

Short communication

Removal of color from textile dyeing wastewater by foam separation

Ke Lu, Xiao-Long Zhang, Yan-Li Zhao, Zhao-Liang Wu*

Department of Bioengineering, Hebei University of Technology, Tianjin 300130, People's Republic of China

ARTICLE INFO

Article history:

Received 3 February 2010

Received in revised form 7 June 2010

Accepted 8 June 2010

Available online 12 June 2010

Keywords:

Foam separation

Color removal

Textile wastewater

CTAB

ABSTRACT

The feasibility of foam separation for color removal from direct dyes-containing wastewater was assessed using actual textile wastewater as the research system and cetyl trimethyl ammonium bromide (CTAB) as the collector. The influences of liquid loading volume, air flow rate, surfactant concentration, and initial pH on the removal efficiency and reuse of CTAB in the foamate were studied. The results indicated that using CTAB as a collector for foam separation can provide good foaming quality and effectively remove color from textile wastewater. Under optimum operational conditions (liquid loading volume 450 mL, gas flow rate of 500 mL/min, CTAB concentration 20 mg/L, and an initial pH of 7.0), the removal efficiency reached 88.9%. The residual dye content met the discharge standard for the dyeing and finishing textile industry (GB4287-92) published by the Ministry of Environmental Protection of the People's Republic of China. Using recycled foamate in untreated wastewater, the removal efficiency of 87.5% was obtained with CTAB concentration 10 mg/L of the wastewater.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In recent years the treatment of colored aqueous effluent streams from textile dye house industries has attracted the attention of environmentalists and entrepreneurs. Colored wastewater not only affects the aesthetic merit and water transparency of receiving water bodies [1,2], but there are also environmental concerns about the possible toxicity and carcinogenicity of some organic dyes. Various techniques for removing dyes from the wastewater have been developed, including flocculation, coagulation [3,4], adsorption [5,6], reverse osmosis [7,8], and chemical oxidation [9,10]. Although these techniques have color removal capabilities, their popularity in application is limited by disadvantages such as significant sludge production, adsorbent regeneration, membrane fouling, and high cost.

Foam separation is a process used to separate surface-active materials based on the differences in their surface activity. Materials that are not surface-active can also be separated using surfactant, which is called a collector [11]. Foam separation has been used as an effective and low-cost method for wastewater treatment and has been widely applied to the removal of proteins [12,13], organic materials [14], and metal ions [15,16]. This technique has also been applied to the removal of dyes. Kabil and Ghazy [17] separated brilliant green, neutral red, eriochrome black T, and eosin from aqueous solutions by flotation using oleic acid as a surfactant. Nearly 100% of the investigated dyes could

be floated. Choi and Choi [18] studied the removal of Direct Red from aqueous solutions by using foam separation techniques of ion and adsorbing colloid flotation. Horng and Huang [19] investigated foam separation of Direct Blue 1 from simulated wastewater; over 98% of Direct Blue 1 was removed in 5 min. We [20,21] reported foam separation of crystal violet and methyl orange from aqueous solutions wherein the removal efficiency reached 93.5% and 99.4%, respectively. Dafnopatidou and Lazaridis [22] investigated foam separation of the reactive dyestuffs from simulated and industrial textile effluents. The residual dye content could be lower than the limit of 300 American Dyestuff Manufacturer's Institute units (ADMI). Although the previous studies demonstrated that foam separation could remove dyes effectively, most focused on ideal single dye solutions or laboratory simulated wastewater. There were few reports on the use of this technique for the removal of dyes from actual textile wastewater. Consequently, it is worthwhile to assess whether foam separation is useful to treat genuine process-generated effluent.

Foam separation, however, cannot be used directly to remove dyes from wastewater because textile wastewater alone cannot produce stable foam when aerated. Direct dyes can be classified as anionic dyes. They carry negative charges in aqueous solutions due to the presence of sulfonate (SO_3^-) groups [23]. Therefore, CTAB was chosen as a surfactant in order to produce stable foam and to promote the formation of dye-surfactant complexes by electrostatic interactions. Fig. 1 presents exemplarily the complex structure formed between Direct Black 17 and CTAB. The complexes are adsorbed on the surfaces of bubbles rising through the liquid. The interstitial water between bubbles is drained out by gravity such that dye-surfactant complexes are concentrated and

* Corresponding author. Tel.: +86 22 26564304; fax: +86 22 26564304.
E-mail address: zhaoliangwu@163.com (Z.-L. Wu).

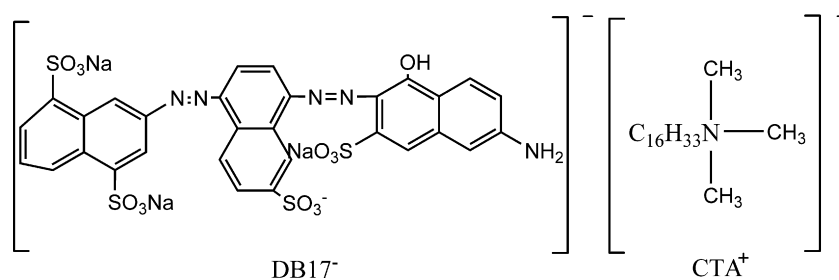


Fig. 1. Structure of DB 17⁻/CTAB complex (molar ratio 1:1).

the remaining liquid is clarified. Precipitation of the dye–surfactant complexes occurs in the foamate because the concentration of dye-complexes in the foamate increases significantly while their solubility decreases.

In this study foam separation was adopted for color removal from actual textile wastewater. Experiments were carried out in a conventional bubble column and CTAB was used as the collector. The effects of process parameters such as liquid loading volume, air flow rate, CTAB concentration and initial pH on the color removal efficiency and reuse of CTAB in the foamate were studied. The objective of our work was to determine the effectiveness of using foam separation to treat actual textile wastewater.

2. Materials and methods

2.1. Wastewater characteristics

The wastewater samples were obtained from a textile mill located in Hebei, China. Table 1 presents the characteristics of the untreated wastewater and the discharge standard for the dyeing and finishing textile industry (GB4287-92) published by the Ministry of Environmental Protection of the People's Republic of China. The samples contained direct dyes (Direct Black 56, Direct Blue 15, Direct Blue 6, Direct Black 17, Direct Yellow 12, Direct Brown 95, and Direct Brown 1) and auxiliary chemicals (NaOH, Na₂CO₃, Na₂SO₄, NaCl, Na₂S₂O₄, CH₃COOH, H₂O₂, brightener, detergent, and swelling agents). Undiluted effluent was used for each study.

2.2. Chemicals and analytical methods

Analytical CTAB, chemicals including hydrochloric acid and sodium hydroxide were purchased from Tianjin Damao Reagent Factory (China). The color in Pt–Co unit was determined using a color meter (Hanna HI93727, Hanna Instruments, Italy) at 470 nm. The chemical oxygen demand (COD) was measured by the standard dichromator closed reflux method (APHA-1989) using a COD analyzer (HACH American). The pH was measured using a pH meter (pHS-25, Shanghai Jingke Instruments, China).

2.3. Equipment

Fig. 2 presents the foam column used in this study. The column was 120 cm high with an inner diameter of 32 mm and was made of organic glass. An air stone diffuser mounted at its bottom was

used as the gas sparger. A rotameter (LZB-3WB, 60–600 mL/min, Wuhuan Instruments, China) was used to control the flow of compressed air, which was passed through the sparger, generating bubbles in the bulk liquid phase. A collection spout was fitted over the top of the column to direct the flow of foam to a collection vessel.

2.4. Experimental procedure

The foam column was operated at room temperature (20 °C). CTAB was added into a certain volume of the wastewater (between 350 and 550 mL) at concentrations ranging from 10 to 30 mg/L. The initial pH of the wastewater was then adjusted to a certain pH value (from 4 to 7) by adding HCl (1 mol/L) or NaOH (1 mol/L). The treated wastewater was then poured into the column. Air flow rate was adjusted to a certain value (between 400 and 600 mL/min). The experiments were run until foam ceased to exit the outlet.

For reuse of CTAB, the foamate was centrifuged at 5000 rpm for 10 min using a high-speed centrifuge (3K18 Sigma, Germany). The dye–surfactant precipitate was collected; the residual foamate and the untreated wastewater with CTAB concentrations from 5 to 15 mg/L were mixed and added into the column to carry out the next operation.

2.5. Performance indicators

Performance indicators used for the foaming process are the removal efficiency (R) and the foamate volume (V),

$$R (\%) = \frac{A - B}{A} \times 100,$$

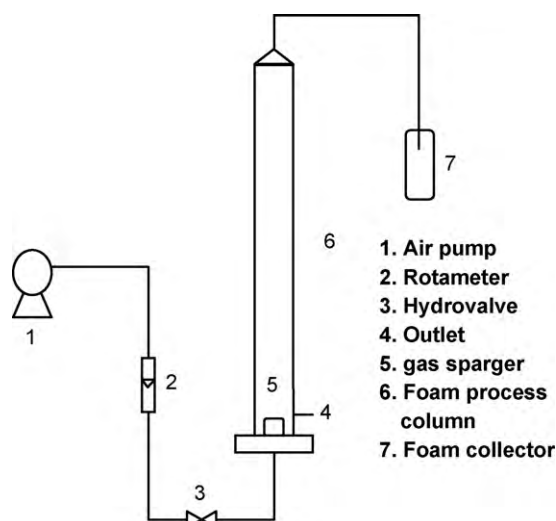


Fig. 2. Experimental apparatus for foam separation.

Table 1
The textile wastewater characteristics.

Parameters	Concentration	Discharge standard
pH	7.2	6–9
Chemical oxygen demand (mg/L)	728	100
Total suspended solids (mg/L)	72	70
Color (Pt–Co)	150	50

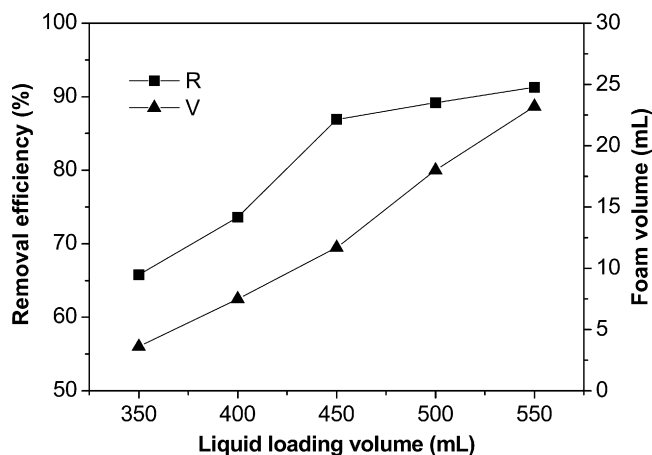


Fig. 3. Effect of liquid loading volume on removal efficiency (R) and foamate volume (V) (CTAB concentration = 30 mg/L, air flow rate = 500 mL/min, initial pH 7.2).

where *A* is the color of initial liquid sample and *B* is the color of the residual liquid sample left in the column at the end of experiments.

3. Results and discussion

3.1. Effect of liquid loading volume

The effect of the liquid loading volume on the removal efficiency and the foamate volume is shown in Fig. 3. As the liquid loading volume increased, the removal efficiency increased from 65.8% to 91.3%. The greater removal efficiency indicated that the increase of liquid loading volume induced greater residence time of bubbles in the bulk liquid phase. Longer residence time ensured sufficient contact between bubbles and the bulk solution, which allowed more surface-active compounds to be adsorbed at the liquid–air interface of bubbles.

Performance indicators of foam separation are commonly presented in terms of the removal efficiency and the enrichment efficiency. The foamate volume can reflect the performance of the enrichment efficiency. A larger foamate volume means a lower enrichment of surface-active compounds due to a higher liquid hold-up in the foam phase. The foamate volume was also found to be larger as a result of more entrainment of liquid in the foam resulting from a shorter foam residence time in the foam phase. Therefore, 450 mL of liquid loading volume was chosen for the subsequent experiments.

3.2. Effect of air flow rate

The air flow rate, which influences the rate of foam formation as well as bubble size and foam residence time, plays a significant role in the process of color removal from wastewater by foam separation. As shown in Fig. 4, the removal efficiency and the foamate volume increased as the air flow rate increased. Higher air flow rate led to a larger quantity of gas bubbles and, thus, more dye–surfactant complexes could be transported into the foam and adsorbed onto the bubble surfaces. When the air flow rate was higher than 500 mL/min, the removal efficiency increased only slightly (from 80.5% to 84.1%). This could be explained that with increasing the air flow rate, the mean bubble radius increased [24,25], thus the interfacial area per unit volume of air decreased and the bubble residence time in the bulk liquid phase also decreased since larger bubbles had higher rise velocities [26]. The production rate and rise rate of bubbles increased and the rate of foam drainage due to gravity remained constant, and thus the foamate volume increased. By balancing both the removal efficiency

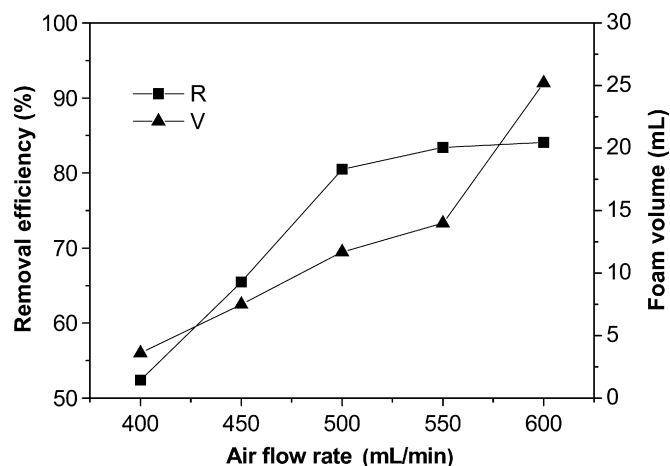


Fig. 4. Effect of air flow on removal efficiency (R) and foamate volume (V) (liquid loading volume = 450 mL, CTAB concentration = 30 mg/L, initial pH 7.2).

and the foamate volume, 500 mL/min was the most suitable air flow rate.

3.3. Effect of concentration of CTAB

The effect of the concentration of CTAB on the removal efficiency and the foamate volume is shown in Fig. 5. By increasing the surfactant concentration, the removal efficiency and the foamate volume increased. This could be attributed to the fact that, at higher CTAB concentration, foam capacity and foam stability became higher and more dyes could be connected to CTAB polar “heads” with a positive charge. When CTAB concentration was higher than 25 mg/L, the removal efficiency increased somewhat (from 83.2% to 92.5%) and the foamate volume increased significantly (from 6.8 to 24 mL). The former may be because the adsorbed surfactant at the liquid–air interface was close to saturation and excessive surfactant could contest the valid liquid–air interface with the formed complexes. The more significant increase in the foamate volume was due to the increase of liquid hold-up in the foam phase. Considering the above factors, 20 mg/L appeared to be the most suitable CTAB concentration.

3.4. Effect of initial pH

The effect of the initial pH of the wastewater on the removal efficiency and the foamate volume is shown in Fig. 6. The increase of the

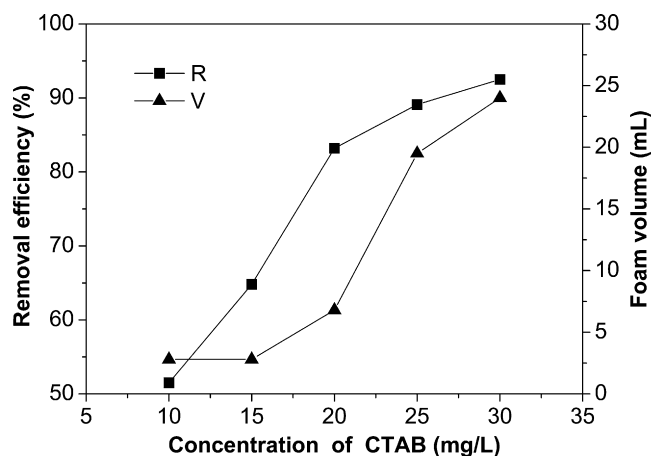


Fig. 5. Effect of concentration of CTAB on removal efficiency (R) and foamate volume (V) (liquid loading volume = 450 mL, air flow rate = 500 mL/min, initial pH 7).

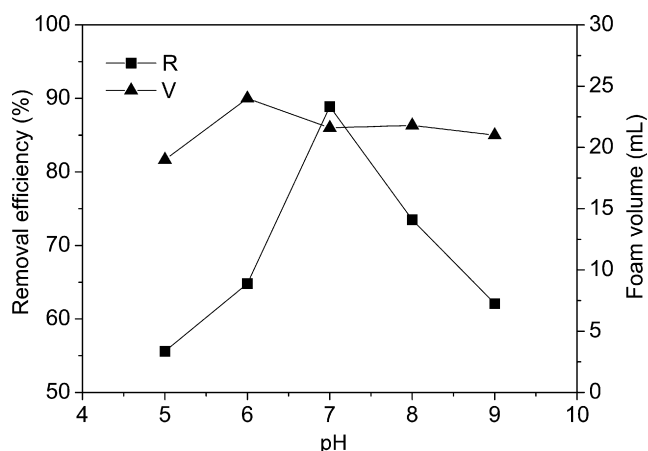


Fig. 6. Effect of initial pH on removal efficiency (R) and foamate volume (V) (liquid loading volume = 450 mL, air flow rate = 500 mL/min, CTAB concentration 20 = mg/L).

initial pH had little effect on the foamate volume, while the removal efficiency reached the maximum value at pH 7. In acidic conditions, the removal efficiency decreased from 88.9% to 55.6%. The reasons for this were: firstly, direct dye anions were protonated, which made the formation of dye–surfactant aggregate difficult [27]; secondly, lower pH induced the decrease of foam quantity and foam stability due to decreased surface tension and viscosity of the solution. We also observed lower color removal in alkaline conditions which agreed with Choi and Choi [18]. It was thought that the presence of excessive OH^- competed with the direct dye anions for CTAB. Thus the most suitable initial pH was 7.

Under the optimum operational conditions the color removal efficiency reached 88.9%, which was roughly the same as the result reported in Dafnopatidou and Lazaridis [22]. However, the concentration of CTAB 20 mg/L used in our study was lower than their CTAB value of 100 mg/L. The difference may be due to different types and concentrations of dyes in the wastewater.

3.5. Reuse of CTAB in the foamate

In the foam separation process CTAB was used as the collector for dyes and formed the complexes that could be precipitated in the foamate. The rest of CTAB was used as foaming agent and remained in the foamate. Therefore, the residual CTAB in the foamate could be reused to treat the untreated wastewater, thereby reducing the total amount of CTAB required and, thus, the expense in an industrial application. Experiments were conducted with the recycled foamate, using 21.8 mL of recycled foamate mixed with 450 mL of wastewater. Small amounts of CTAB (5–15 mg/L) were added to the wastewater prior to the mixing with recycled foamate. The results are presented in Table 2. The removal efficiency reached 87.5% when CTAB concentration of the wastewater was 10 mg/L. By increasing CTAB concentration there was only a slight increase in the removal efficiency. Thus CTAB concentration of 10 mg/L of the wastewater appeared to be the most suitable concentration with recycled foamate. The results suggested that the residual CTAB in the foamate could be reused to treat the wastewater.

Table 2
Effect of CTAB concentration of the fresh wastewater on removal efficiency.

Concentration of CTAB (mg/L)	Removal efficiency (%)	Foamate volume (mL)
5	81.6	10
10	87.5	19.8
15	87.9	22

4. Conclusion

Foam separation, using CTAB as the surfactant, was found to be an effective method for color removal from textile wastewater. Under optimum operational conditions the color removal efficiency reached 88.9% and the foamate volume was 21.6 mL. The color of wastewater decreased from 150 to 17 Pt–Co and met the discharge standard. Wastewater COD decreased about 50%, from 728 to 365 mg/L. Using residual CTAB in the foamate to treat wastewater achieved a removal efficiency rate of 87.5% while the CTAB concentration in the wastewater was only 10 mg/L. Foam separation appears to be a cost effective method for color removal from textile wastewater.

Acknowledgements

This project was supported by The Key Natural Science Foundation of Tianjin, China (No. 08JZDJC25200). We are very grateful to the foundation and for the financial and technical support provided by Hebei University of Technology, Tianjin, China.

References

- W.C. Tinchler, Mills will face new effluent challenges, *Textile World* 5 (1993) 60–62.
- I.M. Banat, P. Nigam, D. Singh, R. Marchant, Microbial decolorization of textile-dye-containing effluents: a review, *Bioresour. Technol.* 58 (1996) 217–227.
- F. El-Gohary, A. Tawfik, Decolorization and COD reduction of disperse and reactive dyes wastewater using chemical-coagulation followed by sequential batch reactor (SBR) process, *Desalination* 249 (2009) 1159–1164.
- V. Golob, A. Vinder, M. Simončič, Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents, *Dyes Pigments* 67 (2005) 93–97.
- S. Karcher, A. Kornmüller, M. Jekel, Anion exchange resins for removal of reactive dyes from textile wastewaters, *Water Res.* 36 (2002) 4717–4724.
- A. Pala, E. Tokat, Color removal from cotton textile industry wastewater in an activated sludge system with various additives, *Water Res.* 36 (2002) 2920–2925.
- N. Al-Bastaki, Removal of methyl orange dye and Na_2SO_4 salt from synthetic waste water using reverse osmosis, *Chem. Eng. Proc.* 43 (2004) 1561–1567.
- C. Suksaroj, M. Héran, C. Allègre, F. Persin, Treatment of textile plant effluent by nanofiltration and/or reverse osmosis for water reuse, *Desalination* 178 (2005) 333–341.
- S.F. Kang, H.M. Chang, Coagulation of textile secondary effluents with Fenton's reagent, *Water Sci. Technol.* 36 (12) (1997) 215–222.
- M. Pérez, F. Torrades, X. Domènech, J. Peral, Fenton and photo-Fenton oxidation of textile effluents, *Water Res.* 36 (2002) 2703–2710.
- S. Boonyasuwat, S. Chavadej, P. Malakul, J.F. Scamehorn, Anionic and cationic surfactant recovery from water using a multistage foam fractionator, *Chem. Eng. J.* 93 (2003) 241–252.
- N.Y. Chan, Md.M. Hossain, M.S. Brooks, A preliminary study of protein recovery from mussel blanching water by a foaming process, *Chem. Eng. Proc.* 46 (2007) 501–504.
- H. Maruyama, H. Seki, A. Suzuki, N. Inoue, Batch foam separation of a soluble protein, *Water Res.* 41 (2007) 710–718.
- Z.D. Chang, H.Z. Liu, J.Y. Chen, Foam separation of tributyl phosphate from aqueous solutions. Part I. Experiment, *Sep. Purif. Technol.* 19 (2000) 131–136.
- M. Moussavi, M. Javidnejad, Separation of Hg (II) by foam fractionation in the acidic range: effect of complexation, *J. Hazard. Mater.* 144 (2007) 187–193.
- Y.H. Qu, G.M. Zeng, J.H. Huang, K. Xu, Y.Y. Fang, X. Li, H.L. Liu, Recovery of surfactant SDS and Cd^{2+} from permeate in MEUF using a continuous foam fractionator, *J. Hazard. Mater.* 155 (2008) 32–38.
- M.A. Kabil, S.E. Ghazy, Separation of some dyes from aqueous solutions by flotation, *Sep. Sci. Technol.* 29 (18) (1994) 2533–2539.
- S.J. Choi, Y.H. Choi, Removal of Direct Red from aqueous solution by foam separation techniques of ion and adsorbing colloid flotation, *Sep. Sci. Technol.* 31 (15) (1996) 2105–2116.
- J.Y. Horng, S.D. Huang, Removal of organic dye (Direct Blue) from synthetic wastewater by adsorptive bubble separation techniques, *Environ. Sci. Technol.* 27 (1993) 1169–1175.
- X.L. Zhang, Z.L. Wu, H.J. Zheng, H.M. Ding, Decolorization of the wastewater containing crystal violet by foam separation, *Chin. J. Proc. Eng.* 8 (6) (2008) 1116–1119.
- X.T. Li, Z.L. Wu, H.J. Zheng, Y.J. Jing, Decolorization process of dye wastewater containing methyl orange by foam separation method, *Chem. Eng. China* 37 (4) (2009) 60–63.
- E.K. Dafnopatidou, N.K. Lazaridis, Dyes removal from simulated and industrial textile effluents by dissolved-air and dispersed-air flotation techniques, *Ind. Eng. Chem. Res.* 47 (2008) 5594–5601.

- [23] C.Y. Kuo, C.H. Wu, J.Y. Wu, Adsorption of direct dyes from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetics and thermodynamics parameters, *J. Colloid Interface Sci.* 327 (2008) 308–315.
- [24] B.K. Gorain, J.P. Franzidis, E.V. Manlapig, Studies on impeller type, impeller speed and air flow rate in an industrial scale flotation cell—Part 1: Effect on bubble size distribution, *Miner. Eng.* 8 (6) (1995) 615–635.
- [25] A. Hasanen, P. Orivuori, J. Aittamaa, Measurements of local bubble size distributions from various flexible membrane diffusers, *Chem. Eng. Proc.* 45 (2006) 291–302.
- [26] Y.J. Lu, J.H. Liu, J. Tang, B. Wei, X.L. Zhang, The removal of humic acids from water by solvent sublation, *J. Colloid Interface Sci.* 283 (2005) 278–284.
- [27] E.K. Dafnolatidou, G.P. Gallios, E.G. Tsatsaroni, N.K. Lazaridis, Reactive dyestuffs removal from aqueous solutions by flotation, possibility of water reuse, and dyestuff degradation, *Ind. Eng. Chem. Res.* 46 (2007) 2125–2132.