protonation. Positively charged surface sites on the MWCNTs do not favor the adsorption of SDBS.

Effect of adsorbent dosage and dispersion time and temperature

The results of adsorption dosage experiments are shown in Figure 2. The adsorption percentage of SDBS increases from 5 to 76% with an increase in MWCNT mass from 0.001 to 0.01 g due to the availability of adsorption sites (Erdem *et al.* 2005; Wang *et al.* 2008). The adsorption capacity was reached with 0.01 g of adsorbent and remained constant.

The results of contact time experiments are shown in Figure 3. In the first 15 min of contact time, the adsorption percentage of SDBS increased from 20 to 80% and the entire SDBS became adsorbed. An agitation time of 15 min was selected for further experiments.

When the experimental temperature was varied, it was found that removal efficiency decreased from 80% at 25°C to 25% at 50°C . This suggests that the removal efficiency

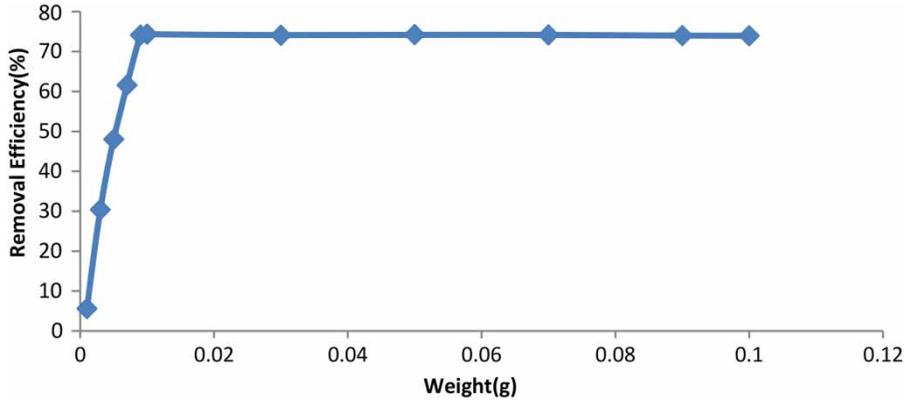


Figure 2 | Percentage of SDBS removal at different MWCNT dosages.

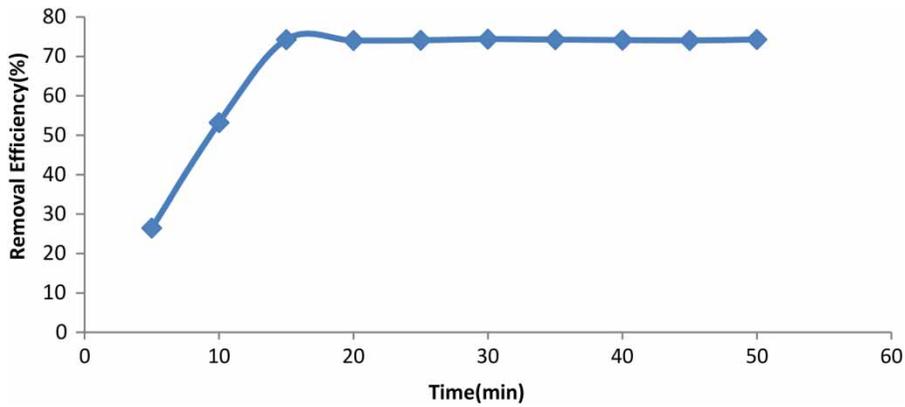


Figure 3 | The effect of contact time on the adsorption of SDBS on MWCNTs.

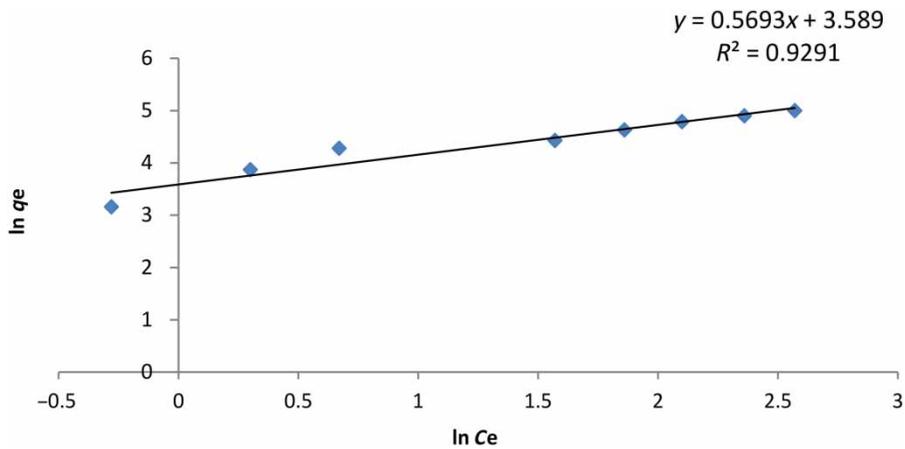


Figure 4 | Freundlich isotherm plot of SDBS adsorption on MWCNTs (MWCNT dosage = 0.01 g, pH = 5.6, contact time 15 min).

depends on the temperature, and that the process is exothermic and occurs by the weakening of bonds between SDBS and MWCNTs at high temperatures (Ribeiro *et al.* 2012).

Adsorption isotherms

The Langmuir and Freundlich isotherms were obtained by using the linear least square regression methods. The results showed that the Freundlich isotherm fitted well with the SDBS adsorption process ($R^2 > 0.92$). The Langmuir and Freundlich correlation coefficients and constants are shown in Table 1.

R^2 of the Langmuir and Freundlich isotherms are 0.9166 and 0.9291, respectively (Figure 4, Table 1). Our results suggest that the adsorption process can be described as a homogeneous distribution onto the MWCNTs' surface, and might occur by a reaction between SDBS and negatively charged groups of MWCNTs (Gao *et al.* 2013).

Adsorption kinetics

In order to investigate the mechanism of adsorption, the first-order and pseudo-second order kinetic models were

used to fit the experimental data, which can be expressed as the following (Ho & McKay 1999):

$$\ln(q_e - q_t) = -k_1 t + \ln q_e$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

where q_e and q_t are the sorption capacity ($\mu\text{g/g}$) at equilibrium and at time t (min), k is the rate constant, $h = k_2 q_e^2$ is the initial sorption rate in the pseudo-second order kinetic model. The R^2 values of the first-order and pseudo-second order kinetics models were 0.6559 and 0.9736, respectively (Table 2). Hence the pseudo-second order model (plot of t/q_t vs. t) better represented the adsorption kinetics (Figure 5), which suggests that the rate-controlling step in the adsorption is controlled by chemical processes (Pang *et al.* 2011).

Table 2 | Kinetic model parameters for SDBS adsorption on MWCNTs

First-order model			Pseudo-second order model		
K_1	q_e , Cal	R^2	K_2	q_e , Cal	R^2
0.001	22.56	0.6559	0.07	125.0	0.9736

CONCLUSIONS

This study demonstrated that the optimum pH for SDBS adsorption by MWCNT was 5.6. Equilibrium adsorption data were very well fitted by the Freundlich model. Adsorption of SDBS obeys a pseudo-second-order equation with good correlation. The results show that MWCNTs may be used effectively for removal of SDBS from aqueous media.

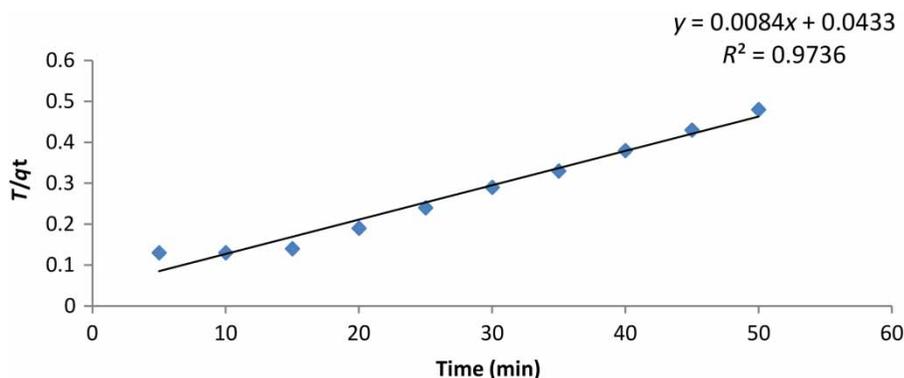


Figure 5 | Pseudo-second order plot for SDBS adsorption on MWCNTs.

REFERENCES

- Brunauer, S., Emmett, P. H. & Teller, E. 1938 Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**, 309–319.
- Eichhorn, P., Rodrigues, S. V., Baumann, W. & Knepper, T. P. 2002 Incomplete degradation of linear alkylbenzene sulfonate surfactants in Brazilian surface waters and pursuit of their polar metabolites in drinking waters. *Sci. Total Environ.* **284**, 123–134.
- Emmanuel, E., Hanna, K., Bazin, C., Keck, G., Clement, B. & Perrodin, Y. 2005 Fate of glutaraldehyde in hospital wastewater and combined effects of glutaraldehyde and surfactants on aquatic organisms. *Environ. Int.* **31**, 399–406.
- Erdem, E., Colgec, G. & Donat, R. 2005 The removal of textile dyes by diatomite earth. *J. Colloid Interf. Sci.* **282**, 314–319.
- Freundlich, H. 1906 Über die adsorption in lösungen. *Zeit. Phys. Chem. (Leipzig)* **57A**, 385–470.
- Freundlich, H. 1926 *Colloid and Capillary Chemistry*. Methuen, London, p. 993.
- Gao, H., Zhao, S., Cheng, X., Wang, X. & Zheng, L. 2013 Removal of anionic azo dyes from aqueous solution using magnetic polymer multi-wall carbon nanotube nanocomposite as adsorbent. *Chem. Eng. J.* **223**, 84–90.
- Gonzalez-Garcia, C. M., Gonzalez-Martin, M. L., Denoyel, R., Gallardo-Moreno, A. M., Labajos-Broncano, L. & Bruque, J. M. 2004 Ionic surfactant adsorption onto activated carbons. *J. Colloid Interf. Sci.* **278**, 257–264.
- Gunister, E., Alemdar, S. A. & Gungor, N. 2004 Effect of sodium dodecyl sulfate on flow and electrokinetic properties of Na activated bentonite dispersions. *Bull. Mater. Sci.* **27**, 317–322.
- Ho, Y. S. & McKay, G. 1999 Pseudo-second order model for sorption processes. *Process Biochem.* **34**, 451–465.
- Khan, M. N. & Zareen, U. 2006 Sand sorption process for the removal of sodium dodecyl sulfate (anionic surfactant) from water. *J. Hazard. Mater.* **133**, 269–275.
- Kowalska, I., Kabsch-Korbutowicz, M., Majewska-Nowak, K. & Winnicki, T. 2004 Separation of anionic surfactants on ultrafiltration membranes. *Desalination* **162**, 33–40.
- Langmuir, I. 1916 The constitution and fundamental properties of solids and liquids. Part. I. Solids. *J. Am. Chem. Soc.* **33**, 2221–2295.
- Li, Y. H., Wang, S. & Luan, Z. 2003 Adsorption of cadmium (II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon* **41**, 1057–1062.
- Lissens, G., Pieters, J., Verhaege, M., Pinoy, L. & Verstraete, W. 2003 Electrochemical degradation of surfactants by intermediates of water discharge at carbon-based electrodes. *Electrochim. Acta* **48**, 1655–1663.
- Long, R. Q. & Yang, R. T. 2001 Carbon nanotubes as superior sorbent for dioxin removal. *J. Am. Chem. Soc.* **123**, 2058–2059.
- Merkoci, A. 2006 Carbon nanotubes in analytical sciences. *Microchim. Acta* **152**, 157–174.
- Murphy, M., Alkhalidi, M., Crocker, J., Oregon, P. & Acott, P. 2005 Two formulations of the industrial surfactant toximul differentially reduce mouse weight gain and hepatic glycogen in vivo during early development: effects of exposure to Influenza B virus. *Chemosphere* **59**, 235–246.
- Pang, Y., Zeng, G. M., Tang, L., Zhang, Y., Liu, Y. Y., Lei, X. X., Li, Z., Zhang, J. C. & Xie, G. X. 2011 PEI-grafted magnetic porous powder for highly effective adsorption of heavy metal ions. *Desalination* **281**, 278–284.
- Purakayastha, P. D., Pal, A. & Bandyopadhyay, M. 2005 Adsorbent selection for anionic surfactant removal from water. *Indian J. Chem. Techn.* **12**, 281–284.
- Ribeiro, R. S., Fathy, N. A., Attia, A. A., Silva, A. M. T., Faria, J. L. & Gomes, H. T. 2012 Activated carbon xerogels for the removal of the anionic azo dyes Orange II and Chromotrope 2R by adsorption and catalytic wet peroxide oxidation. *Chem. Eng. J.* **195–196**, 112–121.
- Savitsky, A. C., Wiers, B. H. & Wendt, R. H. 1981 Adsorption of organic compounds from dilute aqueous solutions onto the external surface of type A zeolite. *Environ. Sci. Technol.* **15**, 1191–1196.
- Shiau, B.-J., Harwell, J. H. & Scamehorn, J. F. 1994 Precipitation of mixtures of anionic and cationic surfactants: III. effect of added nonionic surfactant. *J. Colloid Interf. Sci.* **167**, 332–345.
- Vazquez, I., Rodriguez-Iglesias, J., Maranon, E., Castrillon, L. & Alvarez, M. 2007 Removal of residual phenols from coke wastewater by adsorption. *J. Hazard. Mater.* **147**, 395–400.
- Walton, K. S. & Snurr, R. Q. 2007 Applicability of the BET method for determining surface areas of microporous metal-organic frameworks. *J. Am. Chem. Soc.* **129**, 8552–8556.
- Wang, X., Zhu, N. & Yin, B. 2008 Preparation of sludge-based activated carbon and its application in dye wastewater treatment. *J. Hazard. Mater.* **153**, 22–27.
- Wu, S. H. & Pendleton, P. 2001 Adsorption of anionic surfactant by activated carbon: effect of surface chemistry, ionic strength, and hydrophobicity. *J. Colloid Interf. Sci.* **243**, 306–315.
- Yang, W. B., Li, A., Fan, J., Yang, L. & Zhang, Q. 2006 Adsorption of branched alkyl benzene sulfonate onto styrene and acrylic ester resins. *Chemosphere* **64**, 984–990.
- Yavari, R., Huang, Y. D. & Ahmadi, S. J. 2011 Adsorption of cesium (I) from aqueous solution using oxidized multi-wall carbon nanotubes. *J. Radioanal. Nucl. Chem.* **287**, 393–401.
- Zhang, T., Oyama, T., Horikoshi, S., Zhao, J., Serpone, N. & Hidaka, H. 2003 Photocatalytic decomposition of the sodium dodecylbenzene sulfonate surfactant in aqueous Titania suspensions exposed to highly concentrated solar radiation and effects of additives. *Appl. Catal. B-Environ.* **42**, 13–24.