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COAGULATION AND SEDIMENTATION PROCESSES AS THE FIRST NODE OF TECHNOLOGICAL INSTALLATION FOR TREATMENT OF WASTEWATER FROM TIMBER PROCESSING PLANT

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PROCES KOAGULACJI I SEDYMENTACJI GRAWITACYJNEJ JAKO PIERWSZY WĘZEŁ UKŁADU TECHNOLOGICZNEGO OCZYSZCZANIA ŚCIEKÓW Z ZAKŁADU PRZETWÓRSTWA DREWNA

W niniejszej publikacji przedstawiono wyniki badań chemicznego podczyszczania ścieków pochodzących z przetwórstwa drewna w procesie koagulacji. Wykorzystano trzy różne, najczęściej spotykane koagulanty tj.: wodorotlenek wapnia, siarczan glinowy oraz chlorek żelazowy. Przeprowadzono badania wpływu pojedynczego oraz równoczesnego dozowania przedstawionych odczynników. Wykorzystano układ bloków kompletnie zrandomizowanych w czynnikowej analizie wariancyjnej oraz sformułowano końcowe aproksymacyjne równania matematyczne analityczno-empiryczne metodą punktu centralnego.

Summary

This paper deals with the results of chemical pre-treatment of effluents from Chip Washing by coagulation. Three different, most frequently used coagulants i.e. calcium hydroxide, aluminium sulphate and ferric chloride were applied. Influence of single and simultaneous dosage of the reagents was investigated. Fully randomized block systems were applied in the factorial variance analysis and final approximation analytic-empiric mathematical equations with application of the central point method were formulated.

INTRODUCTION

At Polspan-Kronospan, Szczecinek, timber processing results in the production of effluents at the Chip Washing Station. The effluents produced in quantity of 100 m^3/day are transported to a tank located near the production hall and then to a heap on the solid waste side, located near the plant. This was justified by the necessity to limit dust emission to nearby arable land and the city. In the summer time the dry heap could absorb more post-production effluents than in any high humidity period (autumn, winter, spring) so that the nearby Warynskiego Street was flooded. Attention must also be paid to the hazard of pollution of the nearby Lake Trzesiecko.

The influence of leachate from such heap on ground water quality and the development of a technology for pre-treatment of such effluents (Fig. 1) was investigated in the past years at Technical University of Koszalin, Institute of Water-sludge Technology and Waste Utilization [5-7, 9].

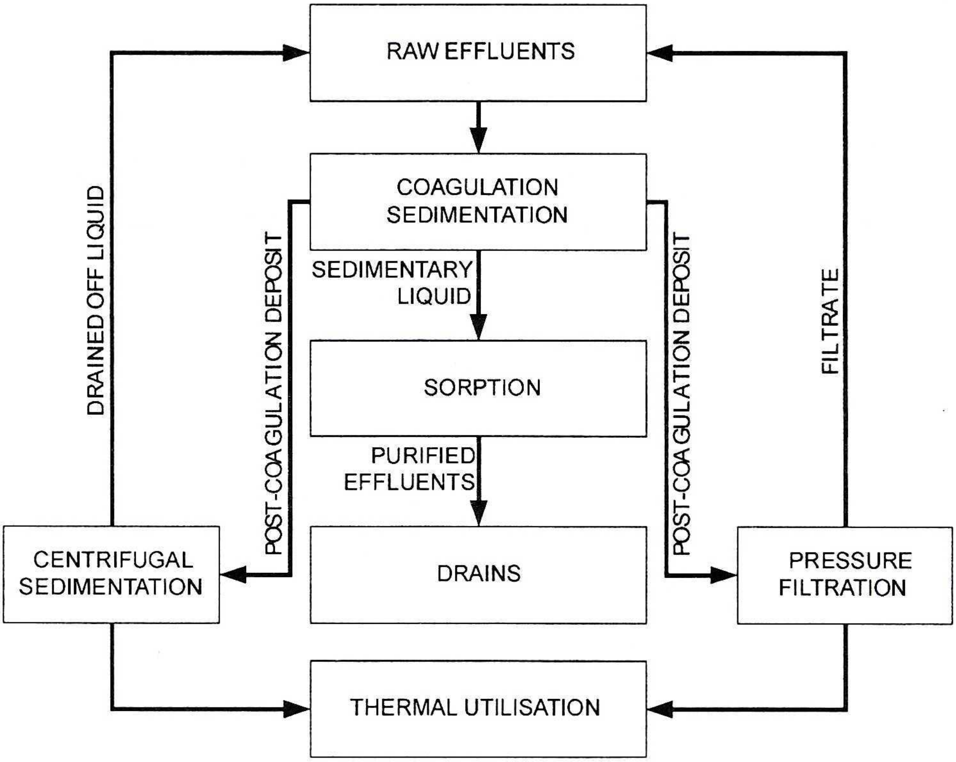

Fig. 1. Block diagram of effluent purification and waste utilization at POLSPAN-KRONOSPAN Szczecinek Plant

There is a number of disposal methods for such effluents from Chip Washing, which can generally be divided into mechanical, chemical, biological methods and those being a compilation thereof [10].

EFFLUENT PROPERTIES

The raw effluent is grey-brown-milky in color, rendering resin acids and terpene odor. The pollutants are toxic or bacteriostatic for micro organisms. The effluent contains huge amounts of organics and minerals of good settling quality and colloidal suspended solids, which affect the chemical and biochemical oxygen demand [3]. The chemical and biochemical oxygen demand ratio is approx. 2.56 therefore the effluent from Polspan-Kronospan Szczecinek Chip Washing Station is not very susceptible to biodegradation [2].

The effluent was fed to a buffer tank where its composition was averaged through natural turbulence. Before sampling (following tank filling) the effluent was mixed with an impeller pump. Each sample was then analyzed. The arithmetic mean is shown in Table 1.

Table 1. Characteristic properties of effluents from Chip Washing

Indicator		Symbol	Dimensions	Raw effluent	Coagulant						Legal requirement*
					$Ca(OH)_2$		$Al_2(SO_4)_3$		$FeCl_3$		
						[%]		[%]		[%]	
1	Reaction	pH	-	5.7	12.3	-	4.14	27	3.39	41	6.5÷9.0
2	Chemical oxygen demand	COD	mg O_2/dm^3	12300	1604	87	9900	20	7536	39	350
3	Biochemical oxygen demand	BOD_5	mg O_2/dm^3	4800	580	88	3100	35	2500	48	200
4	Total suspended solids	TSS	mg/dm^3	23520	1276	95	12861	45	12125	48	150
5	Dissolved matter	DSM	mg/dm^3	2830	2780	2	2725	4	2700	5	1200
6	Total solids	TS	mg/dm^3	26350	4056	85	15586	41	14825	44	1350
7	Ether extract	EE	mg/dm^3	426	320	25	400	6	365	14	40
8	Total organic carbon	TOC	mg/dm^3	14830	1400	91	7642	48	4690	68	40
9	Nitrogen	N	mg/dm^3	75	-	-	-	-	-	-	30
10	Phosphorus	P	mg/dm^3	21.5	-	-	-	-	-	-	5
11	Chromium	Cr^{+6}	mg/dm^3	0	0	-	-	-	-	-	0.2
12	Lead	Pb	mg/dm^3	0.0035	0	-	-	-	-	-	0.5
13	Zinc	Zn	mg/dm^3	0.245	0.11	-	-	-	-	-	2
14	Cadmium	Cd	$\mu g/dm^3$	0.15	0.085	-	-	-	-	-	100

(*) – Contract made with the Water Supply and Sewerage Company for delivery of water and discharge of effluents to municipal sewerage system No 19/95 dated 9 June 1995.

METHODOLOGY

The independent variable parameters in the coagulation process under investigation were: coagulant dose D [g/dm^3] (x_1) and initial effluent temperature [°C] (x_2). The resultant variable parameters were: pH [-] (y_1), chemical oxygen demand COD [mg O_2/dm^3] (y_2), biochemical oxygen demand BOD$_5$ [mg O_2/dm^3] (y_3), total suspended solids TSS [mg/dm^3] (y_4), dissolved matter DSM [mg/dm^3] (y_5), total solids TS [mg/dm^3] (y_6), ether extract E_E [mg/dm^3] (y_7) and total organic carbon TOC [mg/dm^3] (y_8).

In the first series of tests the constant independent parameter was the temperature of effluent fed to coagulation process, being 20°C. The first independent variable parameter under consideration (x_1) the coagulant dose was varied within the range 0.00÷4.00 g/dm^3, in 0.50 g/dm^3 increments – which allowed for fairly accurate observation and then reflection of changes in the resultant parameters ($y_1 \div y_8$).

In the second series of tests the constant independent parameter was the coagulant dose at 2.00 g/dm^3. The second variable independent parameter under consideration (x_2) the initial temperature of effluent fed to the coagulation process was varied within the range of 10÷30°C, in 5°C increments.

A mechanical mixer was used in the coagulation process. The first stage of coagulation, i.e. fast stirring, was being effected during 30 seconds after addition of the chemicals. The number of revolutions was 30 min^{-1}. At the second stage of coagulation, during slow stirring conducted for 20 minutes, the number of revolutions was 4 min^{-1}. Sedimentation time was 2 hours [3].

DESCRIPTION AND ANALYSIS OF THE RESULTS

Coagulation with calcium hydroxide

The effects of calcium hydroxide influence on the indicators under consideration after coagulation are shown in Table 1 and Figure 2. The analysis of the results shows that the optimum dose of $Ca(OH)_2$ is 2.00 g/dm^3 at an initial temperature of the effluent T = 20°C. The chemical oxygen demand, biochemical oxygen demand, total suspended solids, total solids and total organic carbon were reduced by approx. 89%. Reduction of dissolved matter was limited to 2%.

The essence of effluent purification in an alkaline medium consists mainly in use of magnesium hydroxide coagulation and adsorptive features (magnesium hydroxide being precipitated in form of jelly-like sediment). The mechanism of the process can be explained by the fact that with increase of lime dose up to pH approx. 10.4 free carbon dioxide and that compounded in the form of bicarbonates is tied up, i.e. the so called decarbonization takes place resulting in formation of fine crystalline calcium carbonate. Further addition of lime causes, apart from increase of hydroxide ions concentration, formation of magnesium hydroxide.

The optimum pH for sedimentation of magnesium hydroxide depends on magnesium ions concentration in the solution in equilibrium and on temperature of the effluent. To achieve fast sedimentation of magnesium hydroxide excess of hydroxide ions is necessary.

Significant sedimentation of magnesium hydroxide is observed at pH exceeding 10.5. There is a relationship between the degree of effluent clarification and the amount of calcium carbonate and magnesium hydroxide being precipitated in the process of coagulation

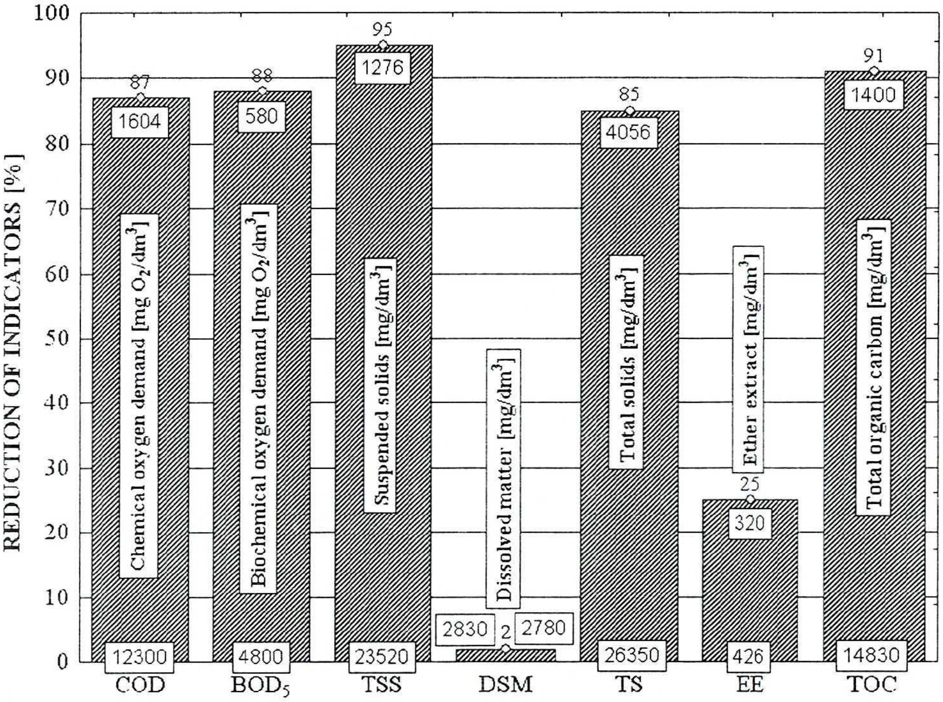

Fig. 2. Reduction of the mentioned parameters by $Ca(OH)_2$

with lime. Clarification of low hardness and alkalinity effluents proceeded only at pH exceeding 11, which can be explained with flocculating influence of magnesium hydroxide.

The efficiency of coagulation processes depends very much on the initial temperature of effluents. Both increase of pH and temperature causes, as already mentioned herein, decrease of magnesium solubility.

Coagulation with aluminium sulphate

The influence of aluminium sulphate on coagulation is shown in Table 1 and Figure 3. The analysis of the results shows that the optimum dose for decreasing of the selected parameters at T = 20°C is 2.00 g/dm^3. The chemical oxygen demand, biochemical oxygen demand, total suspended solids, total solids and total organic carbon were reduced by approx. 38%. In the case of the dissolved matter and ether extract indicators small reduction, 5% on the average, was noted.

The summary reaction of aluminium hydroxide dissolution process consists of the alkaline dissociation reaction in acid reaction water and of acidic dissociation in water showing alkaline reaction. This results in substantial increase of solubility of the hydroxide through dissociation in the low and high pH water. Within the investigated range of pH, cations of aluminium or anions of aluminium hydroxide redissolve.

Solubility of aluminium clearly increases for pH values below 5 and above 9. Within a pH range of 5.5÷7.5 aluminium hydroxide is insoluble. The scope of applicability of the coagulant determined by pH of water therefore is: 5.5÷7.5. Within this range of pH technological efficiency of aluminium sulphate as coagulant is the highest possible and the concentration of aluminium dissolved in water is very much below the admissible value.

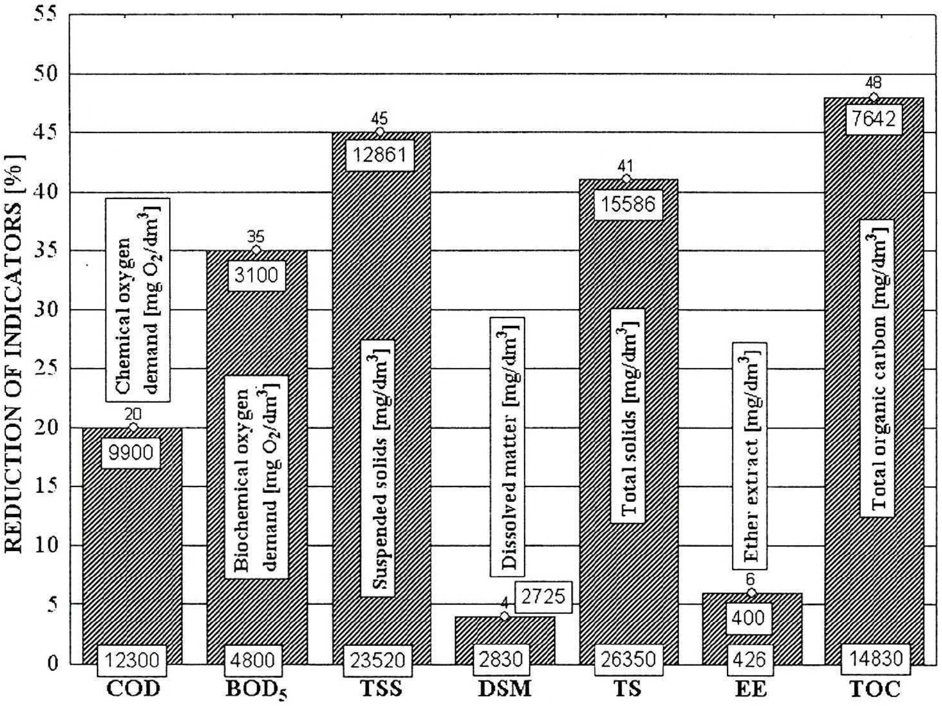

Fig. 3. Reduction of several parameters by coagulation with aluminium sulphate

Coagulation with ferric chloride

The influence of ferric chloride on the precipitation of pollutants is shown in Table 1 and Figure 4.

The results show that the optimum dose of ferric chloride is 2.00 g/dm^3. The chemical oxygen demand, biochemical oxygen demand, total suspended solids, total solids and total organic carbon were reduced by approx. 50%. Dissolved matter and ether extract were reduced by 10% on the average.

Ferric chloride has the greatest coagulation power of all iron salts, besides, the trivalent iron salts feature a specific ability to form flocks of high specific gravity.

However, generated hydrochloric acid caused substantial decrease of pH during treatment. Ferric chloride is applied mostly at pH 4÷7 and above 8.5. Ferric hydroxide has good sedimentation properties [10]. It has been established in practice that phosphate can be well removed at higher pH at the expense of higher coagulant dose.

Positively charged iron ions destabilize suspended particles by neutralization of the negative charge of finely dispersed pollutants. High turbulence followed by gentle stirring during treatment lead to absorption and occlusion of dissolved organic substances and biomass. Ferric chloride is applied worldwide in effluent purification and in slurry treatment. In mechanic-chemical treatment ferric chloride is fed to the location of highest turbulence before the settling tank. Application of tri-valent iron salts improves efficiency at all stages of treatment including anaerobic sludge digestion.

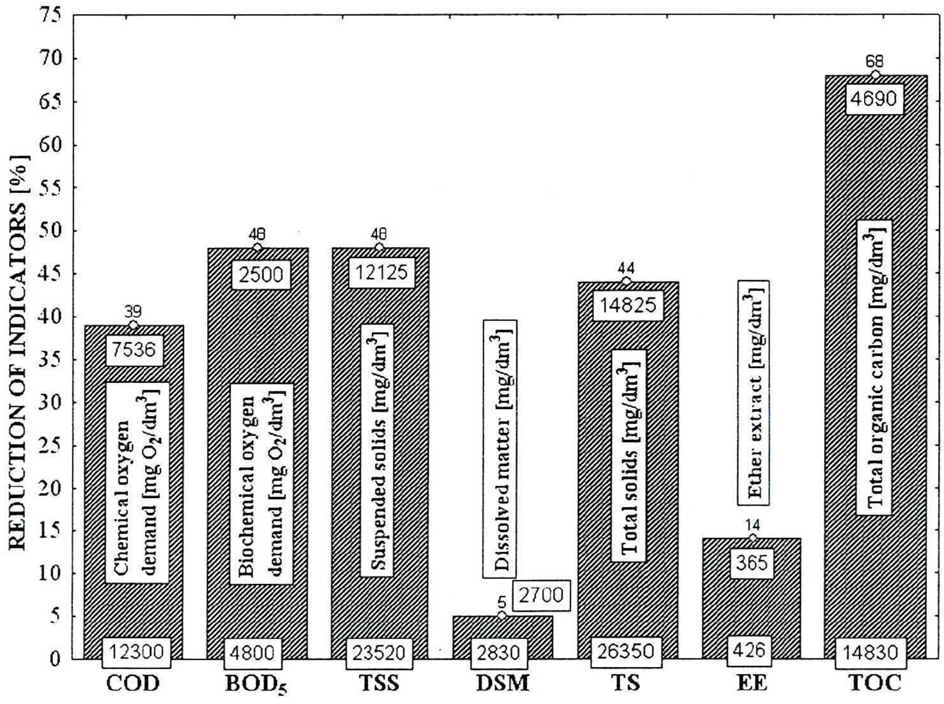

Fig. 4. Reduction of pollutants with ferric chloride

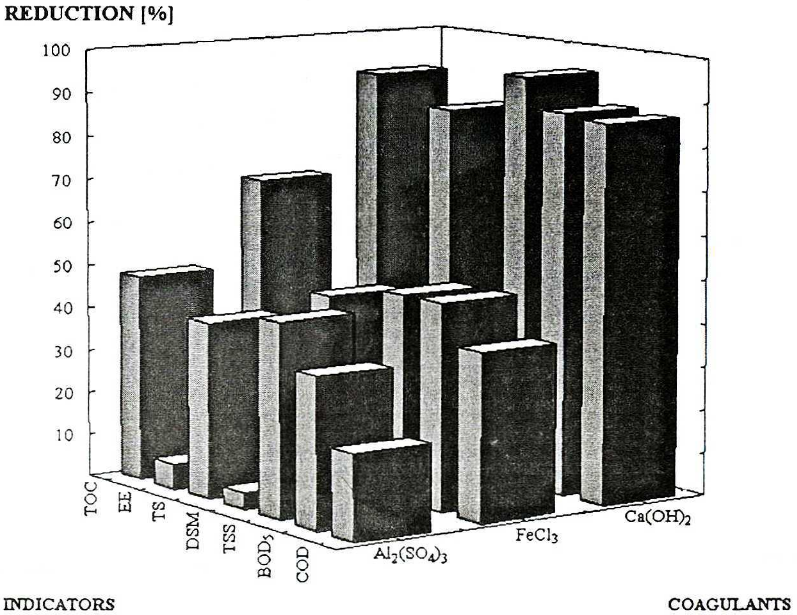

Fig. 5. Reduction of pollutants versus coagulant

Figure 5 shows reduction of the investigated parameters. The graph clearly points out the advantage of $Ca(OH)_2$ over the coagulants ferric chloride and aluminium sulphate.

Mixed coagulation

In a further step of investigation the mutual influence of the additives on coagulation was investigated.

The analysis of the test results for such type of industrial effluents at assumed level of change indicates that the interactions both for 5% of significance level determined with t-Student test and for 1% of significance level are not significant, therefore are negligible for the limits assumed and the admissible error.

QUANTITATIVE SEMI-EMPIRICAL CORRELATION

Research of relationships between several independent variables and a dependent variable was investigated by approximation method of the central point [7, 8]. The method was developed by and applied in his habilitation dissertation by T. Piecuch in 1975 [4].

The general calculation problem to be solved in such analysis consists in matching the curve being a n-degree poly-nominal for a point pattern. The functional relationships between the variables in question are initially determined through approximation with the least squares method, which consists in such selection of an equation being mostly a poly-nominal that the sum of squares of point distances on the dispersion graph from the approximation curve is the smallest possible.

Following completion of a full series of tests certain abstract mathematical space of curve pencil is obtained [7, 8]:

$$y = f(x_1, x_2, \ldots, x_N)$$

where:
y_N – poly-nominal at n-degree of approximation,
c_N – constant value at n-degree of approximation,
x_1, x_2, x_N – input independent values (factors).

A specific feature of this method is that all curves always go through one common central point. Obviously particular curves have their origin and end limited (of course) with change intervals (from ÷ to) in which particular independent variables $x_1, x_2, \ldots, x_N$ were set. Therefore, one can assume that those particular patterns create between themselves a distinct space in which equations obtained as a consequence of such approximation are often sufficiently precise [7, 8].

It must also be noted that in the central point of approximation method a simplifying assumption was adopted that the independent variable parameters tested x_1, x_2, x_3 and x_N do not interact mutually or interaction is negligible when compared with the effect of change of a single factor x_i on the process result that those interactions can be omitted without making a big error.

To verify the above one should proceed with additional few random experiments, after completion of such series of tests and establishment of the final analytic-empiric mathematical equations, with arbitrary selected values of particular variables $x_1, x_2, \ldots, x_N$ falling within the initially tested change intervals that would be selected intentionally in such way as not to be linked with approximation central point but with the space around that point, i.e. the space in which it is assumed that the equations obtained can be applied [7, 8].

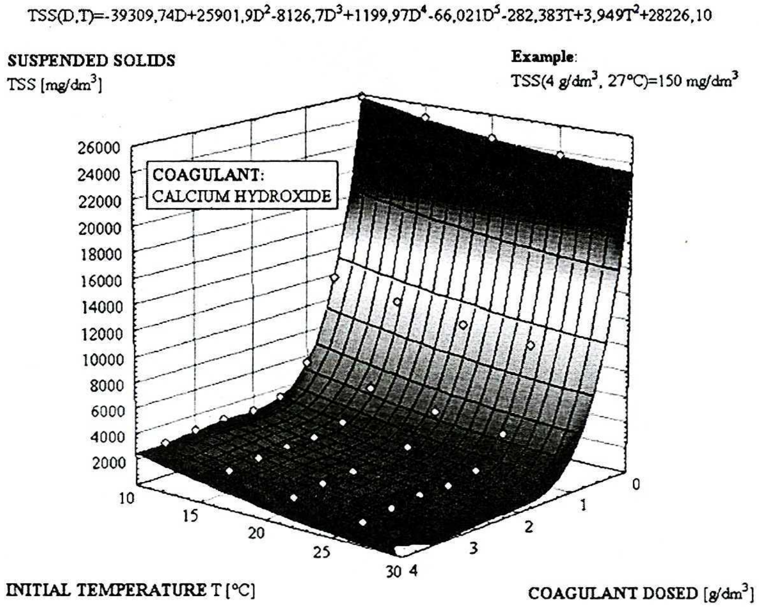

Fig. 6. Coagulation with calcium hydroxide – suspended solids TSS [mg/dm³]

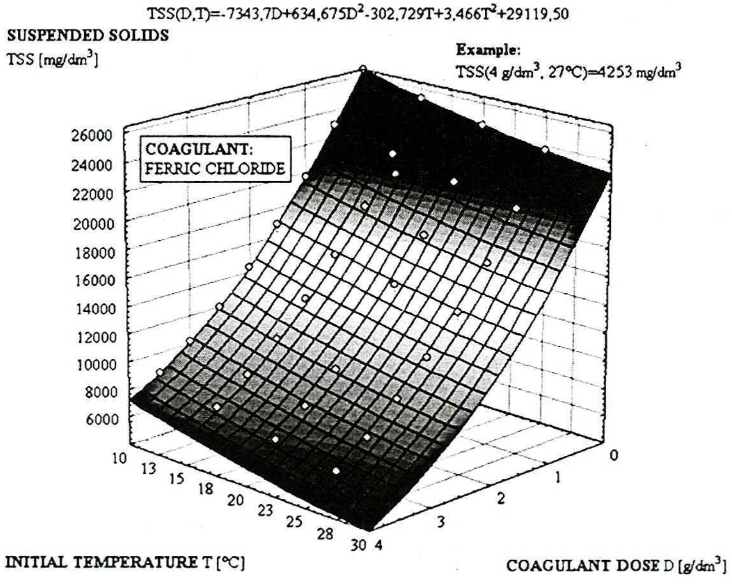

Fig. 7. Coagulation with ferric chloride – suspended solids TSS [mg/dm³]

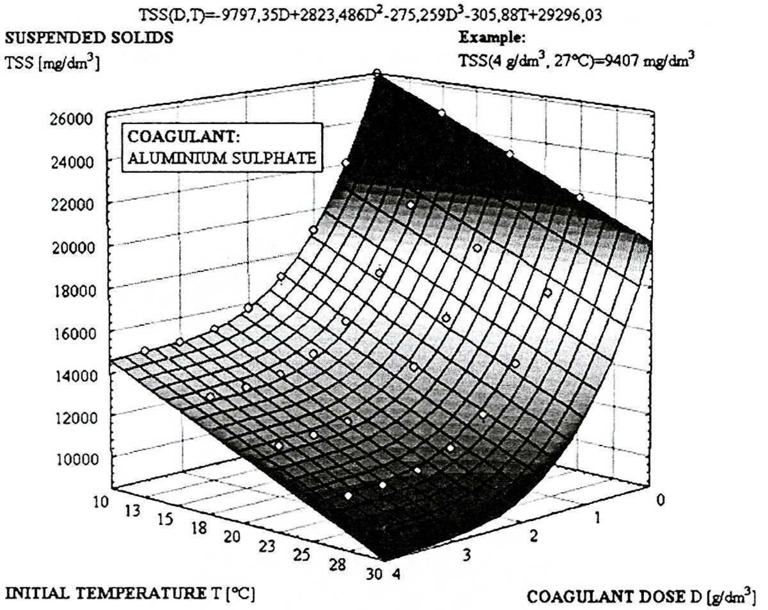

Fig. 8. Coagulation with aluminium sulphate – suspended solids TSS [mg/dm^3]

CONCLUSIONS

The following general conclusions can be drawn from the tests made:

- The best efficiency of pre-treatment of wastewater from timber processing in Polspan-Kronospan Plant in Szczecinek, with separate application in experiments of such coagulants as calcium hydroxide, aluminum sulfate and iron chloride in tested range of their dosage 0÷4 dm^3, was achieved using coagulation with calcium hydroxide. At applied doses of coagulants, in reference to low wastewater reaction after coagulation with aluminum sulfate and iron chloride, it may be assumed that hydrolysis and coagulation process proceeded not fully, which had impact on smaller efficiency of wastewater treatment.
- Using composition of joint dosage coagulants, interactions occurring between calcium hydroxide and aluminum sulfate as well as between calcium hydroxide and iron chloride are not significant for the 5% significance level.

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