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PRECIPITATION AND COAGULATION OF ORGANIC SUBSTANCES IN BLEACHERY EFFLUENTS OF PULP MILLS

S. Beulker and M. Jekel

Technical University of Berlin, Department of Water Quality Control, Straße des 17. Juni 135, Sekr. KF4 1000 Berlin, Germany

ABSTRACT

The formation of chlorinated organic substances in bleachery effluents of pulp mills is avoided by changing the bleaching processes to nonchlorinating agents. However, high concentrations of poorly biodegradable and colored lignins are remaining. Precipitation can be one option in physico-chemical treatment of these waters. The influence of alum, lime and magnesium hydroxide as precipitation agents for two different bleachery wastewaters was investigated under various conditions. Alum prove to be the most effective precipitant. Application at an Al/DOC-ratio of 0.5 (g/g) yields a reduction of about 60 % of the soluble organic matter in chlorine-bleachery effluents at the pH = 5.5. Oxygen-bleachery effluents require only half of this specific dosage. Lime precipitation also causes low residual concentrations, but the high chemical demand leads to problems in application. The precipitation with magnesium hydroxide cannot be applied, because remaining concentrations of organic materials are quite high. The changes in bleaching processes are responsible for a new kind of wastewater, which has a significantly lower demand of precipitant.

KEYWORDS

Precipitation; coagulation; pulp mills; chlorine-bleachery effluents; oxygen-bleachery effluents; alum; lime; magnesium hydroxide; ultrafiltration.

INTRODUCTION

In the bleaching processes of pulp mills, various oxidants and chemicals are applied for removing colored substances from the cellulose fibres. Because of their poor biodegradability bleachery wastewaters are of great concern in water quality control and wastewater treatment (Möbius, 1986). Especially the effluents from chlorine and hypochlorite bleaching are considered to be a great problem due to chlorinated substances present. Therefore, most bleaching processes have recently been changed to nonchlorinating agents, such as oxygen, hydrogen peroxide or even ozone. Even though chlorinated organic substances were widely avoided, the wastewaters are still heavily loaded with organic substances.

Precipitation of the organics by various chemicals can be one way of physico-chemical treatment. The research work presents results on the bench-scale treatment of a chlorine and an oxygen bleachery effluent with alum, lime and magnesium hydroxide.

METHODS

The bleachery wastewaters under investigation can be characterized as follows:

TABLE 1 Origin and compounds of bleachery effluents

Parameter	unit	O_2-bleachery	Cl-bleachery
bleaching steps		EOP-EP-EP*)	C-E-H-D-H*)
pH-value		10.5	1.0
DOC	mg/l	700	1200
COD	mg/l	2000	3000
UV (280 nm)	m^{-1}	800	2000
CU (465 nm,pH 7.6)	m^{-1}	14	140
AOX	mg/l	-	340

*) Employed chemicals: C: chlorine, D: chlorine dioxide,
H: hypochlorite,O: oxygen, P: peroxide, E: alkaline extraction

Precipitation and coagulation were performed in conventional jar-tests (1.8 l beakers) with rapid ($G = 760\ s^{-1}$, 3 min) and slow mixing ($G = 15\ s^{-1}$, 25 min), followed by a 2 h settling (DVGW-Arbeitsblatt W 218). An aliquot of the supernatant was used for turbidity measurements. DOC, COD, UV and color were determined after filtration through a 0.45 μm-membrane. pH-values were adjusted by H_2SO_4 and NaOH. The chemicals used for precipitation were alum, lime and magnesium hydroxide.

Also a streaming current detector (SCD) was used for the determination of flocculant demand. In these investigations, the wastewaters were titrated with a cationic polymer (Poly-di-allyl-di-methyl-ammonium-chloride, DADMAC) to a neutral colloid surface at several pH-values, varying the flocculant concentration.

Ultrafiltration tests were performed with 200 ml-Amicon-systems and membranes between 1,000 u and 30,000 u. The DOC-value of a molecular weight fraction was determined by the difference in the DOC-contents of the permeates (permeate-difference method, Summers 1986).

RESULTS

A part of the tests was performed to obtain the chemical demand necessary to reduce the organic material. Precipitations at various pH-values and with different amounts of alum were tested. The residual concentrations of organic material, measured as COD at the pH-optimum of 5.5 (see below) are shown in figure 1. The abscissa displays the applied amount of alum in relation to the DOC of the raw water. This dimensionless figure is useful, as different batches of wastewater with different amounts of DOC show similar response curves in this kind of graphic presentation.

The COD decreases with rising alum dosages and above a specific Al/DOC-ratio no further reduction can be achieved. While for the oxygen-bleachery effluents the optimum alum dosage is a Al/DOC-ratio of 0.25, the chlorine bleachery effluent needs a ratio of 0.5. The main mechanism of this precipitation is the stoichiometric reaction between organic anions and polymeric aluminium cations. The nonprecipitable fraction of COD is about 40 %. Investigations on precipitation and coagulation of fulvic and humic acids confirm these results. The coagulant demand is proportional to the concentration of a specific humic acid and its concentration of negative functional groups (Hall and Packham, 1965; Albert, 1975; Narkis and Rebhun, 1977; Semmens and Field, 1980; Edwards and Amirtharajah, 1982 and Jekel, 1983). Jekel (1986) described a similarity of the organic material of bleachery effluents, characterized by lignins and their derivatives, with natural humic substances in view of precipitation processes.

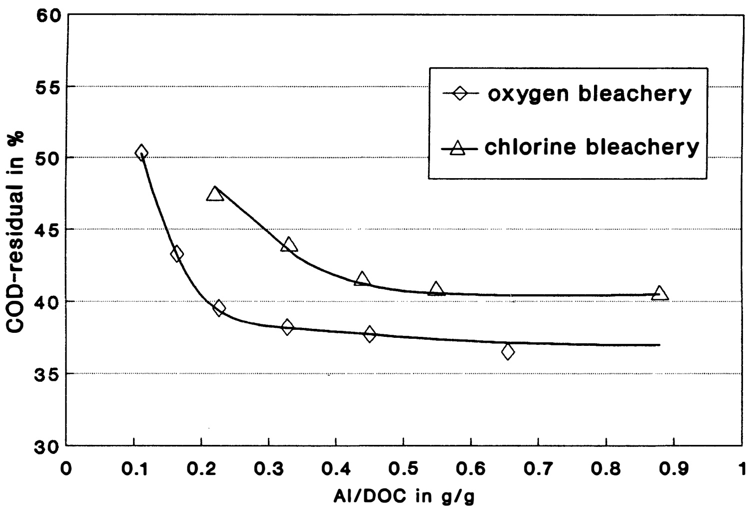

Fig. 1. Influence of alum-dosage on removal of organic substances at pH = 5.5, represented by COD-reduction.

Titrations and measurement of the colloid surface charge by using a SCD should provide information on the necessary chemical demand as a function of various pH-values. The first report on SCD (Gerdes, 1966) described possible applications of the instrument for laboratory titrations and coagulation control in water treatment plants. "In the few years since this was written, SCDs have found a widespread use in water treatment plants" (Dentel and Kingery, 1989).

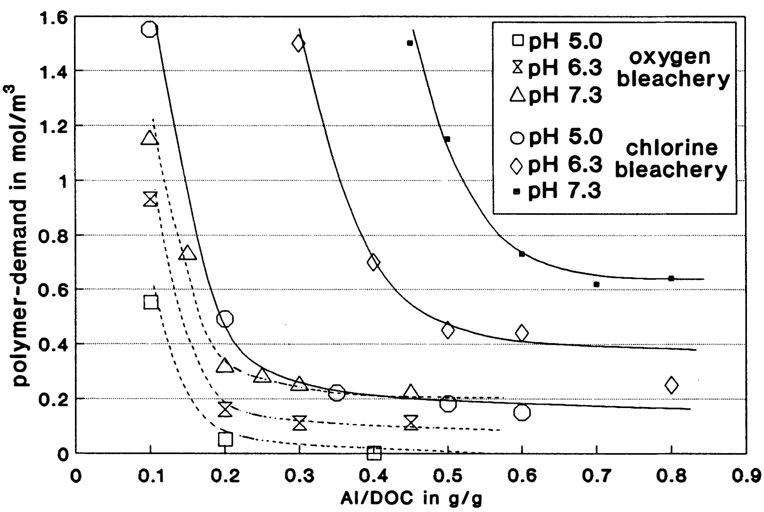

Fig. 2. Polymer demand for destabilization (measured with SCD) at various alum dosages and pH-values, demonstrated with two different bleachery wastewaters. (Polymer-demand in mol/m^3 charge of DADMAC)

As shown in figure 2, the cationic polymer demand decreases drastically with rising alum dosages down to a constant polymer consumption which is necessary to neutralize the residual charges at a certain Al/DOC-ratio. The oxygen bleachery effluents are destabilized at a Al/DOC-ratio of 0.2 to 0.25 and pH = 5, resulting in a very low cationic polymer demand. Chlorine bleachery effluents need more alum for destabilization. The destabilization is strongly dependent on the pH-value, rising from 0.3 (Al/DOC in g/g) at pH 5 up to 0.7 at pH 7.3. In addition, the cationic polymer demand in the SCD is significant at high Al/DOC-ratios, which indicates a fraction that is not removable by alum, but does react with the cationic polymer.

These results have been confirmed in precipitation tests. The lowest concentration of organic material was observed at and above the Al/DOC-ratio, which was necessary for a destabilization in the titration tests. Also the residual turbidities were markedly lower at these conditions and reached values below 2 NTU. The minimum of residual organic material corresponds quantitatively to the minimum of the residual turbidity, because an optimum in precipitation leads to well settlable solids (Jekel 1986).

Figure 3 shows the results of oxygen bleachery effluent precipitation at different pH-values and best alum dosages. There is a wide pH-optimum with the lowest residual concentration of organic matter at pH = 5.5. The residual COD amounts to 37 % and is somewhat lower than the DOC (by about 5 %). The minimum in the UV-absorbing substances is about 22 % at this pH-value. Colored substances can be reduced by more than 90 % and show a precipitation optimum at pH = 6.0. This is due to an accumulation of chromophores in the precipitable fractions. The better COD-removal as compared to DOC-removal is probably caused by the higher degree of oxidation (oxygen content) of the nonprecipitable fraction.

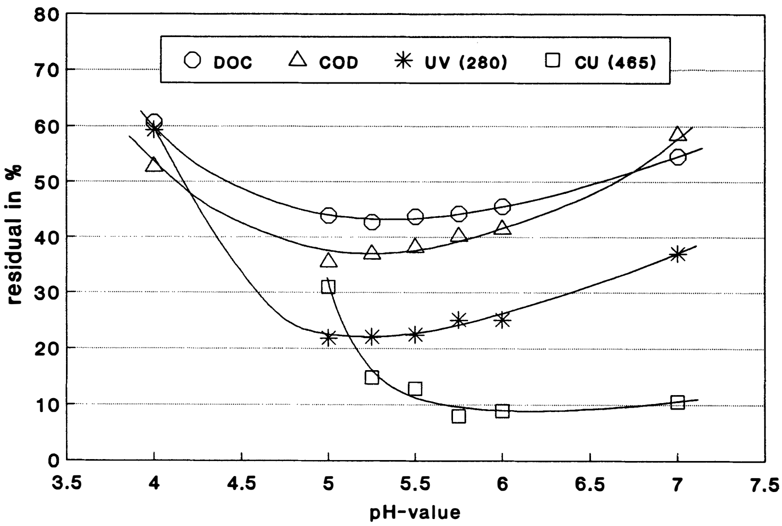

Fig. 3. Influence of the pH-value on the precipitation of oxygen bleachery effluent with alum

These results are comparable to those reported by Jekel (1986). He describes a pH-optimum between 4 and 6 for the precipitation. Using chlorine bleachery effluent he obtained best results at pH 5.2. The elimination rate was between 40 % and 70 %, depending on the applied wastewater.

Ultrafiltration tests were performed to get information on changes of the molecular weight fractions caused by precipitation and coagulation. In figure 4 ultrafiltration results of oxygen bleachery effluent are shown. The original bleachery effluent contains significant amounts in all 4 fractions. The precipitation removes high molecular-weight substances (more than 10,000 u) by more than 90 %, while low molecular-weight substances (less than 1,000 u) are not affected.

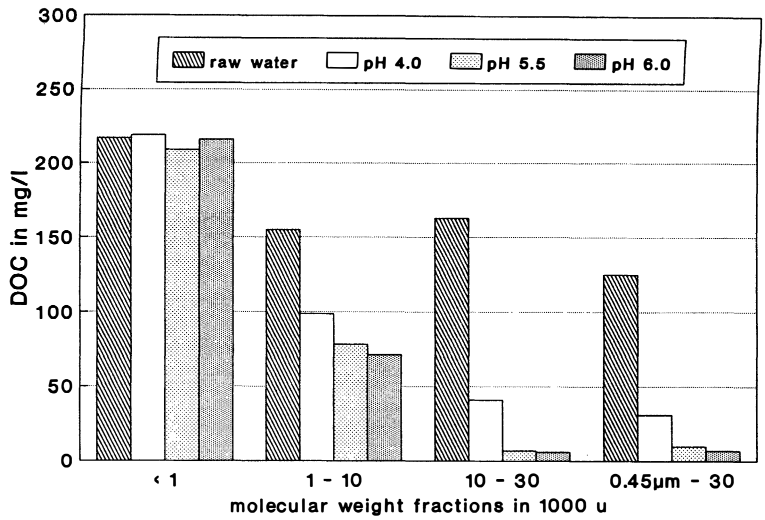

Fig. 4. Ultrafiltration before and after precipitation of oxygen bleachery effluent and the influence of the pH-value

The results of the precipitation of chlorine bleachery effluents are represented in figure 5. There is a wide pH-optimum too, but lowest residual concentrations are achieved at higher pH-values around 7. Both, DOC and COD can be reduced similarly down to 38 %. Remaining UV- and color absorptions are the same as in oxygen bleachery effluents (20 % and 10 % respectively).

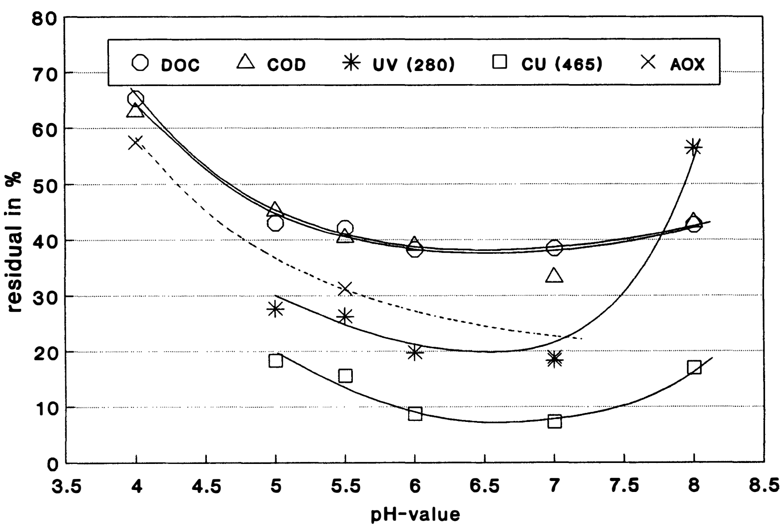

Fig. 5. Influence of the pH-value on the precipitation of chlorine bleachery effluent with alum

The ultrafiltration results concerning chlorine bleachery effluents (figure 6) show a different wastewater composition. The portion of the low molecular weight fraction is significantly higher and it is, in contrast to the oxygen bleachery effluent, partly precipitable. A DOC-elimination of 40 % is obtainable at pH 7. Macromolecular substances can be completely removed under these conditions.

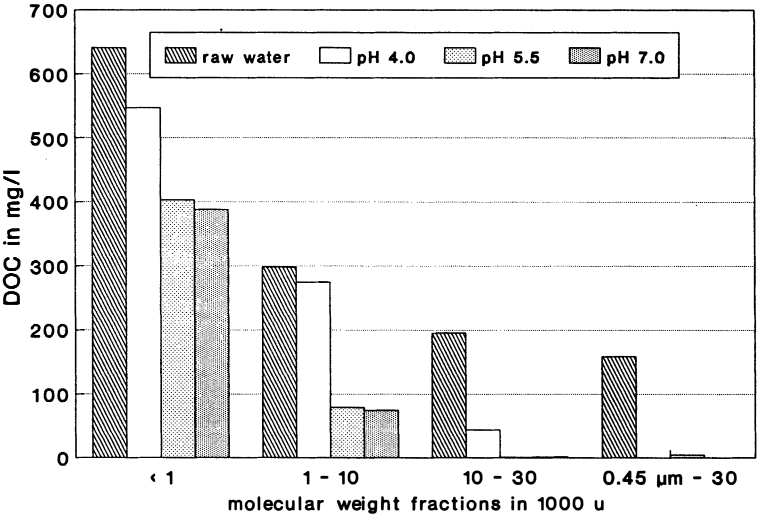

Fig. 6. Ultrafiltration before and after precipitation of chlorine bleachery effluent and influence of the pH-value

Results of additional tests by precipitating the organics with magnesium hydroxide and lime addition at high pH-values are represented in figure 7. Only the application of lime leads to removal rates comparable with alum. It produces similar results with chlorine bleachery effluents at a lime dosage of 6.0 g/l, but is less effective with the organic material of oxygen bleachery effluents (necessary lime dosage, 3.6 g/l). The residual DOC-concentration is 15 % higher and amounts to 55-60 %. Using alum as a precipitant both wastewaters can be treated with similar efficiency in all parameters.

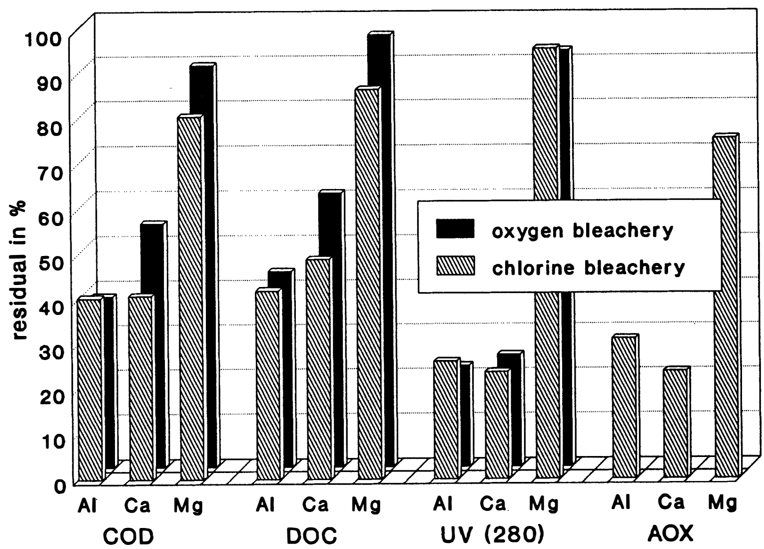

Fig. 7. Precipitation of two different bleachery effluents by alum, lime, magnesium hydroxide. Removal of organic material is represented by wastewater parameters

The use of magnesium hydroxide is not suitable for the precipitation of bleachery wastewaters. Removals of organic matter are only about 10 to 20 %, requiring dosages in the range of lime precipitation.

SUMMARY

The precipitation and coagulation of two different bleachery wastewaters was investigated using alum, lime and magnesium hydroxide. The organic matter in these wastewaters can be reduced to less than 40 % with alum as the most effective precipitant. The nonprecipitable part is mostly in the molecular weight fraction below 1,000 u. Only in chlorine bleachery effluents, can a part of this fraction be precipitated.

Lowest residual concentrations are produced at pH 5.5. The demand of precipitant in chlorine bleachery effluents, expressed as Al/DOC is about two times higher as with oxygen bleachery effluents and increases further at higher pH-values.

The application of lime causes low residual concentrations, but high demands and the resulting quantities of solids lead to problems in separation. Therefore, the application of lime seems questionable. Precipitation with magnesium hydroxide cannot be applied, because remaining concentrations of organic materials are very high.

The changes in bleaching processes are responsible for a new kind of wastewater, which requires significantly less precipitant. Furthermore, the solids contain nearly all macromolecular and color-causing organic substances.

REFERENCES

Albert, G. (1975). Die Elimination organischer Substanzen durch Flockung. In: *Heft 9 der Publikation der Wasserchemie Karlsruhe, "Adsorption"*, ZfGW-Verlag Frankfurt/M., pp 309-324.

Dentel, S.K. and Kingery, K.M. (1989). Using Streaming Current Detectors in Water Treatment, *J. Am. Water Works Assoc., 3*, 85-94

DVGW-Arbeitsblatt 218 (1992): Testverfahren in der Flockung, in preparation.

Edwards, G.A. and Amirtharajah, A. (1982). Color removal domains of the alum coagulation diagram. *J. AWWA Conference,* Miami.

Gerdes, W.F. (1966). A New Instrument- The Streaming Current Detector. *12th National Analysis Instrument Sym.*, Houston, Texas.

Jekel, M. (1983). Die Komplexierung von Aluminium mit Huminsäuren im Flockungsprozeß. In: *Vom Wasser, 61,* 349-361.

Jekel, M. (1986). Physikalisch-chemische Aufbereitung von Bleichereiabwässern der Zellstoffproduktion. *Study for Fa. Philip Müller,* Stuttgart.

Hall, E.S. and Packham, R.F. (1965). Coagulation of organic and color with hydrolyzing coagulants. *J. Am. Water Works Assoc., 57,* 1149-1166.

Möbius, C. H. (1986): Papier- und Zellstoffabriken, In: *Lehr- und Handbuch der Abwassertechnik VI (3. Auflage),* Berlin.

Narkis, N. and Rebhun, M. (1977). Stoichiometric relationship between humic and fulvic acids and flocculants. *J. Am. Water Works Assoc., 69,* 325-328.

Narkis, N. and Rebhun, M. (1983). Inhibition of flocculation processes in systems containing organ. matter. *J. WPCF, 55*, 947-955.

Semmens, M.J. and Field, T. K. (1980). Coagulation: Experiences in organics removal. *J. Am. Water Works Assoc., 72*, 476-484.

Summers, R. C. (1986). Activated carbon adsorption of humic substances: Effect of molecular size and heterodispersity. *Dissertation, Stanford University*, USA.