Reduction of biofouling in paper production processes by using a carbamate-based biocide as a retention agent

Contact times should be around 30 minutes

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BIOCIDES ARE USED in the pulp and paper industry to reduce breakdown time, to prevent formation of spots and specks and other defects and to avoid degradation of wood fibres and additives (starch, glues, etc.) [1]. Microbial growth in suspensions of fibres is not always inconvenient: often, high cell concentrations are found in paper production circuits without causing any special problems. The question arises when the microorganisms attach to the walls of pipes, headbox and couch pit and produce biofilms, that is, when they form a network of extra-cellular polymers which, in turn, tends to incorporate other particles and generate a colored gelatinous biomass (slime). Slime formation, in particular near the headbox, is highly undesirable, mainly when there is no depuration process between the headbox and the paper machine. In fact, the detachment of slime from the walls and its incorporation in the paper sheet causes spots and specks and breaks in the paper when it goes through the presses [1-2]. Furthermore, the biofilm stimulates corrosive attack in the paper machine [3] and odor complaints due to the production of volatile fatty acids (VFA) [1].

Slime formation depends on the concentration of microorganisms, temperature, dissolved oxygen concentration, presence of organic compounds, nutrients and inhibitors, as well as on the hydrodynamic conditions.

Control of oxygen concentration in the paper or pulp production process is virtually impossible. Some measures can be taken in terms of avoiding dead zones and, thus, reducing the probability of biogas production, which causes unwanted odors and dark slime. Closed pulp and paper circuits have been implemented in order to adhere to environmental restrictions. However, this causes an increase in the over-all water temperature [4], as well as in the concentration of colloids and dissolved substances [5], favoring microbial growth and slime deposition. Since the control of the concentration of such substances cannot be achieved by removing water from the system, their retention by the fibres through the use of coagulants and flocculants is also a way of mitigating biofouling problems [6].

Biocides are often used to prevent slime formation. Nowadays, mills use chemicals that are environmentally acceptable, mainly when the excess water is drained through the wastewater-treatment systems.

It is important to know the mechanism of biocide activity in order to be able to apply it properly. It is intended, in general, that the biocide concentration is kept at a suitable level (above a lethal minimum) during a certain time period. This is not always the case when carbamates are used. Therefore, in order to determine the optimum conditions (pH and concentration) to apply these chemicals, tests were run on the adhesion of microbial cells to stainless steel surfaces, as well as on the surface potential of the cells and their retention on the cellulose fibres. The current work presents and discusses the results from those tests and compares them with those obtained through the use of glutaraldehyde (another commonly used biocide).

MATERIAL AND METHODS

The majority of the materials and methods were described elsewhere [7].

The microorganism used was the aerobic bacteria *Pseudomonas fluorescens*, a well known producer of biofilm and a strain widely found in industrial environment [8].

The biocides studied were: 1) a solution composed of sodium dimethyl dithiocarbamate (15% w/v) and disodium ethylene bisthiocarbamate (15% w/v); and 2) a solution of glutaraldehyde (50% w/v).

P. fluorescens initial adhesion to stainless steel (AISI 316) was investigated using epifluorescence microscopy.

The zeta potential was determined according to Loodsrecht [9] using a Zeiss Zetameter System 3.0+. The pH of each experimental system was adjusted by addition of diluted acid or basic solutions according to the desired pH.

The retention assays were carried out using suitable refined pulp bisulphite suspensions (6 g/L). To evaluate the first-pass retention, the total protein concentration of the samples was determined using the modified Lowry method (SIGMA - Protein assay Kit No. P 5656). The values of the first-pass retention were calculated, through the following equation:

$$\%\text{Cell Retention} = \frac{|\text{Protein}|_{\text{suspension}} - |\text{Protein}|_{\text{filtrate}}}{|\text{Protein}|_{\text{suspension}}} \times 100$$

To evaluate the cellular activity, a biological oxygen monitor (BOM) was used to determine the oxygen uptake rates of the biofilms in short term assays. These assays were performed in a Yellow Sprigs Instruments BOM (model 53), and the procedure used was described elsewhere [10]. The cellular activity was assessed in terms of oxygen uptake rates instead of the current plate

FIG. 1. Epifluorescence micrograph (400X) of a stainless steel slide with some bacteria attached, in the absence of carbamate after exposure for 1 h to a bacterial suspension.

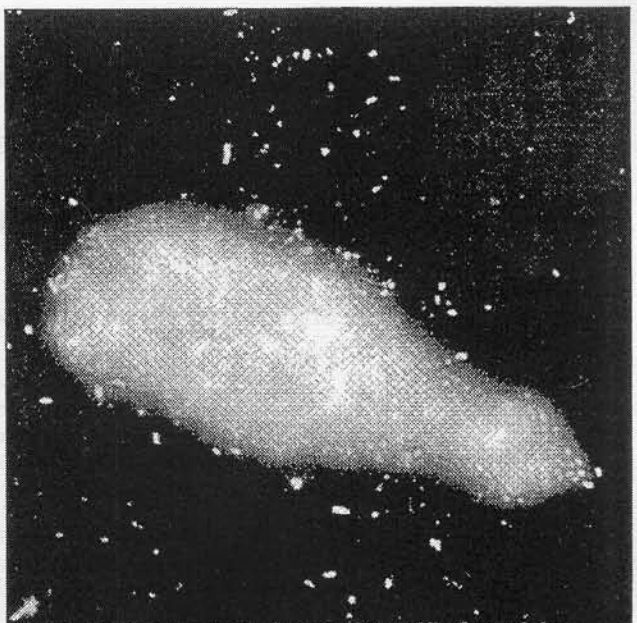

FIG. 2. Epifluorescence micrograph (400X) of a stainless steel slide exposure for 1 h to a bacterial suspension treated with 100 mg/L of carbamate.

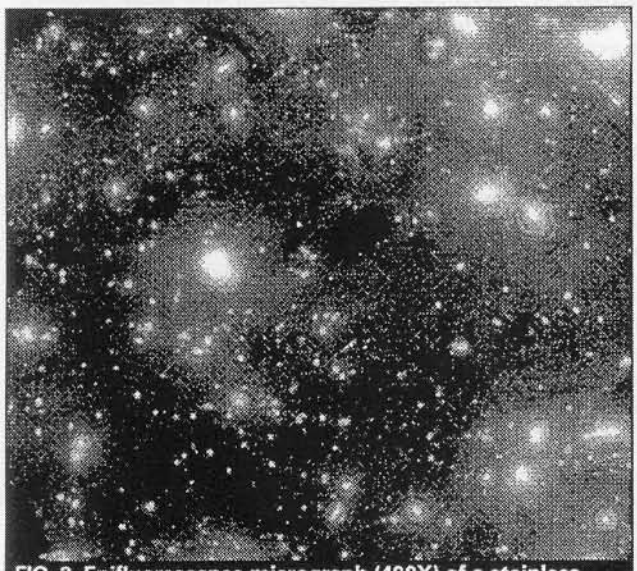

FIG. 3. Epifluorescence micrograph (400X) of a stainless steel slide exposure for 1 h to a bacterial suspension treated with 200 mg/L of carbamate.

FIG. 4. Epifluorescence micrograph (400X) of a stainless steel slide exposure for 1 h to a bacterial suspension treated with 300 mg/L of carbamate.

count method, because some authors [11] have stated that the determination of the oxygen uptake levels is more accurate than the traditional methods of bacterial enumeration by colony formation on agar media. These latter methods may overestimate biocide efficacy since bacteria can continue viable even after biocide application, but may not grow on solid media.

RESULTS

Figures 1 to 4 show the effect of the carbamate-based biocide concentration on the initial adhesion (up to three hours). In the absence of this biocide, the bacterial cells are isolated and randomly distributed on the metal slides, Fig. 1. In the presence of 100 mg/L, some aggregates of cells can be observed, Fig. 2. For biocide concentrations of 200 mg/L, Fig. 3, and 300 mg/L, Fig. 4, the distribution pattern is similar to the one obtained without

Table I. Zeta potential values of stainless steel (SS) when treated with biocides: 300 mg/L of carbamate and 100 mg/L of glutaraldehyde.

System	Zeta potential (mV)	Standard deviation (mV)
Water + SS fillings, pH = 5.8	-15.2	5.1
Water + SS fillings, pH = 8.9	-24.8	6.6
Water + SS fillings, pH = 10.9	-35.3	8.9
Water + SS fillings + 300 mg/L of carbamate, pH = 9.5	-38.1	3.5
Water + SS fillings + 100 mg/L of glutaraldehyde, pH = 5.7	-10.9	3.6

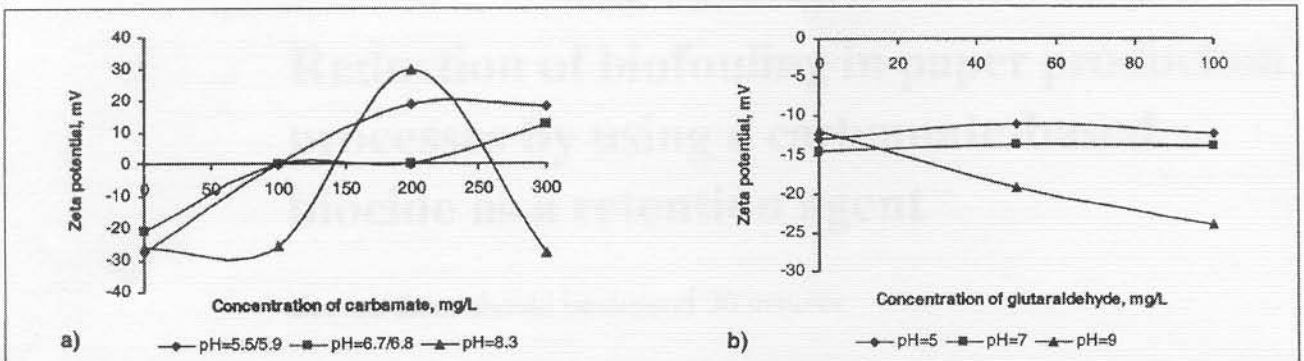

FIG. 5a. Zeta potential variation of suspended cultures of *P. fluorescens* as a function of carbamate (a) and glutaraldehyde (b) concentrations.

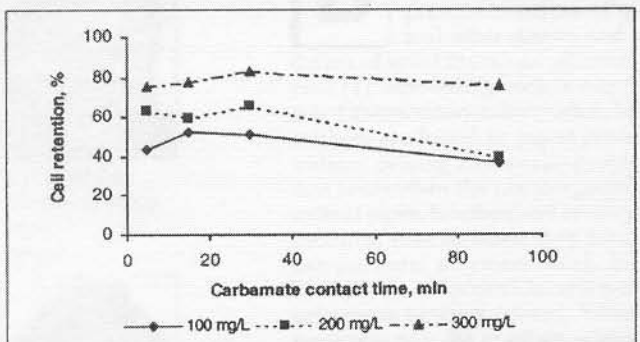

FIG. 6. Cell retention (%) as a function of biocide contact time for different concentrations of carbamate.

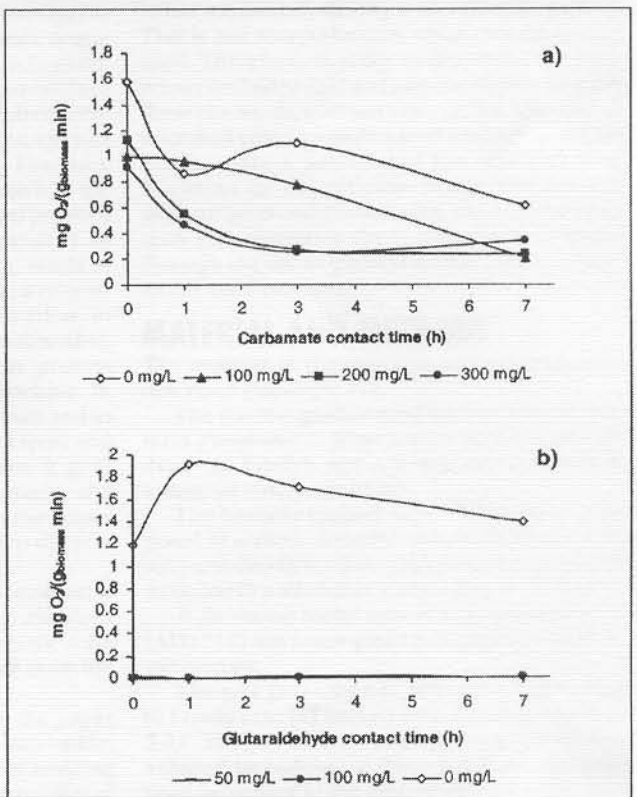

FIG. 7. Oxygen uptake rates of suspended cultures of *P. fluorescens*, when treated with different concentrations of carbamate (a) and glutaraldehyde (b), as a function of time.

biocide — but a higher number of cells can be observed.

Table I presents the potential zeta of the stainless steel fillings when treated with the biocides referred to above. The results show that the electrical charge of the stainless steel is not substantially affected by the addition of any of the two biocides studied. Instead, the registered variations in zeta potential values are essentially a consequence of the system pH variation.

Figure 5 presents the zeta potential values of suspended cultures of *P. fluorescens* treated with different concentrations of the two biocides, respectively, carbamate, Fig. 5a, and glutaraldehyde, Fig. 5b.

The results indicate that with a carbamate-based biocide the presence of this biocide shifts the bacterial electrical charge toward the positive range, depending on the pH value and biocide concentration. For glutaraldehyde, its presence does not alter the sign of the bacterial surface charge. Only when the pH of the bacterial suspended culture is 9, a slight influence of glutaraldehyde concentration on zeta potential is verified.

To evaluate the effect of carbamate on the retention of bacteria by the paper pulp suspension, several assays were carried out using different concentrations of biocide. Figure 6 shows the retention values of *P. fluorescens* by fibrous suspension for different contacting times, in presence of several concentrations of carbamate.

The results obtained indicate that the retention values increased with the increase of biocide concentration — for contact times up to 30 min. The retention values decrease for longer contact times.

To evaluate the activity of the bacteria, respirometric assays were performed in order to measure the oxygen uptake rates by *P. fluorescens* suspended cultures when treated with different concentrations of both biocides. Figure 7 presents the results from the respirometric assays, in presence of the biocides, respectively, carbamate, Fig. 7a, and glutaraldehyde, Fig. 7b.

The results show that the carbamate-based biocide causes a small reduction in the activity of *P. fluorescens*, opposite to what happens with glutaraldehyde that quickly and strongly inactivates the bacteria.

DISCUSSION

The results clearly indicate that, contrary to the glutaraldehyde (Fig. 5b), the carbamate-based biocide modifies the surface electrical charge of the microbial cells, making them more positive (Fig. 5a). Therefore, this biocide may promote cell aggregation when the electrostatic repulsion becomes low or nonexistent (i.e., when the zeta potential is close to zero). This happens for carbamate concentrations of 100 mg/L and 200 mg/L, when the pH is 5.9, and for concentrations of 200 mg/L, when the pH is 6.7.