Poll Res. 40 (May Suppl. Issue) : S250-S256 (2021)

ISSN 0257–8050

DEINKING OF OLD USED PAPERS USING CRUDE RHAMNOLIPID BIOSURFACTANT

ASHUTOSH MISHRA[1] AND RAKESH KUMAR TRIVEDI[2*]

[1]*Department of Chemical Engineering, Dr. Ambedkar Institute of Technology for Handicapped, Kanpur 208 024, (U.P.) India*
[2]*Department of Oil Technology, Harcourt Butler Technical University, Kanpur 208 002, (U.P.) India*

(Received 20 October, 2020; accepted 23 December, 2020)

ABSTRACT

Surfactants are having a great role in world chemical industries majorly used in laundry detergents, household, and personal care products along with pharmaceuticals. Apart from this surfactants have special use in the pulp and paper industry for the deinking process that makes new paper from the old paper. Generally, anionic synthetic surfactants are using for this purpose. As the synthetic surfactants are non-biodegradable and non-eco-friendly, this study was conducted by replacing these surfactants with the rhamnolipid biosurfactant, which was manufactured in the laboratory with the help of *Pseudomonas aeruginosa* MTCC 424 using residual oil from vegetable oil processing industry. After manufacturing the new hand sheet, the brightness % and the ash content were checked. The brightness efficiency and ash content were found 58 percent and 8.97 percent, respectively. The optimum concentration of the crude rhamnolipid biosurfactant of concentration 0.9 g/L was used 0.12 percent at pH 9.

KEY WORDS : Rhamnolipid biosurfactant, *Pseudomonas aeruginosa*, Brightness efficiency, Ash content, Pulp consistency

INTRODUCTION

Surfactants have a vital role in the field of chemical technology. These have major applications in the field of agriculture such as pesticides, herbicides, insecticides, sanitizers, spermicides (nonoxynol-9), and fungicides. Surfactants also have versatile applications in food processing, pharmaceutical, oil, and paint and as well as for industrial and home cleaning solutions (Borchardt, 2003; Bruhn, 2009). These also include applications as emulsifiers, foaming agents or wetting agents for lowering surface tension and interfacial tension. Surfactants are widely used for cleaning, dispersing agents, soaps, adhesives, various detergents, wax related products, paints, softeners, emulsifiers, inks, anti-fogging agents, fabric washing, anti-foaming agent, etc. These also have major applications for personal care and household products like shampoos, shower gel, hair conditioner, and toothpaste, etc (Miranda *et al.*, 2010). For industrial or household safety, surfactants play a vital role such as fire fighting agents and in pipelines as liquid drag-reducing agents. In oil exploration wells, alkali surfactant polymers are used to mobilize oil. Surfactants are also used in plastic industries as plasticizer for making nanocellulose, ferrofluids, and leak detectors. In the current research, surfactants are used with quantum dots for identifying the electrical properties and reactions on their surface which is required for the growth and assembly of dots. Therefore, the mechanism of surfactant arrangement on the quantum dots surface and deinking of recycled papers is required to understand the process. Previously synthetic surfactants are in a wide range application due to their low cost and they can be easy to synthesize the synthetic surfactants in the industries. If the biodegradability of synthetic surfactants is considered, it harms the environment and human health as well. Therefore, with the help of biosurfactants we overcome this problem of environmental issues as well as toxicity towards living organism. In this study we conclude the wide application of biosurfactnat for the deinking of old used papers for recycling as well as for environmental issues related to the paper industry (Allix *et al.*, 2010; Wasserman *et al.*, 1965). Generally inkjets and flexographic water-based inks are difficult to deink. A column flotation cell is designed for the deinking of used paper without the addition of an agitator (Chaiarrekij *et al.*, 2001). The formulated design method is capable of significant savings of electrical energy, capital costs, and maintenance costs which ultimately benefits the environment.

Cellulose is used in place of conventional chemicals for deinking of old used papers (Pelach *et al.*, 2003). In enzymatic treatments the enzyme efficacy is improved with particular consistency and repulping time which is analyzed with shear factor. The office recovered papers were recycled for removing the ink using biological deinking technology with cellulase and resinase enzymes (Viesturs *et al.*, 1999). The enzyme treatment with acidic pH reduces the ink particle size and enhances ink removal effectiveness as compared to alkaline pH. The addition of hydrocarbon oil surfactant eliminates the darkness of pulp and improves the cleanliness of paper. The mechanism of cellulase enzyme for removing the ink particles using biodeinking technology is explicitly explained (Vyas *et al.*, 2003; Lee *et al.* 2007). The Anionic surfactants are generally using for removing the black toner ink from laser-printed paper nowadays. The foam is generated due to the addition of surfactants which tend to decrease surface tension. The efficacy of deinking affects with flotation time, pH and, quantity of fatty acid soap. The problem continues with association of pigments, inks and other paper grade quality. As per the literature of recycling, the surfactants are broadly classified into three stages (Abraha *et al.*, 2019; Allix *et al.* 2008; Zhao *et al.*, 2004). In the first stage, the ink particles are detached from fiber which is dispersed in the system and restricts them to re-deposit on the further deinking process. For the second stage, the ink particles are agglomerated with the case of the surfactant. In this stage, hydrophobicity plays an important role which later absorbs on paper fiber. The surface of fiber is changed from hydrophilic to more hydrophobic. In the third stage the hydrophobic end is attached to the surface during the processing of the flotation stage for achieving the higher yield. Current research emphasizes simple, cheap, biodegradable, and effective recycling of used paper.

MATERIALS AND METHODS

Materials

e The following conventional chemicals were used in this study.

i. Lemon Juice
ii. Baking Soda(1N)
iii. Sodium silicate
iv. Crude rhamnolipid Surfactant
v. C.B.S.X.
vi. Polyethylene Glycol

Methods

The pulping is the first stage of deinking process in which the printed used papers were dispersed in water to release ink and fiber particles. In this research, the conventional process was replaced by the natural process for releasing the ink. The natural lemon juice and baking soda were used in place of toxic chemicals like hydrogen peroxide and crude rhamnolipid biosurfactant was used in place of synthetic surfactant.

Making the oven-dried pulp:

For making the pulp following materials were used

25 % old magazine papers (Cricket Samrat)

25% used newspapers (Times of India)

25% used handwritten copies by students (Classmate brand)

25 % recovered computer printout

For the process of this research, all the materials were well crushed and then soaked overnight in the bucket of distilled water for proper disintegration. Samsung mixer (501 - 750 watts) was used for disintegrating the particles. Then these particles were passed through the centrifuge for dewatering and dewatered material again well mixed into very fine pulp which was dried at room temperature. For the determination of air-dried pulp, consistency of the pulp was calculated using 250g oven-dried pulp. Pulp consistency is expressed as percentage which is defined as follows:

$$\frac{\text{Dry weight of pulp fibers}}{\text{Weight of the suspension}}$$

As the pulping consistency increases, the deinking efficiency decreases. For1-2% of the pulp consistency, the maximum efficacy of deinking was observed.

To find the consistency, a small amount of air-dried pulp is taken, weighed (X) and mixed with water in a small beaker, and suction filtered through a previously weighed filter paper (F). The weighed filter paper with the filtrate was dried in a rapid drier and again weighed (Y).

Consistency (C) = $\frac{X-Y}{X}$ 100

Weight of air-dried pulp needed to get 250 g oven dried pulp = $\frac{250X100}{C}$

PULPING

For calculating 250g oven dried pulp, the weight of air dried pulp was required. Water was added in 90 percent of the total weight of the pulp. In every set of experiments, the amount of water and the weight of pulp were varied according to the batch of raw material or recovered paper used. The oven-dried pulp was assorted properly with sufficient amount of water and kept in a water bath at 60 °C for 30 minutes. After this time, the chemicals were added to the pulp and the pH was measured. Then the mixture was kept in a water bath for another 30 minutes and the resultant pH was measured after one hour at 60 °C.

Floatation: After pulping, the pulp was diluted to 1% consistency to achieve higher microfilament yield and pulp was further transferred to a flotation machine, which could be a mechanical flotation cell or a flotation column. Laboratory flotation cell (as per developed in the lab Fig.1.) was used for the current study to achieve higher consistency.

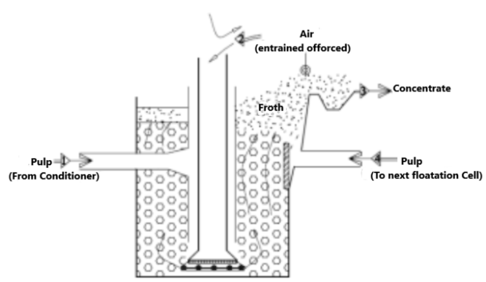


Fig. 1. Floatation cell

After flotation the froth was scraped off and the distilled water was used for washing of deinked pulp. The deinked pulp was dried and for testing it was converted to hand sheets from the pulp. The brightness was measured using brightness tester (Model PCE-WNM 100) made by PCE instruments and ash content was calculated through Muffle furnace.

Making the brightness sheet

The brightness of the initial pulp, the pulp after pulping, and deinked pulp could be found out by making the brightness sheet/ hand sheets of the respective pulp. The Technical Association of the Pulp and Paper Industry (TAPPI), TAPPI Test Method T218om91 (Buchner Funnel Procedure) provided the technique by which the hardness sheets were prepared.

RESULTS AND DISCUSSION

The current study was performed to achieve better deinking of used paper as well as to achieve higher consistency in the floatation phase. The effect of water based ink for different values of pH is given in Table 1.

Table 1: Effect of pH on removal of ink

The alkaline medium generates dark colored froth (Fig. 2a),whereas the acidic medium generates lighter color froth (Fig. 2b). The study establishes the fact that alkaline medium has the ability to agglomerate the ink particles while medium forces ink particles to disperse. The color difference is monitored for the pH values of 6 and 10 which are acidic and alkaline regions respectively.

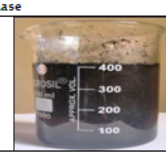
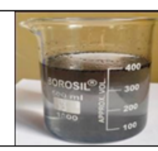
Water based ink	Water based ink (pH 9-10)	Water based ink (pH 6-7)
Froth		
	Fig 2.a. Dark colored foam	Fig 2.b. Light colored foam
After deinking	Rear phase + sedimentation of agglomerated particles in dense phase	Continuous phase ink
		

Fig. 2(a) and Fig. 2(b) show the agglomerated ink particles after flotation by application of alkaline and acidic medium, respectively. The difference in the colors of two froths is visible.

Various important surface characteristics has been shown by the FTIR spectra of rhamnolipid biosurfactant treated pulp. The rhamnolipid treated pulp is in good agreement with the previous studied literature. The –OH stretching corresponding to hydrogen bonding is depicted by the band at 3477.92 cm^{-1}. The streaching can be attributed to increase cellulase content of the pulp. The band at 3041.24 cm^{-1} corresponds to asymmetric

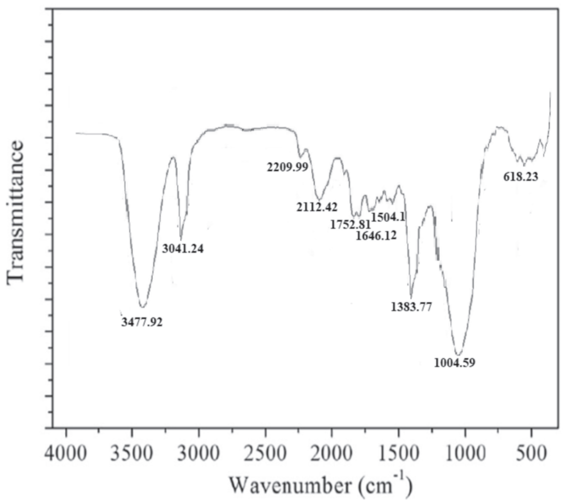


Fig 3. FTIR spectra of Rhamnolipid Biosurfactant treated pulp

–CH vibrations of CH, CH_2, CH_3. The band at 1752.81 cm^{-1} was assigned to vibrations of C = O stretching in ester, COOH, β-C= O indicating the enrichment of spent lignin in functional groups after rhamnolipid treatment . This variation can be due to the aliphatic chain degradation. The band at 1646.12 cm^{-1} can be attributed to C=O stretching of carbonyl groups, due to bio surfactant action on aromatic ring of lignin. The sharp band at 1504.01 cm^{-1} can be attributed to $–CH_3$ stretching combined with skeletal aromatic vibrations with deformation in the plane, which shows that some $O–CH_3$ has been removed during rhamnolipid treatment. The band at 1383.77 cm^{-1} has been assigned to C–H aliphatic stretching in phen–OH and CH_3. Appearance of band at 1004.59 can be attributed to syringyl groups degradation.

Distribution of detached ink before floatation is presented in Fig 4.a the diameter of the ink was measured by using dot analyzer (Beta Breye Braille Dot Print Ananyzer by Beta Screen Corporation). Majority o the detached ink has been reported less than 10 µm. With the decrement in the ink diameter, there observed a rapid increase in number of ink. Furthermore, the Fig. 4.b suggests that number of inks lesser than 3 µm might be larger than the reported value. If the growth of bubble goes along with surfacing, the ink removal might get effected. So, the distribution of bubbles starting from the lower position to upper position was measure. It was observed that in pulp slurry, same even distribution at upper and lower position and less growth of bubbles was occurred. The result might be attributed to the retardation of bubble growth in presence of pulp.

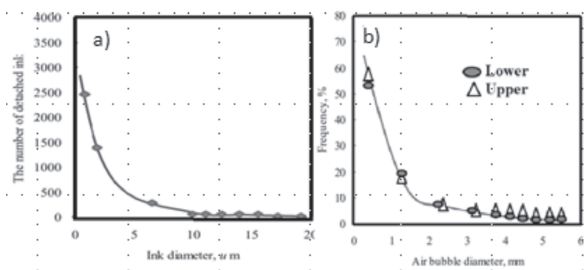


Fig. 4(a). Size distribution of detached ink before floatation**; (b)** distribution of bubbles at different positions in pulp slurry

Fig. 5 shows the effect of rhamnolipid concentration and brightness percent on the flotation process. Deinking efficiency increases with increasing concentration up to 0.9 g/l. The brightness was 58 using 0.9 g/l of crude rhamnolipid. Since the anionic species of surfactants and the ink particles form a micelle which has the same polarity. The negatively charged particles are strongly favored as compared to alkaline pH range particles by the flotation process. The two adjacent surfaces are interconnected through the bridging mechanism in which the calcium is predominant. As a result, there is a strong bonding between surface functional groups and carboxyl groups which exist on ink particles and collector, respectively. Higher surfactant concentration reduces the floatability but increase the collision frequency. This effect can also

Table 2. Ink removal results using various Deinking solution at different times

Deinking solution	Ink removal					
	20 min	40 min	60 min	80 min	100 min	>120 min
Biosurfactant* (0.12%)	90%	100%	100%	100%	100%	100%
Lemon juice (0.5%)	14%	25%	35%	40%	60%	100%
Baking soda (1N)	100%	100%	100%	100%	100%	100%
Sodium silicate (0.1%)	15%	24%	36%	48%	52%	63%
C.B.S.X. (1%)	10%	12%	14%	14%	14%	14%
PEG (0.08%)	5%	7%	7%	7%	7%	7%

results above CMC for the biosurfactant. Rhamnolipid supported the formation of admicelles on carbon black as well as paper which indicates the carboxylate group and carbon surface strongly interacted. With the help of this phenomenon we resulted in the wider application of soaps in flotation deinking operations.

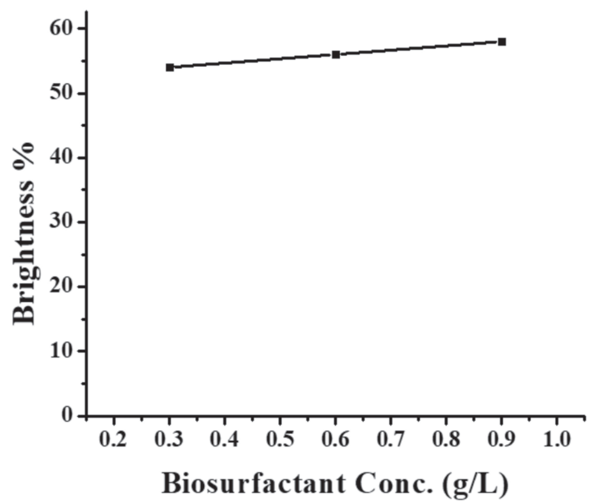


Fig. 5. Effect of Biosurfactant conc. on brightness of the floating product.

Table 2 shows the percentage removal of ink with different time duration for different deinking solutions. The area covered with alkaline agents is immediately cleaned in alkaline medium by adding the drop of surfactant. Crude Rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* is used for this purpose. Acidic agents had lower removal of water-based ink. This research studied the sustainable application of biosurfactant on the recycling of paper during the deinking process.

In the current study we observed the effect of biosurfactant on the removal of ink from pulp. Biosurfactnt having a pH of 6.3 is used which is found to be best. It is observed that Acidic solutions showed poor deinkbility as well as behaves as poor dispersants. However, biosurfactants showed better ability to deink from the pulp surface, but the negative effect shows by scattering the ink particles in the environment. Table 3 shows the effect of deinking for different pH values in the solutions.

Measurement of brightness (%) ISO

As brightness is the prime indicator of the Deinking efficiency. The brightness pads (Fig. 6 and 7) made both from the deinked pulp treated with synthetic surfactant and from the deinked pulp samples treated with crude rhamnolipid biosurfactant were compared for optical property, in order to evaluate the influence of biosurfactants on the deinking of old used papers. The pulp brightness (%) is measured on an ISO brightness color tester according to the TAPPI (Technical Association of Pulp and Paper Industry) standard T452 om 87. Pulp brightness (ISO) is defined as follows:

$$\frac{\text{Radiance of wavelength 457 nm of a paper specimenn}}{\text{Perfect refelcting diffuser}}$$

Magnesium oxide is taken as a perfect reflecting diffuser. Before taking the brightness, one filter paper is peeled off from one side of the brightness sheet. The percentage of brightness is also referred to as brightness index (BI). The brightness is measured with Elrepho' Photo-electric reflectance photometer. At different places of the sheet prepared, the brightness is measured and the values are calculated as the mean of all (TAPPIT 452 om 92). The digital value presented the percentage value of the brightness of the sheet prepared. Table 4 shows the brightness and dirt count for different deinking agents.

Fig. 6. Handsheets made from synthetic surfactant

Fig. 7. Handsheets made from Rhamnolipid Biosurfactant

Table 3. Effect of deinking for different pH values in the solutions

Deinking solutions	pH	Observations
Surfactant*	6.3	Good for deinking but No. agglomeration
Lemon Juice	3	Good for deinking but No. agglomeration
Baking Soda (IN)	11	Good for deinking but No. agglomeration
Sodium silicate	9	Good for deinking but No. agglomeration
C.B.S.X. & Polyethylene Glycol	2-4	No ink detachment/Good ink agglomeration

Table 4. Brightness (%) and dirt count (ppm) for different deinking agents

Deinking Agent	Handsheet	
	Brightness %	Dirt Count (ppm)
Biosurfactant*	67	50
Baking Soda (1N)	38	98
Sodium silicate	34	107
C.B.S.X.	25	227
Polyethylene Glycol	16	243

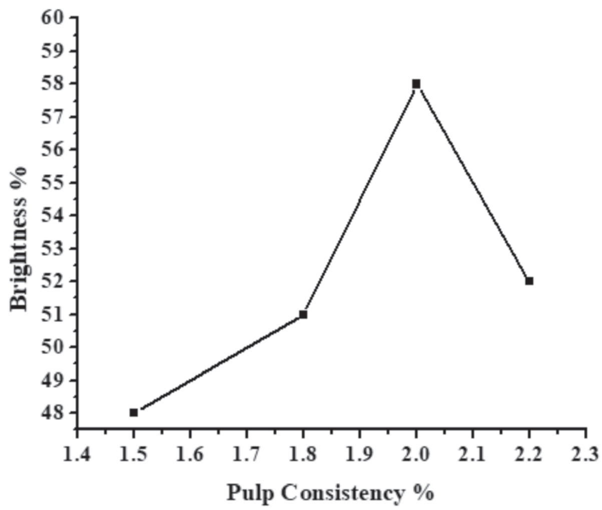


Fig. 8. Effect of Pulp Consistency on brightness.

Fig. 8. shows the effect of the consistency of paper pulp with biosurfactants in the stage of pulping. A brightness of 58% was obtained with 0.9 g/L of rhamnolipid biosurfactants. The brightness is almost constant with pulping consistency up to 2% and then decreased.

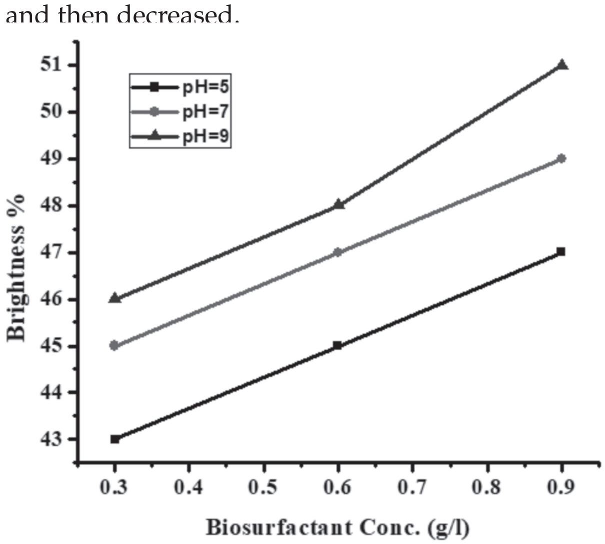


Fig. 9. Effect of Biosurfactant conc. and pH on brightness of 13% pulp.

Fig. 9. shows the effect of biosurfactant concentration and pH on the brightness of paper pulp. The higher brightness is achieved by with increasing the concentration of biosurfactant. The maximum brightness is obtained at 0.9 g/L for crude rhamnolipid biosurfactant. The brightness increases with increasing pH up to 9, which means a higher alkaline medium is to be maintained. Alkalinity enables the swelling of the fibers which results in easy removal of printing ink by the effect of breaking the bond between fibers and print. It also supported increasing final brightness and hydrolysed ester groups in print particle networks.

Ash content Mesurement (%)

Ash content calculation is another very important parameter to know deinking efficiency. Ash content is obtained by burning the pulps in a Muffle furnace(Make : Nabertherm, Model : L3/12) according to TAPPI standards. Both initial and deinked pulps in a quantity of 100 ml are taken for this measurement. The brightness pads and consistency sheets are prepared similarly to the previous method. Empty and pulp containing the weight of crucibles are measured and then put in a desiccators. The ready consistency pads are positioned in every crucible and kept in the furnace for 45minutes (the set temperature for ashing was around 600 ^{o}C). After ashing, weights of the crucibles are measured and the ash present is calculated in percentage by the formula, weight of ash/ weight of oven dried pulp×100. Fig.10. describes the effect of biosurfactant concentration on brightness and ash content of pulp.

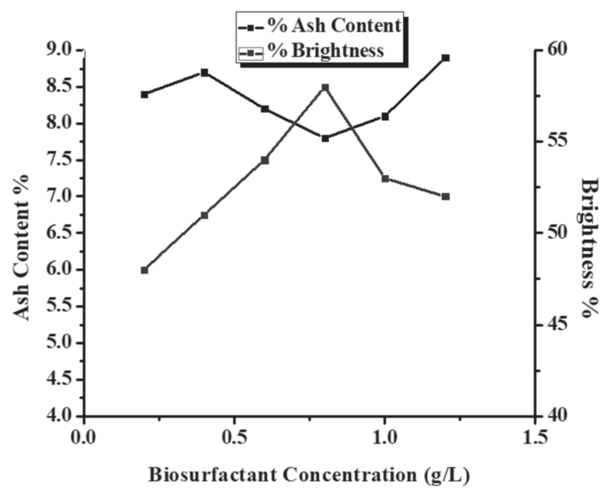


Fig. 10. Effect of Biosurfactant conc. on brightness and ash content of pulp.

CONCLUSION

Optimization of the most efficient biosurfactant concentration

The optimum concentration of rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* MTCC 424 preparing using residual rice bran oil as a sole substrate for the deinking of old used papers is found to be 0.9g/l. A decrease in the percentage of brightness is observed with an increase in biosurfactant concentration. The percentage of ash is also found to be lowest when 0.9 g/l of biosurfactant is added to the pulp before deinking.

ACKNOWLEDGEMENTS

We are thankful for M/S- Bajaj Kagaj Limited Unnao for providing us guidance and laboratory facilities for this research. We are also grateful to Indian Institute of Technology Kanpur and for facilitating laboratories.

REFERENCES

Abraha, M. and Kifle, Z. 2019. Deinking of Black Toner Ink from Laser Printed Paper by Using Anionic Surfactant. *Biomol. Eng.* 4 (1) : 23-30.

Allix, J., Beneventi, D., Carré, B., Nortier, P., Zeno, E. and Angelier, M.C. 2008. Understanding the role of surface active substances in flotation deinking mills by coupling surfactant and ink balance with process simulation *TAPPI J.* 9 : 31.

Allix, J., Beneventi, D., Zeno, E. and Nortier, P. 2010. Flotation de-inking of 50% ONP/50% OMG recovered papers mixtures using nonionic surfactant, soap, and surfactant/soap blends. *Bioresour.* 5 (4) : 2702-27019.

Borchardt, J.K. 2003. Recent developments in paper deinking technology. *Pulp Paper Can* 104 (5) : 32.

Bruhn, C.M. 2009. Understanding' green' consumers. *Food Technol- Chicago.* 63 (7) : 28-35.

Chaiarrekij, S., Gupta, H., Amato, W. and Ramarao, B. 2000. Experimental results in deinking of recycled fibers by column flotation. Faculty of science and engineering, University of New York. 4.

Lee, C., Darah, I. and Ibrahim, C. 2007. Enzymatic deinking of laser printed office waste papers: some governing parameters on deinking efficiency. *Bioresour. Technol.* 98 (8) : 1684-1689.

Miranda, C. R., Bobu, E., Grossmann, H., Stawicki, B. and Blanco, S.Á. 2010. Factors influencing a higher use of recovered paper in the European paper industry. *Cellul. Chem. Technol.* 44 (10) : 419-430.

Pelach, M., Pastor, F., Puig, J., Vilaseca, F. and Mutje, P. 2003. Enzymic deinking of old newspapers with cellulase. *Process Biochem.* 38 (7) : 1063-1067.

Viesturs, U., Leite, M., Eisimonte, M., Eremeeva, T. and Treimanis, A. 1999. Biological deinking technology for the recycling of office waste papers. *Bioresour. Technol.* 67 (3) : 255-265.

Vyas, S. and Lachke, A. 2003. Biodeinking of mixed office waste paper by alkaline active cellulases from alkalotolerant *Fusarium* sp. *Enzyme Microb. Technol.* 32 (2) : 236-245.

Wasserman, A.E. 1965. Absorption and fluorescence of water-soluble pigments produced by four species of Pseudomonas. *Appl. Microbiol.* 13 (2) : 175-180.

Zhao, Y., Deng, Y. and Zhu, J. 2004. Roles of surfactants in flotation deinking. *Prog. Pap. Recycl.* 1 : 41-45.