TONER RECOVERY FROM SUSPENSIONS WITH FIBER AND COMPARATIVE ANALYSIS OF TWO KINETIC MODELS

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Abstract: This paper studies kinetic aspects of toner flotation in a mechanical cell with methyl isobutyl carbinol (MIBC) as a frother by using a synthetic toner sample 212+0 µm in a size at variable pH. The effect of the MIBC dosage and pH value on the flotation behavior of the toner has been investigated in terms of toner recovery and fiber recovery. Two kinetic models, the classical first order model and a modified first order model, have been tested and compared. It was established that the achieved optimal parameters of flotation were MIBC 1.5 mg/dm³ and pH from 7 to 12. The obtained results indicate that the toner floats rapidly and that flotation kinetics fits well the modified first order model with a very good correlation coefficient compared to the correlation coefficient for the classical first order model.

Keywords: toner, flotation rate, toner recovery, fiber recovery, kinetic model

Introduction

For the first time flotation was applied to the separation of mineral ores at the end of 19th century the beginning of 20th century. It became the primary method of recovery for a large variety of minerals (Schmidt, 1996). Today, it is used for recovering different types of metallic and nonmetallic minerals and it has a wide range of applications in a number of areas other than mineral processing. These include technologies such as oil recovery (Ramaswa et al., 2007), waste water treatment (Rubio et al., 2002; Bogdanovic et al., 2013), soil remediation (Dermont et al., 2010), plastic separation (Hui et al., 2012) and deinking - flotation of ink (Jameson, 1998; Trumic et al., 2007; Vashisth et al., 2011).

Flotation is a dynamic process caused by an interaction of forces acting in the bubble-particle-water system (Kowalczuk et al., 2011). In the ink flotation, the air is blown into the fiber suspension creating air bubbles to which the hydrophobic ink particles are attached. The attached particles are carried to the top of the flotation.
vessel, where they are removed as deinking froth (Pan et al., 1996; Rutland and Pugh, 1997). The purpose of the ink flotation process is to separate the hydrophobic ink particles from the hydrophilic fibre by using the differences in their chemical properties (Labidi et al., 2007).

To improve the hydrophobicity of floated particles, it is very common to apply flotation reagents. The laser and photocopy toner particles are hydrophobic and do not need the use of any collector, but a frother must be used in order to obtain a stable foam layer to remove the toner particles (Schmidt, 1996; Zhao et al., 2004). It is shown that the froth stability and the recovery of ink particles are closely related as the ink recovery increases with the increase of froth stability (Bajpai, 2014). Nonionic surfactants are widely applied as frothers in the flotation of ink due to their excellent foamability and they are not sensitive to water hardness (Zhao et al., 2004). The research has shown that the concentration of the nonionic frother should be between 0.1 and 5 mg/dm$^3$ in order to avoid the decrease in the hydrophobicity of the toner particles, as well as to minimize the loss of fibers and fillers in froth (Doriss and Sayegh, 1994).

The recovery of ink particles can be affected by many factors. Generally, all significant factors can be classified in three groups: chemistry (collectors, frothers, activators, depressants, pH), equipment (cell design, agitation, gas flow rate) and operation parameters (feed rate, mineralogy, particle size, pulp density, temperature) (Theander and Pugh, 2004). The way these factors affect recovery is measured in terms of the toner flotation kinetics.

Kinetics is a very important aspect of flotation, and its main purpose is to study the role of the flotation rate constant. The flotation rate is measured by the recovery change of the floating material in the product per unit time and is characterized by the rate constant and the kinetics order (Li et al., 2013). Different functions can be used for delineation of kinetics of flotation. The most widely used is the first order model (Pan et al., 1996; Pelach Serra, 1997; Presta Maso, 2006; Labidi et al., 2007; Shemi, 2008, Allix et al., 2010; Doriss et al., 2011).

Pan et al. (1996) in his research described the flotation kinetics of ink particles under laboratory conditions by the classical model of the first order kinetics using the expressions

$$ln \frac{1}{1-I} = kt \quad (1)$$

$$I = \frac{C_0-C}{C_0} \quad (2)$$

where

$I$- flotation recovery of ink particles in froth product

$t$- flotation time

$k$- kinetic constant of flotation
concentration of particles at \( t=0 \) in sink product
\( c \) - concentration of particles at time \( t \) in sink product.

According to Pan et al. (1996) for a constant bubble flow through the stationary suspension of homogeneous particles and for a short flotation time, the particle flotation process follows the first order kinetics. However, for a longer flotation time, for all particle sizes, a sharp break is observed in the plots (no straight line for a given particle size at the plot of \( \ln \frac{1}{1-I} \) vs. \( t \)). This implies that no single value of the constant \( k \) suffices to express the data. According to Pan the break between the two linear portions of each curve implies that for any given particle size two flotation mechanisms operate: one is a short-time mechanism and the other is a longer-time mechanism.

Generally, many scientists agree that the value of \( k \) can be determined from the expression (1) as long as the flotation time is short and the diameter of the ink particles is constant (Pan et al., 1996; Pelach Serra, 1997; Labidi et al, 2007). In this work, the flotation rate data were subjected to the curve fitting procedure in order to compare two models: the classical first order model and a modified first order model. This was done to determine which model better describes the kinetics of the toner flotation.

**Material and methods**

**Toner**

According to the material safety data sheet (MSDS), the toner inside the cartridge CB435A is mainly composed of a styrene/acrylate copolymer (<55 wt %) with ferrite (<45 wt %) and wax (<10 wt %). Its solubility in water is negligible, and it is partially soluble in toluene and xylene. The material should soften between 100 and 150°C. The density of the toner is 1.5 g/cm\(^3\). The average particle size of toner inside the cartridge is about 10 µm and particles have a spherical shape (Fig.1a). The polymerization of toners during the printing process results in the formation of larger particles (Fig.1b). This process might lead to the chemical bonding between the cellulose fiber and the new large toner particle and/or the physical entrapment of the cellulose fiber within the large toner particle. The toner can be separated from paper fiber in a disintegration process, but particles shapes will be flat or cubic (Nie et al., 1998). The surface roughness and shape of the toner particle have been changed after the printing process, as it can been seen in Fig.1b. In order to obtain a realistic synthetic sample, the toner from the cartridge has been thermally treated in an oven at 90 degrees for 60 minutes, and then it has been ground and screened to obtain three different fractions of different particle sizes. Screens used had 212, 150, 106 micrometers openings. The used toner fractions were -212+150 µm, -50+106 µm -106+0 µm, and their masses were 0.25, 0.25 g, and 0.5 g, respectively. The particle shape is given in Fig.1c.
Fig. 1. Scanning electron microscopy (SEM) photographs of toner from:
a) cartridge, b) laser printed sample and c) synthetic sample; (20 kV, 250x). Samples were coated with
gold

Paper fiber
The paper fiber was prepared by soaking the alkaline copy paper (MAESTRO
standard, A4, 80 g/m², the total filler content 28.8 wt. %) in distilled water for 16
hours and then disintegrated in an overhead stirrer. The operating conditions, during
the disintegration stage, were held constant for all experiments (5% consistency, 45
°C, 400-900 rpm agitation speed, 120 min, pH 8).

Flotation
After the disintegration, toner was added to the paper fiber to obtain the suspension for
flotation experiments. Flotation was carried out in a 2.2 dm³ laboratory flotation cell
(Denver D12). The operating conditions of the flotation stage were held constant for
all experiments (1100 rpm agitation speed, 270 dm³/h air flow rate). The frother MIBC
(methyl isobutyl carbinol) was added during the conditioning stage. The condition
time was 10 min, and the MIBC dosage varied from 0.5, 1.5, 3 to 6 mg/dm³ to find the
optimum concentration. The pH value of the suspension was varied from highly acidic
(pH 3) to highly alkaline (pH 12). The pH was maintained by sodium hydroxide and
hydrochloric acid during the flotation. Deionized water was used in flotation. The
samples were extracted from the froth at 1, 2, 4, 6 and 10 min to study the kinetics during the flotation process. Subsequently, the float (toner particles in froth) and nonfloat (cellulose fiber in suspension) products were carefully filtered through a Buchner funnel, then dried at the room temperature and weighed to determine the fiber recovery.

The dried froth filter pads were then heated at 550 °C in a muffle furnace to determine the ash content. At this temperature, the calcination of calcium carbonate present in the alkaline paper was negligible. The ash was analyzed for iron by x-ray fluorescence (XRF). With toners of high iron oxide content, the percentage of iron in the froth allowed a reasonably good assessment of the toner content in the froth (Dorris and Sayegh, 1994; Li et al., 2011).

**Results and discussion**

It is apparent that a high recovery of toner (I) in the froth and a high recovery of fiber (Y) in the sink product are two important requirements (Huber et al., 2011). From economic and environmental points of view, the flotation process has to be optimized in terms of both high ink recovery and high fiber recovery and for the analysis of such results it is convenient to use the Fuerstenau plot (Bakalarz and Drzymala, 2013). The values of the ink and fiber recoveries, being also efficiency indicators, should be around 90 % (Suss et al., 1994). Many factors have an influence on these indicator value. The stability of the foam is one of the most important factor. The stable foam layer must be obtained for a high toner removal, but on the other hand, it causes high fiber losses, so it is necessary to determine the optimal frother concentration (Dorris and Sayegh, 1994; Deng and Abazeri, 1998).

Table 1 shows the values of the fiber and toner flotation recovery values obtained experimentally in the laboratory flotation tests.

<table>
<thead>
<tr>
<th>pH</th>
<th>MIBC Dosage, mg/dm³</th>
<th>0.5</th>
<th>1.5</th>
<th>3</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I, %</td>
<td>Y, %</td>
<td>I, %</td>
<td>Y, %</td>
<td>I, %</td>
</tr>
<tr>
<td>3</td>
<td>60.10</td>
<td>95.45</td>
<td>79.31</td>
<td>90.64</td>
<td>81.35</td>
</tr>
<tr>
<td>5</td>
<td>76.70</td>
<td>93.86</td>
<td>84.51</td>
<td>92.23</td>
<td>87.68</td>
</tr>
<tr>
<td>7</td>
<td>82.69</td>
<td>92.36</td>
<td>92.09</td>
<td>91.23</td>
<td>89.91</td>
</tr>
<tr>
<td>9</td>
<td>85.38</td>
<td>93.55</td>
<td>96.33</td>
<td>93.77</td>
<td>95.34</td>
</tr>
<tr>
<td>12</td>
<td>84.41</td>
<td>92.77</td>
<td>94.27</td>
<td>88.27</td>
<td>90.73</td>
</tr>
</tbody>
</table>

It can be seen from Table 1 that a high recovery of fiber of over 90 % was achieved at MIBC dosages of 0.5, 1.5 and 3 mg/dm³, under all pH conditions. Under neutral and highly alkaline conditions (pH 7, 9 and 12), with increasing dosages of MIBC from 3
to 6 mg/dm$^3$, there was a fiber loss, i.e. fiber recovery reduction of about 22, 16, 20\%, respectively. During the experiments, by the visual analysis of froth, it was observed that there was a physical entrapment of fiber in the bubble network of the foam due to the formation of a high stable foam layer (Fig.2). Many authors have postulated that the fiber loss in toner flotation depends not only on the fiber surface chemistry, but also strongly depends on the froth stability, froth structure and fiber geometry. Experimental results suggest that both true flotation and physical entrainment contribute to the total fiber loss, but the physical entrainment is the dominating factor. Thus, the fiber loss in flotation can be controlled by varying the froth height (Ajersch, 1997; Deng and Abazeri, 1998; Luo et al., 2003; Huber et al., 2011). An effective surfactant for toner particles flotation should be used, and the foam should be controlled in a way that does not affect the toner removal but in can reduce the fiber entrapment. It is an imperative to control toner hydrophobicity, toner removal efficiency and fiber entrapment in the froth.

![Fig. 2. Stable foam layer during toner flotation with MIBC, a) top view b) side view](image)

The pH factor plays an insignificant role in the recovery of fiber, but the toner recovery response is strongly affected by pH of flotation. It was shown that the removal of the toner is significantly improved under the neutral to alkaline pH conditions in comparison to the results of flotation under acidic conditions. The high value of the flotation recovery of about 90\% was achieved for 1.5, 3 and 6 mg/dm$^3$, at pH 7, 9 and 12, as it can be seen from Table 1. Generally, a pH between 8 to 10 is reported to be optimum for the toner flotation (Samasundaran et al., 1999; Theander and Pugh, 2004; Bajpai, 2014). However, Alzevedo et al. (1999) reported that the acidic flotation conditions increase the removal of the toner and the maximum removal about 90\% is achieved between pH 5 and 7. Taking into consideration the fact that the author used a collector based on oleic acid for the toner flotation, which also
has good foaming properties, more studies are needed to determine the optimal pH conditions, because the influence of a surfactant type is obvious and is not negligible.

The effect of frother dosages on flotation recovery of toner in froth product and recovery of fiber in the sink product is shown in Fig. 3.

Fig. 3. The Fuerstenau plot: relationship between flotation recovery of toner \((I)\) in the froth product and recovery of fiber \((Y)\) in the sink product.

It can be observed in Fig. 3 that a very good selectivity of toner separation from the fiber suspension was achieved at the MIBC dosage in the range of 1.5 to 3 mg/dm\(^3\). The best separation selectivity \((I=96.33, Y=93.77\%)\) was obtained at MIBC dose of 1.5 mg/dm\(^3\) and pH 9 (Table 1, Fig.3).

**Kinetic flotation tests**

Flotation recoveries of the toner are shown in Fig. 4 as a function of time. Figure 4 indicates recoveries between 90.57\% and 95.56\% within 6 min, depending on the pH. These results were obtained using a fixed MIBC dosage of 1.5 mg/dm\(^3\) to provide a good and stable foam to allow high recovery of the toner.

Fig. 4. The flotation recovery of toner \((I)\) in froth product and recovery of fiber \((Y)\) in the sink product as a function of time at different pH values and MIBC dosage of 1.5 mg/dm\(^3\)
The recoveries of fiber are also given in Fig. 4. In general, such a low fiber recovery loss, less than 5%, is due to a low and stable foam layer with a fine texture. Comparing the values of the flotation recovery of toner and the recovery of fiber at pH 7 and 9 for a short flotation time (2 min) and a longer flotation time (6 min), it can be noticed that the flotation recovery of toner has increased by about 13% and fiber recovery decreased by about 2% in both cases. Analyzing the flotation efficiency indicators at pH 12, it can be seen that there is a flotation recovery increase of toner and recovery of fiber decreases about 5%. Basing on the all presented results, it can be concluded that the pH value between 7 to 9 is the optimum value in flotation.

The flotation data plotted in Fig. 4 have been utilized from the kinetic point of view for comparison of the two kinetic models: the classical first order and the modified first order model proposed by Trumic and Magdalinovic (2011). The kinetics models for the toner flotation will be tested for a MIBC dosage of 1.5 mg/dm\(^3\) at pH 7, 9 and 12.

**Classical first order model**

The extent of fitting the kinetic responses to Eq. (1) can be seen in Fig. 5, which shows a high flotation rate observed in this study.

![Fig. 5. The classical first order fitting of flotation responses under various pH. Fitting for the total flotation time: a) 4 min, b) 6 min](image-url)
The data presented in Figure 5 indicate that with the prolonged flotation time, the value of correlation coefficient, $R^2$, depending on the pH, is reduced from about 0.12 to 0.16, for the total flotation time experiment of 4 min and for all pH values and $R^2$ is between 0.775 and 0.935, which indicate a weak correlation (Fig. 5a). For a longer flotation time of 6 min (Fig. 4b), the correlation is even weaker with $R^2<0.885$. According to Volk (1965) the minimum $R^2$ value for a correlation to exists for 3 data point (4 min) is 0.994, while for 4 points (6 min) is 0.903. These data confirm the Pan et al. (1996) observation that only for short flotation time the particle flotation process follows the first order kinetics with a very good correlation.

**Modified first order model**

Trumic and Magdalinovic (Trumic, 1999; Trumic and Magdalinovic, 2011) have suggested a model which represents a modification of the first order kinetic model. Milosevic (2004) applied successfully this model for delineating the kinetics of oiled water by using equation

\[
\frac{dc}{dt} = -kck_f
\]  

(3)

where $k$ is a kinetic constant of flotation, while $k_f$ is a coefficient of changing the probability of floating (the formation of particle-bubble aggregate and levitation into the foam).

Taking into consideration the fact that the decrease of the floating probability, during a certain period of time, occurs because the easily floating particles are floated first at the beginning and then the poorly floating particles, the authors assumed that the coefficient of changing probability $k_f$ can be defined by the relation:

\[
k_f = \frac{c}{c_0}
\]  

(4)

When the expression for $k_f$ from Eq. 4 is included in the differential Eq. 3, after the integration within the limits from $c_0$ to $c$, and 0 to $t$ we get:

\[
\frac{l}{1-l} = kt
\]  

(5)

where flotation recovery $I$ is as in Eq. (2).

Equation 5 represents the first order kinetic model modified by Trumic and Magdalinovic. It provides straight lines for $\frac{l}{1-l}$ vs. $t$ plots for a given particle size with $k$ as the slope of the straight line. The fit of the kinetic responses to Eq. 5 can be seen in Fig. 6.
Comparing the correlation coefficients for both models for shorter flotation time (4 min), it may be argued that for the neutral and highly alkaline flotation conditions, a modified model considerably better describes the kinetics with the $R^2$ of 0.993 for pH 7 and 0.994 for pH 12, with respect to the $R^2$ values obtained by the classical model of first order, 0.894 and 0.775 respectively (Fig. 5a and Fig. 6a). The values of $R^2$ for the modified model are in the range of minimum $R^2$ for a correlation to exists.

The longer flotation time (6 min) resulted in reduced $R^2$ from 0.01 to 0.03, depending on the pH value (Fig. 6b), referring to the shorter flotation time. By comparing these values with the coefficient values, obtained by the classical model of first order, it can noticed that the modified model gives much better correlation with $R^2$ between 0.953 and 0.976 when compared to the classical model of the first order, where the value of $R^2$ ranged between 0.598 and 0.886. The values of $R^2$ for the modified model are above minimum $R^2$ for a correlation to exists.

Based on the data discussed above, it can be concluded that the modified model gives a better correlation for obtained flotation results.

Table 2 lists the correlation coefficients, $R^2$ and rate constants, $k$ which were obtained under various pH conditions. The rate constants were estimated from the plots for all experiments.
Table 2. Kinetics of flotation of investigated samples with obtained $R^2$. Note: minimum $R^2$ for a correlation to exist for 3 data points is 0.994 while for 4 points is 0.902 (Volk, 1965)

<table>
<thead>
<tr>
<th></th>
<th>pH=7</th>
<th>pH=9</th>
<th>pH=12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 min</td>
<td>6 min</td>
<td>4 min</td>
</tr>
<tr>
<td>classical first</td>
<td>$k$</td>
<td>0.607</td>
<td>0.472</td>
</tr>
<tr>
<td>order model</td>
<td>$R^2$</td>
<td>0.893</td>
<td>0.763</td>
</tr>
<tr>
<td>modified model</td>
<td>$k$</td>
<td>1.925</td>
<td>1.720</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.992</td>
<td>0.975</td>
</tr>
</tbody>
</table>

When the kinetic behavior of toner flotation was analyzed, it was observed that the flotation rate constant $k$, depended on pH. With the increase alkalinity, there is an increase in the value of the flotation rate constant for the flotation time of 4 min. So, the maximum value was achieved at pH 12, while for a longer flotation time, the maximum value of $k$ was obtained for pH 9. Obtaining and interpreting kinetic constant $k$ must be done with the same caution, since there are many parameters that affect this constant. For the toner flotation for flotation time of 6 min, the constant increases when the pH increases until it reaches a maximum value. From this maximum value, any increase in the pH causes a small decrease of the kinetic constant.

In order to optimize the flotation process, it is not only necessary that the constant should have the greatest value, but also the influence of the parameters on the final product quality must be taken into account. For example, in addition to the flotation recovery, the influence of pH values should be considered from the standpoint of brightness, a parameter which defines the quality of fiber. With this viewpoint, pH 12 causes yellowing of fibers which leads to the reduction of brightness, so the toner flotation is carried out in the alkaline range of pH up to 10 (Ferguson, 1992; Bajpai, 2014).

**Conclusions**

The best selectivity of separation of ink from fiber was obtained at the MIBC dose of 1.5 mg/dm³ and pH 9.

In general, the flotation efficiency is considered to follow the first order kinetics. In the comparative study on the flotation kinetics of toner, involving two models, i.e., the classical first order and the first order modified by Trumic and Magdalinić, the modified model was proved to represent the data better than the classical first order model, both for short and long flotation time.

In literature, there are several studies that report the first order kinetics for the toner flotation with the smallest particle sizes in a short flotation time. So, there are no experimental data to be compared with the results obtained in this paper.

The contribution of this work is in demonstrating that there is a good model to describe the kinetics of flotation toner with the largest particle sizes for short and long flotation time, with a very good correlation coefficient.
Further research should focus on testing the modified model by changing different flotation parameters.

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References


