Removal Of Color And COD From Synthetic Paper Mill Effluent Using Coagulation/Acid Precipitation Process

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ABSTRACT

Synthetic wastewater (chemical oxygen demand (COD) = 4800 mg/l, pH = 8.2 8.6) representing pulp and paper mill effluent has been treated using coagulation and acid precipitation processes. The synthetic wastewater comprised of alkali lignin (3000 mg/l), phenols (150 mg/l) and sulphides (10 mg/l). To perform coagulation studies, $FeCl_3$, $FeSO_4$ and polyaluminum chloride (PAC) have been used as coagulants. Use of PAC exhibits the highest color removal from the wastewater (97.22 %) whereas $FeCl_3$ addition into the wastewater shows 81% color removal with the same amount of coagulant dose (i.e., 1.2 g/l). However, no significant difference in COD removal (~86%) has been noted with both coagulants. On the contrary, $FeSO_4$ reduces only 23% COD from the wastewater (final COD = 2880 mg/l) and no color removal has been observed. This may possibly be due to poor floc formation (not easily settleable) and color imparted by ferrous ions. In acid precipitation study, the addition of H_2SO_4 keeps increasing the COD reduction due to lignin precipitation at pH in acidic range. The detailed experimental results are presented in the paper. Applicability of pinch analysis to maximize water reuse/recycle of the treated water is also discussed.

Introduction

Paper and pulp mills are one of the most water intensive industries worldwide, generating an enormous amount of extremely polluting wastewater. In India, pulp and paper industries consume around 900 million m^3 of water out of which around 75% emanates as wastewater[1]. This wastewater cannot be disposed into the water bodies without any treatment due to the presence of several organic and inorganic pollutants. As an alternative, the wastewater can be treated onsite and reused in the industrial unit itself to decrease the freshwater requirement.

In a paper and pulp mill, several unit operations including raw material preparation, pulping, bleaching and paper making are employed. The wastewater generated from different units has varying nature of pollutants, hence a suitable physico-chemical and/or biological treatment process can be adopted for dealing with a waste stream coming out from a specific unit. The wastewater generated from pulping section is highly colored and usually contains not easily biodegradable compounds like lignin, phenols and sulfides. This waste stream requires some kind of physico-chemical treatment prior to conventional biological processes. In the present work, the efficacy of coagulation and acid precipitation processes is observed for the treatment of wastewater containing lignin as a major component.

In earlier studies, it has been demonstrated that iron (Fe), copper (Cu) and aluminum (Al) salts are promising coagulants for the treatment of pulp and paper mill wastewater. Fe and Al salts were used for the treatment of paper and pulp mill effluent (chemical oxygen demand (COD) = 2520 – 7930 mg/l, biochemical oxygen demand (BOD) = 1500 – 3500 mg/l and total carbon (TC) = 1065 – 3560 mg/l)[2]. Ferric chloride was found to be the most efficient coagulant with 88 % reduction in TC and 97 % reduction in color. In another study, chemical coagulation was used for an effluent with COD of 50 mg/l and color of 40 Pt-Co units as a tertiary treatment[3]. The treatment with alum (dose = 90 mg/l) and a polymer as a flocculant (dose = 2 to 3 mg/l) showed the best results with 70 % and 90 % reductions in COD and color, respectively, in the pH range of 5.6 to 5.8. Alum and polyaluminum chloride (PAC) were used as coagulants with polyacrylamide (PAM) as flocculants for treatment of the paper and pulp mill effluent (COD = 3087 mg/l, TSS = 5240 mg/l, turbidity = 4770 NTU and pH = 6 - 8.3)[4]. Overall reductions of 99.8 %, 99.4 % and 91 % were achieved in turbidity, TSS and COD, respectively, with an optimum dose (1000 mg/l) of PAC. Garg et al[5] performed coagulation (using aluminum- based chemicals and ferrous sulphate) as well as acid precipitation (using H_2SO_4) processes for the removal of COD and color from diluted black liquor (COD = 7000 mg/l). The maximum COD and color removals of 63 and 90 %, respectively, were reported at pH of 5.0 with an alum dose of 5 g/l. The effectiveness of coagulation process was investigated for the treatment of agri- based pulp and paper mill wastewater (pH = 7.23, COD = 460 mg/l, TOC = 123 mg/l) in the presence of $FeCl_3$ and alum coagulants[6]. The addition of $FeCl_3$ showed an overall reduction of 65 % in COD and

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97 % in color at an optimum dose of 200 mg/l though lower reductions in COD and color (58 % and 51 %, respectively) were observed after alum addition.

Most of the previous reported work was aimed to treat the composite wastewater generated from pulp and paper mill without emphasizing on a specific waste stream. Besides, acid precipitation process is not used by many researchers.

Therefore, the aim of the present study was to demonstrate the effectiveness of coagulation and acid precipitation processes for the treatment of the synthetic wastewater similar to the effluent generated from the pulping section (having large amount of lignin) of a pulp and paper mill. Three iron and aluminum based coagulants, namely $FeCl_3$, $FeSO_4$ and PAC, were used for the treatment. The effectiveness of the coagulants was adjudged by determining COD and color reductions. In addition, COD and color removals from the wastewater due to acid precipitation (lowering the pH by adding H_2SO_4) were noted. The settling characteristics of the sludge were also determined for the coagulants showed good efficiency. A cost comparison of different treatment options was also done taking chemical costs into account. The applicability of pinch analysis in the treated water reuse/recycle scenarios is also discussed.

Materials And Methods:

Materials

Pulp and paper mill wastewater was synthetically prepared in the laboratory. Alkali lignin was used as the model compound for lignin. Ammonium chloride, sodium phosphate monobasic anhydrous and sodium sulphide were added in the wastewater as a source of nitrogen, phosphorus and sulphides, respectively. In addition, phenol was also used as another organic compound present in the wastewater. All the chemicals were dissolved in tap water and the resulting mixture was used for the treatment study after characterization.

The details related to the wastewater constituents and various coagulants (like purity and purpose) are summarized in Table 1.

TABLE - 1

DETAILS OF THE CONSTITUENTS USED TO PREPARE THE WASTEWATER

Chemical used	Purpose	Purity	Vendor
Lignin alkali, with low sulfonate content	As lignin compound	_	Sigma Aldrich
Sodium phosphate monobasic anhydrous	For phosphorus	Extra pure analytical grade	Sisco Research Laboratory
Ammonium chloride	For nitrogen	?99%	Merck
Phenol	To represent phenolic compounds	?99%	Merck
Sodium sulphide	Sulphides	_	Merck
Ferric chloride	Coagulant	98%	Qualigens fine chemicals
Ferrous sulphate	Coagulant	99%	Merck
Polyaluminum chloride	Coagulant	_	_
Sulfuric acid	For acid precipitation	98%	Merck

Experimental Methods

Coagulation studies

Coagulation was performed using a jar test apparatus (Cintex Floculatior, Cintex Industrial Corporation, Mumbai). Typically, 250 ml of wastewater was taken in 500 ml beaker and pre-determined quantity of the coagulant or H_2SO_4 (for acid precipitation process) was mixed with the wastewater. Then, the beaker contents were agitated rapidly at 120 rpm stirrer speed for 30 seconds and then slowly at a stirrer speed of 20 rpm for another 15 minutes. The sludge formed was then allowed to settle for 30 minutes. pH, COD and color of the treated wastewater were determining the efficiency of treatment process.

Analytical methods

COD of the wastewater (before and after treatment) was determined by standard closed reflux method[7] using a COD reactor (Hach, DRB200 COD reactor, USA). pH of the wastewater was measured using Microprocessor pH stat/Analyzer (Polmon, LP-1395, India). Color reduction was calculated from the absorbance data obtained at 363 nm wavelength using UV-vis spectrophotometer (ThermoSpectronic Genesys 20, USA)[5].

To determine the total solids (TS) in the wastewater, 100 ml of the wastewater was taken in a dried beaker and kept for 24 h in an oven at a temperature of 105 ºC for evaporation of water. After attaining the constant mass, the beaker was shifted to the dessicator for cooling before weighing. Total dissolved solids (TDS) in the wastewater (before and after treatment) was measured after filtering the sample through whatman filter paper (pore size = 1.2 µm). The similar oven conditions were used for determining TDS as that for TS. The total suspended solids (TSS) in the wastewater were taken as the difference between TS and TDS.

Results And Discussion:

Composition and characteristics of synthetic wastewater

Synthetic wastewater was produced by mixing various organic and inorganic constituents mentioned in 'Material and Methods' section. The concentration of various constituents and major characteristics of the wastewater are presented in Table 2. The wastewater contained 3000 mg/l alkali lignin and 150 mg/l phenol as organic components. Inorganic salts containing desired amounts of nitrogen, phosphorus and sulphides were also dissolved in the wastewater. The concentrations shown in the Table were decided on the basis of information available in the literature[8-10]. The wastewater analysis results showed the COD and pH of the synthetic wastewater were 4800 mg/l and 8.2 - 8.5, respectively, whereas, TS concentration in the wastewater was found to be 2980 mg/l, out of which around 94 % was in dissolved form.

TABLE - 2
COMPOSITION AND CHARACTERISTICS OF THE WASTEWATER

Materials / Parameters	Values (mg/l)	Reference
Lignin	3000	Jain *et al*[13]
Phenol	150	Raj *et al*[14]
Nitrogen	24	Buzzini and Pires[15]
Phosphorus	4	Buzzini and Pires[15]
Sulphides	10	Buzzini and Pires[15]
COD	4480 – 4800	-
pH*	8.2 – 8.6	-
Total solids (TS)	2979.5	-
Total dissolved solids (TDS)	2789.5	-
Total suspended solids (TSS)	190	-

* pH is a unitless parameter.

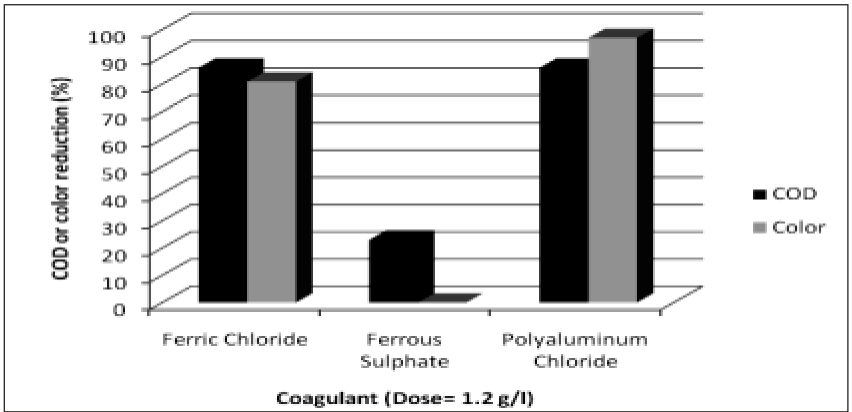

Figure 1 COD And Color Removals Obtained With Different Coagulant (Coagulant Dose = 1.2 g/l, Initial COD = 4800 mg/l)

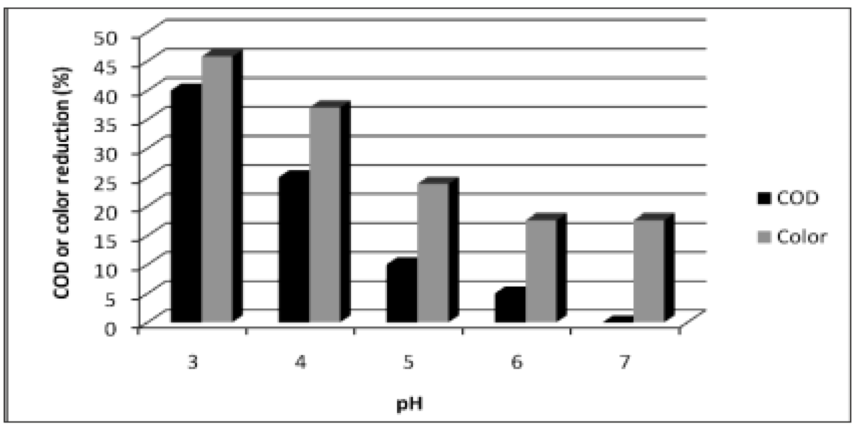

Figure 2 Effect Of pH (Adjusted By Adding H_2SO_4) On COD And Color Removals (Initial COD = 4800 mg/l, Initial pH = 8.37)

pH	Volume of acid used (ml)	Final COD (mg/l)
3	0.57	2880
4	0.38	3600
5	0.23	4320
6	0.17	4560
7	0.13	4800

Table - 3 The Amount of Acid (10% H_2SO_4) Used For pH Reduction (Initial COD = 4800 mg/l, Initial pH = 8.37)

Effect of different coagulants on COD and color of the wastewater

The coagulation study with different coagulants was conducted with a dose of 1.2 g/l. From the results (Figure 1), it was found that PAC and $FeCl_3$ were equally effective for COD reduction (~ 86 %, Final COD ~ 700 mg/l) though the maximum color reduction was obtained (~97 %) with PAC. The addition of $FeCl_3$ showed a color reduction of 81%. Treatment of wastewater with $FeSO_4$ could reduce COD by only 23 % without having any change in original color of the wastewater. The final pH values of $FeCl_3$, $FeSO_4$ and PAC treated wastewaters were dropped to 3.11, 4.92 and 4.49 (in acidic range), respectively.

Effect of acid addition on COD and color removal

The effect of pH on the COD and color removals from the synthetic wastewater was also studied. The pH of the wastewater was adjusted in the range of 3 - 7 by the addition of 10 % H_2SO_4 (v/v) solution. It can be seen from Figure 2 that COD and color removals were continuously increased with drop in pH of the wastewater with the exception of pH 7.0. At this pH, no COD reduction could be found though around 15 % color removal was observed. The physical appearance and absorbance data confirmed the change in color at this pH. With the drop in pH from 7.0 to 5.0, COD was reduced by only 20 % from its initial value of 4800 mg/l and color removal was less than 10 % of the color of the wastewater at pH of 7.0. By further drop in pH to 4.0, overall COD and color reductions were found to be around 25 % and 35 %, respectively. Furthermore, total COD and color reductions enhanced to 40 % and 45.8 %, as the pH was reduced to 3.0. The reductions in these parameters were clearly much lesser than that obtained with the addition of PAC and $FeCl_3$ coagulants. The volume of acid required per unit of pH drop increased as it shifted towards more acidic region (i.e., 7.0 to 3.0) (Table 3). For instance, the volume of acid required to drop the pH by one unit from 7 to 6 was 0.04 ml in comparison to 0.06 ml for pH reduction to 5.0 from a pH value of 6.0.

Settling Characteristics

The uniform suspensions obtained after the treatment with $FeCl_3$ and PAC coagulants were used to study the settling characteristics of the sludge. Since only poor or almost no floc formation was observed with addition of $FeSO_4$ and H_2SO_4 (during acid precipitation) the settling patterns of the treated wastewaters with these chemicals were not recorded.

The settling test was done using a 1000 ml graduated glass cylinder. For both PAC and $FeCl_3$, the slurry was mixed slowly for preparing uniform suspensions before pouring it into the glass cylinder. The suspensions were then allowed to remain in undisturbed position. The height of the interface between clear supernatant and the solids was noted as a function of time. The settling curves thus obtained are illustrated in Figure 3.

On the basis of curves shown in the Figure, this can be suggested that $FeCl_3$ treated wastewater showed slightly better settling than PAC treated suspension. The settled sludge was also found to be more compact for $FeCl_3$ treated suspension. Total settled sludge volumes for $FeCl_3$ and PAC treated wastewaters were 150 ml and 205 ml, respectively (Initial total volume = 500 ml).

Both the curves followed the similar pattern and can be divided into three zones: hindered zone (fast settling), transition zone and the compression zone (slower settling). It is evident from the Figure 3, the hindered settling zone lasted in about 700 minutes, followed by transition zone for next 700 minutes. The consolidation of the sludge occurred for much longer duration (~ 1900 minutes) in the compression zone.

For both these suspensions, TDS in the wastewater were also determined. It was found that the addition of PAC reduced TDS by 61 % (Final TDS = 1086 mg/l) whereas with $FeCl_3$, an overall TDS reduction of 45.11 % (Final TDS = 1531 mg/l) could be achieved.

Cost comparison

The comparison of the costs of wastewater treatment using three coagulants and H_2SO_4 is presented in Table 4. For determining the economics of each option, only the market prices of the chemicals (at the optimum COD reduction) were taken into account. The analysis revealed that among three coagulants, PAC use in the reaction exhibited the highest cost (Rs. 7.20 /- per kg of COD removed) whereas using $FeSO_4$ as coagulant incurred the least cost (Rs. 4.80 /- per kg of COD removed). However, the COD removal with $FeSO_4$ was significantly lower than the other two coagulants (PAC and $FeCl_3$). By increasing higher $FeSO_4$ dose for achieving better removal, the sludge quantities will be increased and the sludge disposal costs will be high. Therefore, it cannot be chosen as the best coagulant for COD reduction. The COD removal from $FeCl_3$ was seen to be slightly lower than that with PAC but the cost was lesser (Rs. 5.3/- per kg of COD removed; 0.74 times the cost with PAC). Hence, $FeCl_3$ can be suggested as the most preferred option for the treatment of wastewater by coagulation process. Acid-precipitation with H_2SO_4 showed the least cost per kg of COD removal (only Rs. 2.2/ kg COD removed). Nevertheless, the pH of the treated water was reduced to 3.0 for achieving 38– 40 % COD reduction that can cause problems with sludge disposal due to its corrosive nature and thus cannot be considered as the best option.

TABLE - 4 COMPARISION OF TREATMENT COSTS

	$FeCl_3$	$FeSO_4$	PAC	H_2SO_4
Unit Cost (Rs/kg)	18	4	25	18.4*
Coagulant/ acid used (mg)	300	300	300	0.57 **
COD removed (mg/l)	4100	1000	4150	1920
Approximate Cost per kg of COD removed (Rs/kg)	5.3	4.8	7.2	2.2

*Rs/l (for 98%), **ml (of 10%)

Water Pinch Analysis:

Due to ever increasing water demands and the increasing stress in the water bodies, the recycling/ reusing of water has become very necessary. In addition to that, there is an urgent need to reduce the wastewater discharge into the water bodies due to the environmental regulations. Therefore, the recycling/ reusing of the water after treatment has become very important in the process industries.

Water pinch analysis (WPA) is a systematic technique which deals with the reduction of freshwater consumption and wastewater generation through integration of various water-using processes. WPA deals with two main issues: optimum allocation of reusable water to minimize the freshwater requirement, and optimal treatment of wastewater generated to meet the environmental regulations[11]. Traditionally, the mills used to use freshwater to satisfy water needs. However, due to depleting water sources, most of the mills are looking for maximizing reuse/recycle of the wastewater within the plant. A typical WPA solution is divided into two parts: setting the targets for minimum wastewater and freshwater as well as

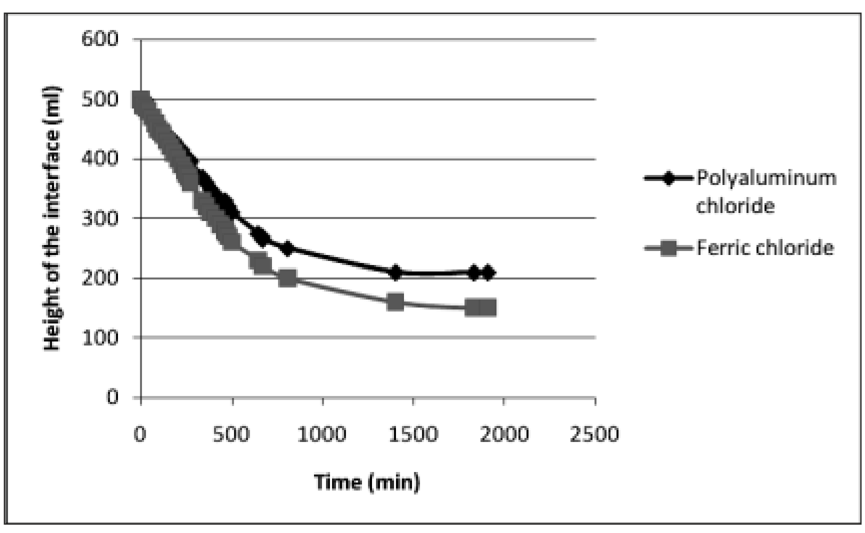

Figure 3 Comparison Of Settling Curves For $FeCl_3$ And Pac Treated Suspensions

the design of the water allocation network according to the targets that were set. If there are several water-using processes in an industry, a network of interconnections is determined such that the overall freshwater consumption is minimized and the unit processes receive water of desired quality. There are two main types of operations in a process plant: fixed contaminant load (example: washing process) and fixed flow rate (example: cooling tower or boiler).

WPA was first introduced by Wang and Smith[12]. They initiated the water pinch technique as a generalized problem of mass exchange network synthesis. They explored reuse, regeneration-reuse and regeneration-recycle opportunities. The limited composite curve was introduced to locate the minimum fresh water and wastewater flow rates prior to the detailed water network design. In this approach, the water using processes were modeled as mass transfer operations with fixed contaminant loads. However, this might not be always sufficient. There are some processes like cooling tower make up and reactor effluent where the water quantity is more important than the contaminant load. Water surplus diagram was developed for targeting minimum freshwater consumption and wastewater generation[13]. This process overcomes the problems in mass transfer based approach. However, this process involves a lot of tedious iterations through graphical drawings. Tan *et al*.[14] came up with a numerical approach called the water cascade table (WCT). Bandyopadhyay *et al*.[15] proposed a novel source composite curve to minimize freshwater and wastewater requirements considering the environmental norm for discharge. Bandyopadhyay and Cormos[8] extended the source composite curve approach with regeneration and recycle while satisfying the environmental norms. WAP technique may be applied to optimize the total water system in a paper and pulp mill.

Conclusions:

The synthetic wastewater from pulp and paper wastewater was treated by coagulation (using $FeCl_3$, $FeSO_4$ and PAC) and acid precipitation (using H_2SO_4) processes. It could be seen from the results that $FeCl_3$ and PAC showed similar COD reductions (~ 86 %) at a dose of 1.2 g/l while the PAC showed greater reduction in color (97 %) than $FeCl_3$ (81 %). Use of $FeCl_3$ exhibited slightly better settling than PAC treated wastewater. The COD reduction shown by $FeSO_4$ was much less (23 %) than that with $FeCl_3$ and PAC at the same dose and there was no apparent color reduction. Adjustment of pH of the wastewater using H_2SO_4 to 3.0 reduced the COD and color by 40 % and 45.8 %, respectively. The economic analysis made on the basis of market price of chemicals added for coagulation or precipitation showed that the treatment with H_2SO_4 was the most cost effective option but can not be suggested as the best option due to insufficient COD removal and corrosive nature of treated water and sludge. $FeCl_3$ has been suggested as the best option due to its low cost and effective COD reduction. Water pinch analysis can be applied for reuse/ recycle of the treated water to find out the minimum freshwater requirement and the minimum amount of wastewater for disposal. Future research work will investigate the efficacy of adsorption process as a post treatment step for the removal of residual COD and color. In addition, identification of different water reuse/recycle scenarios for treated water using source composite curve (WPA) is also proposed for future studies.

Acknowledgment:

To carry out the reported research work, the financial support from Department of Science and Technology (DST), New Delhi under 'Fast Track Scheme for Young Scientists' is acknowledged.

Literature Cited:

1 CPCB (Central Pollution Control Board), "Development of guidelines for water conservation in pulp and paper sector", 2006.
2 Stephenson, R.J. and Duff, S. J., *Water Research* **30** (1996)781-792.
3 Chen, W. and Horan, N.J., *Environmental Technology* **19** (1998)173-182.
4 Ahmad, A.L., Wong, S.S., Teng T.T., and Zuhairi, A., *Chemical Engineering Journal* **137** (2008)510-517.
5 Garg, A., Mishra, I.M. and Chand, S., *Journal of Hazardous Materials* **180** (2010)158-164.
6 Yadav, B.R. and Garg, A., *IPPTA*, 2010. (Accepted for publication)
7 APHA (American Public Health Association), "Standard Methods for the Examination of Water and Wastewater",20th Ed. 2005.
8 Jain, R.K., Dixit, A.K., Janbade.V.A. and Mathur, R.M., *Indian Pulp and Paper Technical Association* **21** (2009)169-173.
9 Raj, A., Reddy, M.M.K., and Chandra, R., *Journal of Chemical Technology and Biotechnology* **82** (2007)399-406.
10 Buzzini, A.P. and Pires, E.C., *Bioresource Technology* **98** (2007)1838-1848.
11 Bandyopadhyay, S. and Cormos, C.C., *Industrial & Engineering Chemistry Research* **47** (2008)1111-1119.
12 Wang, Y.P. and Smith, R., *Chemical Engineering Science* **49** (1994)981-1006.
13 Hallale, N., *Advances in Environmental Research* **6** (2002)377-390.
14 Tan, Y.L., Zainuddin, A.M. and Foo, C.Y., *9th Asian Pacific Confederation of Chemical Engineering (APCChe 2002) Congress*, 2002.
15 Bandyopadhyay, S., Ghanekar, M.D., and Pillai, H.K., *Industrial & Engineering Chemistry Research* **45** (2006)5287-5297.