

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Colloidal Titanium Dioxide Separation from Water by Foam Flotation

Yun-Hwei Shen

To cite this Article Shen, Yun-Hwei(1998) 'Colloidal Titanium Dioxide Separation from Water by Foam Flotation', Separation Science and Technology, 33: 16, 2623 — 2635

To link to this Article: DOI: 10.1080/01496399808545323

URL: <http://dx.doi.org/10.1080/01496399808545323>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Colloidal Titanium Dioxide Separation from Water by Foam Flotation

YUN-HWEI SHEN

DEPARTMENT OF ENVIRONMENTAL SCIENCE AND ENGINEERING
NATIONAL PINGTUNG UNIVERSITY OF SCIENCE & TECHNOLOGY
PINGTUNG, TAIWAN, REPUBLIC OF CHINA

ABSTRACT

Colloidal titanium dioxide (TiO_2) was separated from an aqueous suspension (1000 ppm) by foam flotation using cationic or anionic surfactants. The effects of surfactant dosage, suspension pH value, suspension ionic strength, and gas flow rate on the dispersed-air flotation of colloidal TiO_2 were investigated. TiO_2 separation was almost complete in optimum conditions. It was found that the coulombic interaction between charged TiO_2 particle surfaces and ionic collectors plays a dominant role in this system. Both flotation rate and foamate volume are dependent upon the gas flow rate. Foam flotation may find application in the separation of submicron TiO_2 particles in suspend-photocatalyst systems.

INTRODUCTION

Heterogeneous photocatalysis has recently received widespread attention for the treatment of anthropogenic compounds in water. A number of photocatalysts have been studied, including titanium dioxide (TiO_2), iron oxide, zinc oxide, and cadmium sulfide. TiO_2 is commonly used because it is very photoactive, stable in comparison to other photocatalysts, and has a low cost. Although extensive studies have been conducted on the mechanisms and pathways of the photocatalytic degradation of anthropogenic compounds (1–3), photocatalytic process engineering has received little attention.

In the photocatalytic degradation process, two modes of TiO_2 application are favored: TiO_2 suspended in aqueous media and TiO_2 immobilized on support materials, e.g., quartz sand, glass, activated carbon, or a noble metal. The efficiency of reactors with immobilized photocatalysts seems to be gener-

ally lower than those designs using dispersed TiO_2 particles (slurry) due to reactant mass transfer influence (4). In the case of dispersed TiO_2 , an increase of photocatalytic degradation efficiency by at least a factor of 10 is reported (5) compared to TiO_2 applied in fixed-bed configurations (6, 7). However, because recovery of colloidal TiO_2 particles from treated liquid may be an awkward process (4), the optimal process design for the photocatalytic degradation process has not yet been established. An economic and efficient strategy for solid separation of suspended submicron TiO_2 is essential for the process development of continuous-flow stirred-tank and plug-flow suspend-photocatalyst systems.

As the size of a particle becomes smaller, the surface-to-volume ratio increases and it become advantageous to use surface-dependent properties for separation. Foam separation processes have been utilized to separate or concentrate a variety of constituents from aqueous solution. This technique is based on the fact that a surface-active material tends to concentrate at the gas-liquid interface. On bubbling air through the solution, one adsorbs the surface-active material at the surface of the rising bubbles, which then separate themselves from the solution as foam. If the substance to be removed is submicron size particles which are not surface active by themselves, the separation is called microflotation (8). In this case a surfactant (collector) is then added. The surfactant adsorbs onto the surface of the particle (colloigend) and renders it hydrophobic. The particles then concentrate at the gas-liquid interface and are removed normally by air flotation. From the solid/liquid separation point of view, flotation techniques appear to possess distinct advantages (9): small energy requirements, high efficiency of solid removal, small space requirements, production of small volumes of sludge with low water content, and moderate cost. Although foam flotation techniques have been applied to separate various solids from water such as talc (10), calcite (11), powder activated carbon, (12) and fine-particle coal (13), to my knowledge the application of this technique for the separation of submicron TiO_2 particles in suspend-photocatalyst systems from water has not been investigated.

The objective of present study was to evaluate the foam flotation technique as a possible treatment process for the separation of TiO_2 particles from water and to examine the major operating parameters that may control the process. These parameters include collector type and dosage, ionic strength of solution, solution pH, and gas flow rate.

EXPERIMENTAL

The TiO_2 particles (P25 anatase, particle size 30–70 nm, density $3800 \text{ kg}\cdot\text{m}^{-3}$, $4.02 \times 10^{18} \text{ particle}\cdot\text{kg}^{-1}$ at a mean diameter of 50 nm) used in this study were purchased from Degussa Corp. Reagent-grade sodium dodecylsul-

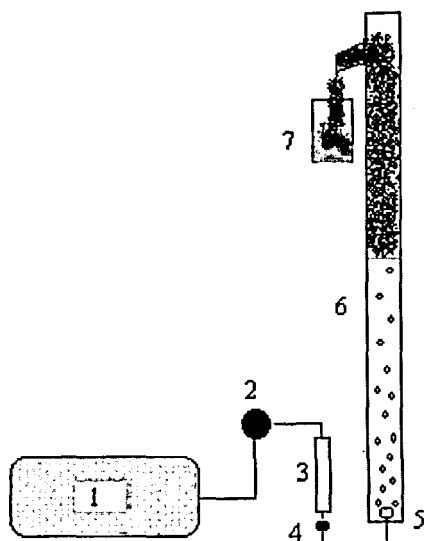


FIG. 1 Schematic diagram of the experimental system. (1) Air tank, (2) regulator, (3) air flowmeter, (4) needle valve, (5) sparger, (6) flotation column, (7) discharge foam.

fate (SDS, Tokyo Chemical Industry, Japan) and dodecylpyridinium chloride (DPC, Tokyo Chemical Industry, Japan) were used as collectors and frothers without purification. Reagent-grade NaOH, HCl, NaCl, and distilled water were used to prepare samples of TiO_2 suspension.

A schematic diagram of the foam separation apparatus is shown in Fig. 1. The flotation column was made of Pyrex tubing, inside diameter 3.5 cm, length 90 cm. The bottom of the column was closed with a rubber stopper with holes for a gas sparger and a stopcock to take samples and to drain the column. The gas sparger was a commercially available 12M gas dispersion tube (pore size 10–15 μm). A lipped side arm near the top of the column served as a foam outlet. Nitrogen gas was supplied by a nitrogen cylinder with a pressure regulator. The gas flow rate was adjusted using a single tube flowmeter with a needle valve.

For foam flotation runs, a 500-mL suspension with a TiO_2 concentration of 1000 ppm, which is a typical concentration used in suspend-photocatalyst reactors, was prepared in a stirred glass beaker. To ensure complete homogeneity, it was sonicated for 10 minutes in an ultrasonic tank. The suspension pH and ionic strength were adjusted using NaOH or HCl solutions and NaCl, respectively. The appropriate amount of surfactant was added and the solution was stirred at 200 rpm for an additional 5 minutes of conditioning. The solu-

tion was then poured into the flotation column, and the timer was started. The air flow rate was adjusted to 83 mL/min before the sample solution was poured into the separation column. The duration of air flow was 12 minutes for each flotation run. All the experiments were performed at room temperature.

Sample turbidities were measured on a Hach ratio turbidimeter (model 18900). The concentration of TiO_2 in suspension was estimated by absorbance measurement taken with a Shimadzu UV-160A spectrophotometer using 10-mm cuvettes at a wavelength of 650 nm. A calibration curve of the absorbance vs TiO_2 concentration was obtained (Fig. 2). Samples were taken before and after flotation, and the absorbance was determined. The percentage of TiO_2 removal was calculated as usual. Foamate volume for each flotation run was estimated by the displacement of the solution–froth interface during flotation. In order to understand the effect of solution pH on the surface charge of TiO_2 particles, electrokinetic measurements were conducted by using 50 ppm TiO_2 suspensions at different pH values using a Zeta meter (Zeta-Meter Inc.). A total of 10–20 particles was tracked. The average velocity of the particles was calculated at a known applied voltage to determine the ζ potential. The relationships between the ζ potential of TiO_2 particles used in this study and pH at two different ionic strength are shown in Fig. 3. It clearly shows that the TiO_2 particles used in this work have a point of zero charge (pzc) at a pH around 6.2. Similar pzc values for TiO_2 were obtained by other investigators (14–16).

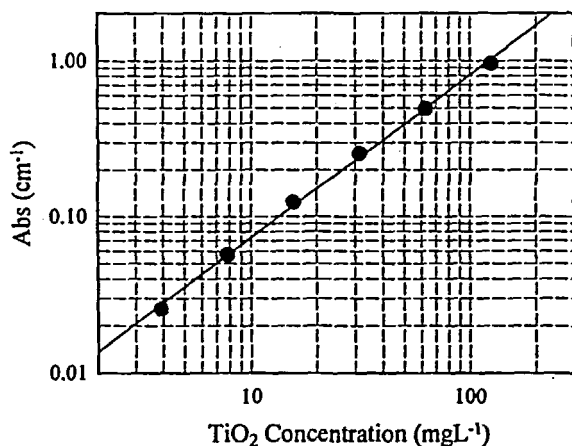


FIG. 2 Calibration curve of absorbance vs $\text{mg}\cdot\text{L}^{-1}$ TiO_2 .

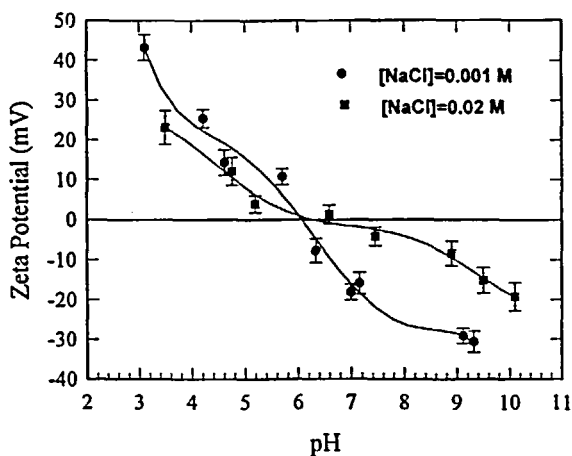


FIG. 3 Zeta potential of TiO_2 as a function of pH.

RESULTS AND DISCUSSION

Effects of Collector and pH on Separation

TiO_2 separation with SDS at three different pH values are presented in Fig. 4. In this instance, the three pH values of TiO_2 suspension, 4.2, 6.0, and 8.6, represent a strong positive, weak positive, and strong negative surface charge of the TiO_2 particles in suspensions, respectively (Fig. 3). SDS proved to be effective only when TiO_2 is positively charged (pH below 6.2). At a pH value of 4.2, maximum separation was obtained, recovery being over 99.9% and residual turbidity being below 10 ntu at a 120 ppm SDS dosage. At pH 8.6, SDS was totally ineffective for TiO_2 separation. In this case, anionic collector ions (SDS) only adsorb on a positively charged TiO_2 surface via coulombic interaction and thereby render it hydrophobic. It is also worth noting that as the TiO_2 surface becomes less positively charged (from pH 4.2 to pH 6.0), separation is slightly reduced and the foamate volume after separation increased. As the surface charge of TiO_2 becomes less positive, adsorption of SDS on TiO_2 surfaces decreases. As a result, the hydrophobicity of the surface is impaired and separation is slightly reduced. On the other hand, increasing the free SDS concentration in solution results in an increase of foamate volume. At pH 8.6, SDS is not expected to adsorb significantly on the strongly negatively charged TiO_2 surface, thus leaving all the SDS in solution. It is thus expected that the foamate volume will be maximum at pH

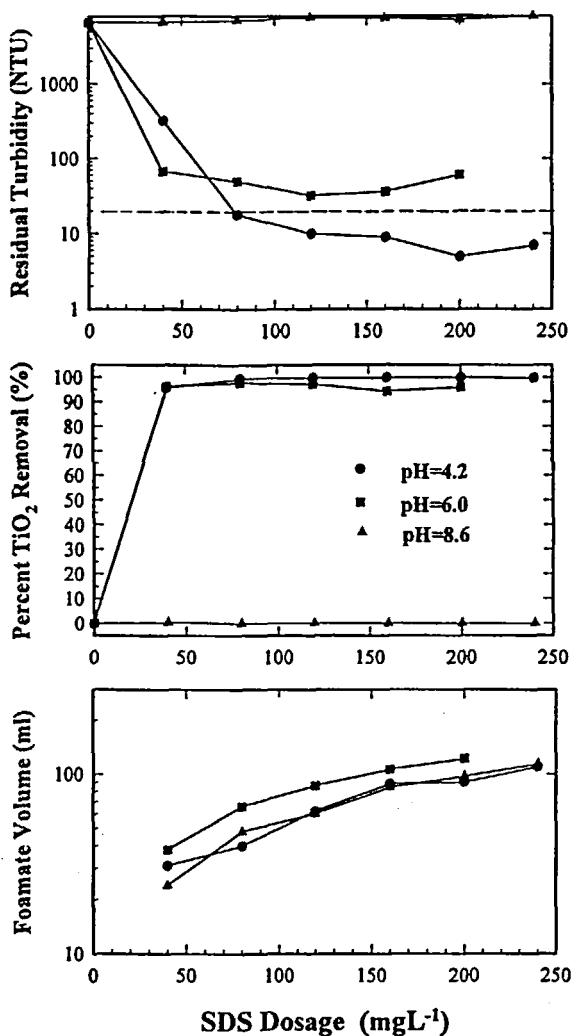


FIG. 4 Effect of SDS dosage on TiO₂ separation at different pH values of the TiO₂ suspension.

8.6, but this is not the case in our experiments. This is possibly due to a lack of solid for stabilizing the foam layer at pH 8.6 adversely affecting foaming ability. Moolman et al. (17) found that hydrophobic particles stabilized froth, whereas completely wetted particles had no effect on froth stability.

TiO₂ separation with DPC at three different pH values is presented in Fig. 5. The flotation mechanisms in this case are very similar to separation with SDS. Cationic DPC proved to be effective only when TiO₂ is negatively charged (pH above 6.2). At a pH value of 10.2, maximum separation was

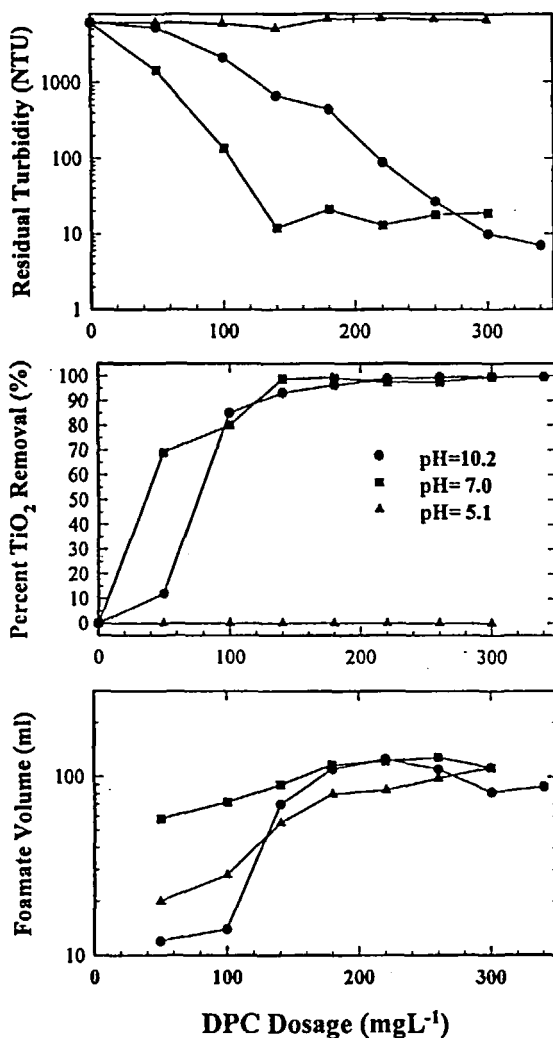


FIG. 5 Effect of DPC dosage on TiO₂ separation at different pH values of the TiO₂ suspension.

obtained, recovery being over 99.9% and residual turbidity being below 10 ntu at a 300 ppm DPC dosage. In this case, cationic collector ions (DPC) adsorbs only on a negatively charged TiO_2 surface via coulombic interaction and thereby render it hydrophobic. It can further be seen from Fig. 5 that at a DPC dosage below 300 ppm, the separation efficiency for a weakly negatively charged TiO_2 (pH 7.0) was better than that for a strongly negatively charged TiO_2 (pH 10.2). This is presumably due to the fact that a weakly negatively charged TiO_2 requires a lesser amount of cationic DPC to neutralize the surface charge and render it hydrophobic. This phenomenon was also observed in separation with SDS (Fig. 4) at low SDS dosages. Finally, the effect of solid particles on foam layer stability was demonstrated again by the foamate volume data shown in Fig. 5.

Effect of Ionic Strength on the Separation

The effects of ionic strength on the separation of TiO_2 with SDS and DPC are shown in Figs. 6 and 7, respectively. At high surfactant dosage, the separation efficiency decreases with increasing ionic strength of solution, presumably due to a decrease of the surface charge of TiO_2 by the compression of the electrical double layer around the TiO_2 particles such that the surface charge of TiO_2 is no longer enough for a sufficient amount of reverse-charged surfactant to be adsorbed. For example, the residual turbidity after separation with 160 ppm SDS was 2, 10, and 20 ntu for solutions with ionic strengths of 0, 0.002, and 0.085 M NaCl, respectively. However, in the low surfactant dosage range, in which the amount of surfactant adsorbed was inadequate to render TiO_2 completely hydrophobic, increasing the ionic strength definitely increased the efficiency of separation. For example, the residual turbidity after separation with 80 ppm SDS was 925, 18, and 40 ntu for solutions with ionic strengths of 0, 0.002, and 0.085 M NaCl, respectively. This result, similar to the pH effect on separation discussed previously, is due to TiO_2 being weakly charged by electrical double layer compression and thus requiring a lesser amount of reverse-charged surfactant to neutralize it and render it hydrophobic. It can also be seen from Figs. 6 and 7 that a weaker charged surface caused by increased ionic strength leaves more unadsorbed surfactant molecules in solution and increases the amount of foamate recorded.

Effect of Gas Flow Rate on the Separation

Flotation experiments were performed at three different gas flow rates (27, 83, and 153 mL/min) with the results shown in Fig. 8. The suspensions for the SDS and DPC tests were maintained at pH values of 4.2 and 10.2, respectively. SDS and DPC dosages were also held constant at 160 and 260 ppm, respectively, while the ionic strength was constant at 0 M NaCl. The separa-

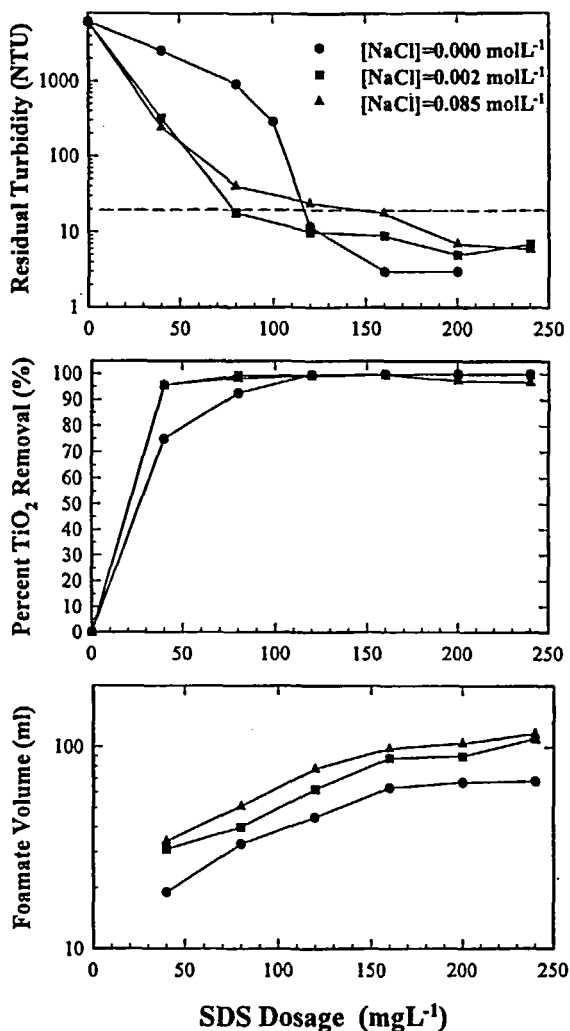


FIG. 6 Effect of ionic strength on TiO₂ separation with SDS at pH 4.0.

tion of TiO₂ in this system seemed to be insensitive to variation of the gas flow rate except that the use of higher flow rates resulted in a greater amount of foamate. A high gas flow rate generally results in fast rising foam in the column and very poor foam drainage. In addition, TiO₂ flotation kinetic data for the different gas flow rate experiments are presented in Fig. 9. The flotation

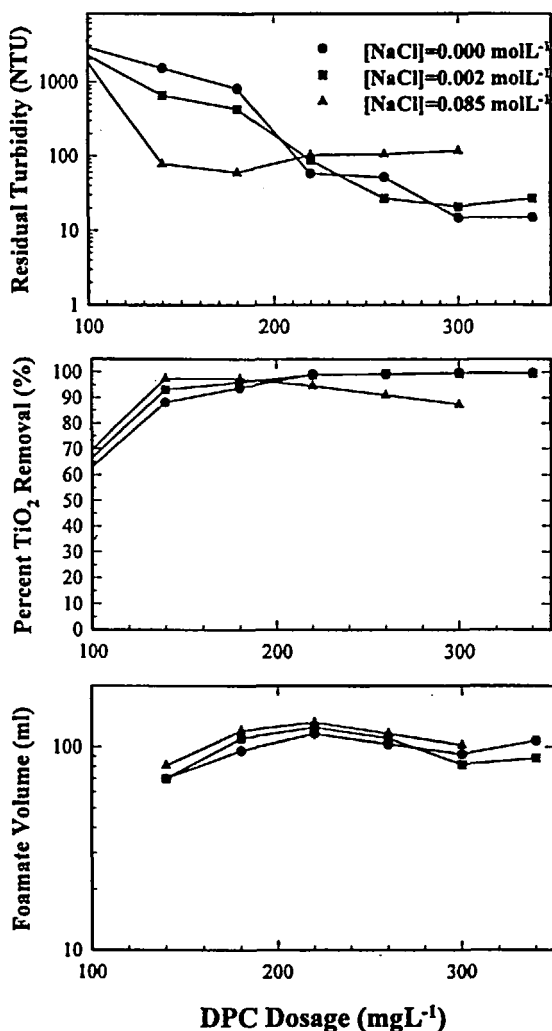


FIG. 7 Effect of ionic strength on TiO₂ separation with DPC at pH 10.4.

of TiO₂ apparently follows a simple first-order rate model which agrees with the literature on floatation kinetics (18). The observed value of first-order rate constants (k) in this study was in the range of 3.74–0.69 min⁻¹. These results shown that both SDS and DPC are capable of TiO₂ separation in a

short time (less than 6 minutes) even at a relatively low gas flow rate (27 mL/min). Also, Fig. 9 indicate that the TiO_2 flotation rate increases with increasing gas flow rate, and flotation runs with SDS generally have a faster kinetic constant than runs with DPC.

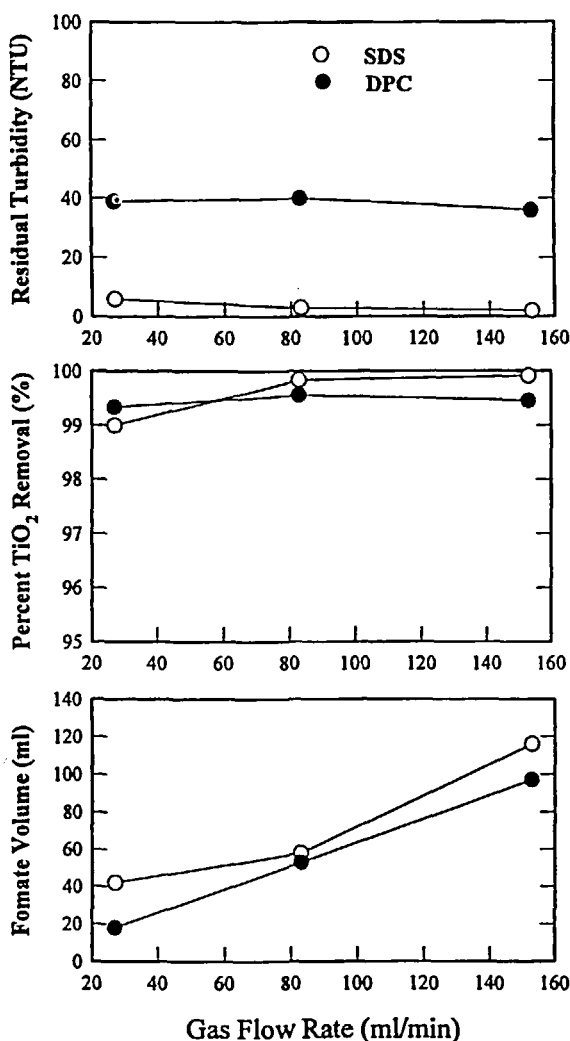


FIG. 8 Effect of gas flow rate on TiO_2 separation with SDS and DPC.

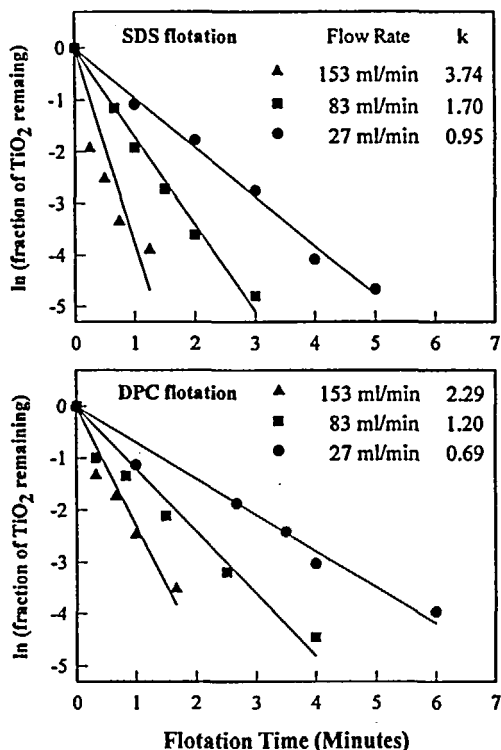


FIG. 9 Flotation of TiO_2 with SDS and DPC as a function of time at different gas flow rates.

CONCLUSIONS

The results of this study demonstrate the feasibility of separation of suspended submicron TiO_2 from water using foam separation with anionic and cationic collectors. Under the appropriate operating conditions, nearly 100% TiO_2 recovery could be achieved. It was found that coulombic interaction between the charged TiO_2 particle surface and the ionic collectors plays a dominant role in this system. Variation of TiO_2 surface charge conditions by changing the solution pH and the ionic strength affects adsorption of ionic collectors onto TiO_2 particles and further affects separation. The rate of foam flotation of TiO_2 is fast in this system. Both flotation rate and foamate volume are dependent upon the gas flow rate. It is concluded that foam flotation with ionic surfactants is an effective process which could be applied to the separation of submicron TiO_2 particles in suspend-photocatalyst systems.

The major concerns for the proposed method are the recovery and reuse of surfactant and TiO_2 . Slapik et al. (19) investigated recovery of surfactant from the collapsed foamate by displacement of SDS surfactant from $\text{Fe}(\text{OH})_3$ floc surface with hydroxide ion. The same process may be applied to SDS- TiO_2 and DPC- TiO_2 systems. This process permits recycle of the surfactant and causes the surfactant-loaded TiO_2 surface to become clean and reusable. Further work is needed to demonstrated this feasibility of surfactant and TiO_2 recovery for this system.

ACKNOWLEDGMENT

This research was supported in part by the National Science Council of the Republic of China and Department of Environmental Protection, Kaohsiung Municipal Government, Republic of China.

REFERENCES

1. K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, and A. Haya, *Bull. Chem. Soc. Jpn.*, **58**, 2015 (1985).
2. W. H. Glaze, J. F. Kenneke, and J. L. Ferry, *Environ. Sci. Technol.*, **21**, 224 (1987).
3. D. F. Ollis and C. S. Turchi, *J. Catal.*, **119**, 483 (1989).
4. D. F. Ollis, E. Pelizzetti, and N. Serpone, *Environ. Sci. Technol.*, **25**, 1523 (1991).
5. A. M. Braun, in *Proceedings of the 8th International Conference on Photochemical Conversion and Storage of Solar Energy*, Palermo, Italy, 1990.
6. K. Hofstadler and R. Bauer, *Environ. Sci. Technol.*, **28**, 670 (1994).
7. V. Brezova, M. Ankovicova, M. Soldan, A. Blazkova, M. Rehakova, I. Surina, M. Ceppan, and B. Havlionova, *J. Photochem. Photobiol. A: Chem.*, **83**, 69 (1994).
8. P. Somasundaran, *Sep. Sci.*, **10**, 93 (1975).
9. A. N. Clarke and D. J. Wilson, *Foam Flotation: Theory and Applications*, Dekker, New York, NY, 1983.
10. C. J. Kho and H. J. Shon, *Int. J. Miner. Process.*, **27**, 157 (1989).
11. P. Mavros, N. K. Lazaridis, K. A. Matis, and G. A. Stalidis, *Sep. Sci. Technol.*, **25**, 155 (1990).
12. A. I. Zouboulis, N. K. Lazaridis, and D. Zamboulis, *Ibid.*, **29**, 385 (1994).
13. A. J. Rubin and R. J. Kramer III, *Ibid.*, **17**, 535 (1982).
14. M. C. Lu, G. D. Roam, J. N. Chen, and C. P. Haung, *J. Photochem. Photobiol. A: Chem.*, **76**, 103 (1993).
15. G. A. Parks, *Chem. Rev.*, **65**, 177 (1965).
16. F. F. Apland and D. W. Fuerstenau, in *Froth Flotation* (D. W. Fuerstenau, Ed.), AIME, New York, NY, 1962, p. 170.
17. D. W. Moolman, J. J. Eksteen, C. Aldrich, and J. S. J. Van Deventer, *J. Miner. Process.*, **48**, 135 (1996).
18. K. A. Matis, G. A. Stalidis, and A. I. Zouboulis, *Sep. Sci. Technol.*, **23**, 347 (1988).
19. M. A. Slapik, E. L. Thackston, and D. J. Wilson, *J. Water Pollut. Control Fed.*, **54**, 238 (1982).

Received by editor April 30, 1997

Revision received April 1998