**New insights on the ozone reactive flotation: fundamental study using virgin fibers to model recovered cellulosic fibers**

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**Highlights**

* Strength properties of fibers are not altered by O3 and drainability is improved
* O3 decomposition into water is predominant
* Remaining O3 mainly reacts with soluble contaminants decreasing the effluent COD

**1. Introduction**

Nowadays recovered papers and boards constitute the major cellulosic fiber raw material used in papermaking but the utilization rate of recovered paper depends on the paper grade. The production of white graphic papers uses in average a maximum of 10% of recovered paper (CEPI, 2016).To obtain high quality final products, deinking, i.e. ink removal, is required. Flotation process is the most common practice for deinking (Kemper, 1999): it is a physico-chemical unit operation using air bubbles flow to collect and drain ink particles out of the fiber suspension. To improve the efficiency and the sustainability of paper deinking lines, the idea is to add ozone (O3) as a reactive gas into the gas flow (Marlin et al., 2013). Indeed, O3 is a well-known oxidant applied for process and urban water treatment (Wei et al., 2016)and also for fiber bleaching in the pulp and paper industry (García et al., 2009). Addition of O3 in the gas stream during flotation gave promising results with the reduction of COD effluent with 30% and an increase of the fiber yield of 1 point, whereas no effect on ink removal efficiency has been observed (Almeida et al., 2010). However, O3 may theoretically also depolymerize the cellulosic chains of the fibers (Mishra et al., 2013; Pipon et al., 2007). To investigate more fundamentally the action of O3 during the flotation process, and especially to examine the reactivity of O3 with both the contaminants present in solution and the cellulosic fibers, flotation trials have been conducted on model recovered cellulosic fibers free of ink and with tap water or model process water to simulate the presence or not of soluble contaminants.

**2. Methods**

Recovered cellulosic fibers have been simulated by a mixture of virgin fibers representative of the fiber composition of office waste papers: 90% bleached chemical pulp and 10% mechanical pulp. Before flotation, the pulp models were diluted to 1% consistency (w dry fibers/w suspension) with a conventional alkaline chemistry (Marlin et al., 2013). Flotation trials were performed in a batch pilot flotation cell specially designed to run with corrosive gas such as O3 (Beneventi et al., 2009), in the following conditions: 2.785 TPN L/min gas flow, 10 minutes flotation time, 40°C, using air or a O2/O3 mix as gas flow. In the case of O2/O3, O3 concentration in the gas stream was 160 g/Nm3, i.e. 4.46 g of O3 in one trial. Flotation trials have been carried out either with tap water and industrial model water containing contaminants commonly found in process effluent of recovered paper recycling lines (sodium oleate 0.4 g/L, carboxymethyl cellulose 0.7 g/L and slightly anionic starch 3.15 g/L). Pulp strength properties have been measured on pulp handsheets of 60 g/m2 prepared according to the standard ISO 5269-3, 2008 method. Tensile strength (Ir) gives the strength of the whole fiber web (ISO 1942-2, 2008) and zero-span strength (Ir0) measured on wet handsheets, the strength of one isolated fibers (ISO 15361, 2000). The papermaking ability of the pulp was evaluated in terms of pulp drainability via the Schopper-Riegler index °SR (ISO 5267-1, 1999). The global quality of flotation effluents was examined through Chemical Oxygen Demand (COD, mg/L - Hach method). The O3 consumption (Cons.), expressed in g of O3 during the trial, has been calculated using the O3 concentration in the gas phase measured at the inlet and outlet of the flotation cell.

**3. Results and discussion**

Table 1. Pulp and effluent properties after air and O2/O3 based flotation processes

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | °SR | Ir (N.m/g) | Ir0 wet (N.m/g) | COD (mg/L) | pH | Cons. (g) |
| Air - tap water  | 40 | 42 ± 2 | 50 ± 2 | 372 | 9.9 | - |
| O2/O3 - tap water  | 43 | 48 ± 3 | 51 ± 3 | 240 | 7.6 | 3.18 |
| Air - model water  | 55 | 48 ± 4 | 50 ± 2 | 643 | 9.2 | -  |
| O2/O3 -model water | 44 | 46 ± 1 | 48 ± 2 | 564 | 7.0 | 3.76 |

 *Inlet pulp properties: pH = 9.6, COD inlet suspension, tap water: 400, air model water: 680, O2/O3 model water: 868 (mg/L), °SR=39, Ir: 43±3, Ir0 wet = 52 ±3 (N/mg)*

Before any flotation, it can be observed that the use of model process water reduced the pulp drainability by increasing the °SR from 39 to 55. Air flotation does not modify the pulp drainability (°SR=40) whereas ozone improves it by reducing the °SR from 55 to 44, probably due to the consumption of the soluble contaminants by O3. This is confirmed by COD and pH results: after air flotation, COD does not change whereas more than 30% COD reduction is obtained after O2/O3 flotation (tap or model water); on the same, after air flotation, pH is maintained at 9-10 whereas it decreased to 7-8 when O3 is used which proves that acidic products are formed. Concerning pulp strength properties, Ir and Ir0 are conserved showing that neither the fiber web nor the fiber itself is degraded by O3. Besides, 3.76 g of O3 is consumed in the trial with model water. As the O3 consumption into water alone (no fiber, no soluble contaminant) is 3.00 g, O3 is mainly decomposed by water; contaminants only consumed 0.58 and fibers 0.18 g of O3.

**4. Conclusions**

Although O3 is mainly decomposed into water, the remaining O3 principally reacts with soluble contaminants thus (1) reducing the COD and (2) preserving the cellulosic fiber from degradation: deinked pulp papermaking ability and strength properties are not altered (Ghorbel et al., 2018).

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