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UTILIZATION OF WASTE LIGNOSULPHONATE IN THE PRODUCTION OF COAGULATING AGENTS FOR THE RECOVERY OF PROTEIN FROM SLAUGHTERHOUSE WASTEWATERS

The problem of preparation of lignosulphonate coagulants and their application to coagulation of slaughterhouse wastewaters has been presented. The coagulants were prepared from raw sulphite liquor by means of membrane methods and from vanillin lignin using its solution in sodium hydroxide or sodium carbonate. The obtained lignosulphonate coagulants have a higher efficiency during precipitation of proteins and fats from slaughterhouse wastewaters than klutan which is now used for this purpose.

1. INTRODUCTION

Slaughterhouse wastes are disposed into the municipal sewerage system after merely preliminary treatment (screens, strainers), causing a number of undesirable processes in water reservoirs due to the high consumption of dissolved oxygen in the water. This inhibits the mineralization of organic compounds and causes the settling of sediments at the bottom of the reservoir. Therefore, various methods of biological and physicochemical treatment of slaughterhouse wastes have been developed [1].

One of them is coagulation by means of lignosulphonates, which do not exert any harmful influence on the quality of the protein and fat precipitated from the wastes. Thus, the application of lignosulphonates to the coagulation of slaughterhouse wastes makes it possible to utilize the precipitated sediments as components of feed for farm animals.

A rich and easily available source of lignosulphonates are waste sulphite liquors obtained through the sulphite method of wood pulping. For the production of coagulants both raw sulphite liquor and the so-called vanillin lignin may be used. Vanillin lignin is the waste resulting from the process of vanillin production from

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sulphite liquor. The sulphite liquor, a source of extremely noxious and troublesome waste, is partly used as a binder in the metallurgy of copper, although no complex method of its utilization has been found so far. The problem of utilizing the vanillin lignin, even though about 3,000 t of it are produced in Poland every year [2], has not been solved yet. For many years attempts have been made to utilize this waste material, but without positive results, as it contains a considerable amount of inorganic compounds and loosely bounded sulphur dioxide.

The aim of these investigations was to find a method allowing us to obtain coagulating lignosulphonate agents from waste sulphite liquor and vanillin lignin. They can be applied to coagulation of slaughterhouse wastewaters in order to recover protein. In order to isolate and purify the lignosulphonate from liquor, ultrafiltration and diafiltration were applied. In the case of vanillin lignin, which is a solid or greasy substance insoluble in water, a method of dissolving it had to be found, and the obtained solutions were the proper coagulating agent. Moreover, attempts have been made to apply both these coagulants to precipitation of protein and fats from the slaughterhouse wastes.

2. PREPARATION OF COAGULATING LIGNOSULPHONATE AGENT FROM RAW SULPHITE LIQUOR BY MEANS OF MEMBRANE METHODS

From the viewpoint of the coagulation of wastes, high-molecular lignosulphonates are the most important components of waste sulphite liquor. Besides them the liquor contains many substances which are not active in this process, e.g., low-molecular lignosulphonates, sugars and inorganic compounds.

The preparation of the lignosulphonate coagulant from raw liquors consists in their concentration and fractionation by means of ultrafiltration, after which the obtained lignosulphonate concentrates are purified by diafiltration [3]. The concentrate of lignosulphonate compounds was obtained, using Danish large-scale membrane module "DDS-Lab-Modul", discussed in [4]. This module was equipped with non-cellulosic flat membranes made of polyacrylonitrille (symbol PAN-20) of the author's own make. The production process and physicochemical properties of membranes have been described elsewhere [5], [6].

Before the set of membranes was used for concentration, fractionation and diafiltration of the wastes, it had been tested and conditioned, i.e., distilled water (for 12 hours at a pressure of 0.4, 0.5 and 0.6 MPa), then raw liquor (for 8–12 hours at a pressure of 0.4 and 0.5 MPa), and finally aqueous solutions of dextrans (concentration 1 kg/m^3) with given molecular weights (2 hours each) were successively let through the module. These tests were carried out at a temperature of 293 K in order to determine the permeability of the membranes and the rejection ratios of the dextrans. The total working time of the membranes applied to the

Table 1

Characteristics of sulphite liquor from Niedomice Pulp Plant

Parameter	Sulphite liquor
Total solids, kg/m^3	103
Ash, kg/m^3	13.4
Volatile matter, kg/m^3	89.8
Sugar, kg/m^3	26.0
Lignosulphonates, kg/m^3	52.4
pH	2.7
Specific conductance, cm^{-1}, ohm^{-1}	0.0068
COD, kg O_2/m^3	146
Density (293 K), kg/m^3	1043
Colour, kg Pt/m^3	41.4

Table 2

Characteristics of polyacrylonitrile ultrafiltration membranes, PAN-20 type

I. Structure

Membrane	Porosity %	Thickness μm	Mean pore radius nm
PAN-20	69.9	75	6.4

II. Permeability data (temp. 293 K)

Pressure MPa	Water permeability $m^3/m^2 \cdot d$	Sulphite liquor flux rate $m^3/m^2 \cdot d$
0.4	1.47	0.647
0.5	1.72	0.803
0.6	1.90	0.929

III. Cut-off data (temp. 293 K, pressure 0.5 MPa, concentration of dextrans 1 kg/m^3)

Molecular weight of dextran	Flux rate $m^3/m^2 \cdot d$	Rejection ratio %
3000	1.26	64.2
20000	1.12	91.5
40000	1.11	92.6
80000	1.08	97.9
100000	1.06	99.3

ultrafiltration and diafiltration in the testing and conditioning amounted to 34 hours, enabling the membranes to attain their final structures.

The process of obtaining coagulating lignosulphonate agents was carried on continuously and comprised three stages. During the first stage raw waste sulphite liquor was subjected to ultrafiltration until its initial volume decreased twice. Next diafiltration was started. This process consisted in the continuous supplying of a given volume of water (the ratio of the volume of water used for diafiltration to the initial volume of the liquor was 1:2) at a rate equal to that of the obtained filtrate. A repeated ultrafiltration, the final stage of this process, proceeded until a concentrate was composed of 20% of the initial volume of the waste sulphite liquor. Both the obtained coagulant and the raw liquor were subjected to physicochemical analysis, and the dissolved solids [7], sugars [8], lignosulphonates [9] and chemical oxygen demand (COD) [7] were determined. The coagulating agent was obtained from a sulphite liquor coming from the Cellulose Plant at Niedomice. Before entering the ultrafiltration system, the liquors were preliminarily filtered through a ceramic filter with a mesh of ca. 10 μm. The average physicochemical characteristics of the sulphite liquor from Niedomice plant have been gathered in tab. 1.

Table 2 shows the characteristics of the polyacrylonitrile membranes applied to the preparation of the coagulating agent, whereas tab. 3 presents the conditions and results of this process. Test investigations of the membranes enabled us to determine their permeability as well as the rejection ratio of dextrans. The PAN-20 membrane is compact, the minimum molecular mass of the substances retained by this membrane, the so-called "cut-off", amounted to approximately 20,000. Due to

Table 3

Preparation efficiency of lignosulphonate coagulant by means of ultrafiltration and diafiltration processes

I. Process rate (temp. 293 K, pressure 0.5 MPa)

Process step	Average flux rate, $m^3/m^2 \cdot d$
Ultrafiltration I	0.792
Diafiltration	0.888
Ultrafiltration II	0.689

II. Characteristics of coagulant and sulphite liquor

Parameter	Raw sulphite liquor	Coagulant
Dissolved solids, kg/m^3	90.5	139
Lignosulphonates, kg/m^3	42.8	94.2
Sugars, kg/m^3	21.3	3.33
COD, $kg\ O_2/m^3$	13.6	209
Lignins to sugars ratio	1.95	28.3

application of this membrane lignosulphonate coagulants were obtained with a high efficiency. The process aimed at removing from the liquor as much sugar and low-molecular lignosulphonate as possible, as they are inactive components in the coagulation of slaughterhouse wastes. The increase of the ratio of the lignin content to the sugar content in the raw liquor and the coagulating agent have been assumed as a measure of the efficiency of this process. The ratio of the content of lignin to that of sugar increased from 1.95 in the case of raw liquor to 28.3 in the case of the coagulating agent.

3. PREPARATION OF THE LIGNOSULPHONATE COAGULANT FROM VANILLIN LIGNIN

The vanillin lignin applied to our investigations was produced in the Kujawy Plant of Concentrated Food, Włocławek. It was an amorphous pasty substance, insoluble in water. In order to dissolve it, aqueous solutions of calcium hydroxide and sodium carbonate were used.

The application of saturated calcium hydroxide solutions as a solvent of vanillin lignin did not yield satisfactory results. Positive results were obtained, however, with aqueous solutions of sodium hydroxide and sodium carbonate.

As far as sodium hydroxide is concerned, a batch of 0.25 kg of air-dry vanillin lignin was dissolved in 0.050 m^3 of sodium hydroxide solution, concentrations of which were 0.01, 0.05, 0.1 and 0.2 kmol/m^3, respectively. As air-dry lignin we understand lignin humidity of which ranged from 7.7 to 10%, obtained after drying it for a few days in aerial atmosphere at ambient temperature. The aforesaid amount of lignin was completely dissolved only in a sodium hydroxide solution of 0.2 kmol/m^3 concentration.

Attempts at dissolving lignin in solutions of higher concentrations yielded negative results, because an undissolved residue was left then. It has been found that the maximum amount of air-dry lignin dissolved in 1 m^3 sodium hydroxide solution of 0.2 kmol/m^3 concentration amounts to 10 kg. In order to coagulate slaughterhouse wastes, vanillin lignin solutions of a concentration of 10 kg/m^3 were used.

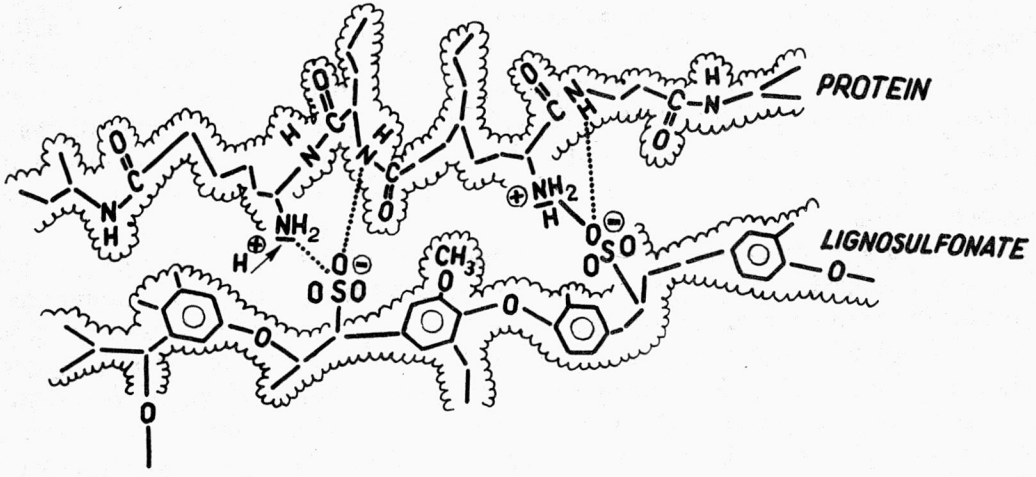
There is much to be said for the application of sodium carbonate to dissolve vanillin lignin because of its lower price and better availability if comparing with sodium hydroxide. Although that lignin dissolves easily in sodium carbonate solution, the method applied has essential disadvantage, i.e., precipitation of calcium carbonate. The calcium contained in the vanillin lignin combines with the carbonate ions of the soda. The sediment of the carbonate must be removed from the solution of the coagulating agent.

The coagulant is obtained from vanillin lignin dissolved in sodium carbonate solution as follows: 10 kg of air-dry vanillin lignin is disintegrated and mixed with 0.125 m^3 of water. A 4–5% sodium carbonate solution is added into the suspension

stirring it all the time. As soon as the pH of the solution has reached the value of 9, no further solution must be added, though the stirring is to be continued for 15 min, then the suspension is put aside for 30 min and the sediment can settle down. Now the solution is separated from the sediment by decantation. The concentration of the solution obtained in such a way amounted to about 10% (total solids – 99.05 kg/m^3). The precipitated, easily sedimenting calcium carbonate was cream-coloured (almost white) and dissolved quickly and completely in hydrochloric acid solution of 1 kmol/m^3 concentration. Vanillin lignin solutions prepared in this way were applied in the coagulation of slaughterhouse waste.

4. COAGULATION OF SLAUGHTERHOUSE WASTE

A lignosulphonate molecule consists of p-hydroxy-m-metoxy-phenylpropane units, which have been sulphonated in the propane chain, mostly in α position. The presence of sulphone groups facilitates the reaction of lignosulphonates with compounds containing amine groups, i.e., also with substances containing proteins. The precipitation of proteins by means of lignosulphonates is presented in figure. In



Precipitation mechanism of lignosulphonate–protein complex

wastes containing proteins the electronegative sulphone groups are arranged towards the electropositive groups of the peptide chain, forming a soluble complex by means of hydrogen bonds and due to van der Waals forces joining the hydration water. After acidification the anion groups in the protein particle bond the protons, obtaining a positive electric charge, and form strong bonds with negatively charged

sulphone groups of lignin. The hydration water is separated, precipitating a lignin–protein complex, which may be filtered off or separated by means of flotation. The efficiency of the precipitation of proteinaceous substances is affected by various factors, the most essential among them being the degree of sulphonation and the structure of the lignin particles. The lignosulphonates contained in waste sulphite liquors are characterized by a great heterogeneity resulting from the variety of wood and the method of pulping. Not all the components of waste sulphite are active in the coagulation of wastes. To these belong, first of all, carbohydrates and inorganic compounds.

In Poland, for objective reasons, slaughterhouse wastewaters are treated in the existing installations of the "Alwatech"-type (imported from Norway) making use of a lignin preparation called "klutan" which is produced for completely different purposes. Its application involves some difficulties, because it is an unrefined waste sulphite liquor, partly devoid of carbohydrates and dried.

The aim of investigations was to check the obtained lignosulphonate coagulants in the process of precipitating the protein from slaughterhouse wastes. For this purpose we used wastes from the slaughterhouse in Opole after their preliminary mechanical treatment (by means of screens and strainers). These investigations were carried out in laboratories in order to compare the precipitation efficiency of protein and fats by means of the obtained lignosulphonate coagulants with the efficiency of their precipitation by means of klutan. To the tested sample of wastewater a definite dose of the coagulating agent was added (calculated in relation to the total solids), then it was acidified with a 10% solution of sulphuric acid to a pH of 3, being stirred firmly all the time. The solution with the precipitated sediment of protein and fats was put aside for 2 hours, so that the sediment might settle down. Efficiency of precipitation in the liquid above the sediment, the chemical oxygen demand as well as the total solids were determined. Next the sediment was filtered off and dried, and weighed. In the case of raw waste also the chemical oxygen demand and the content of dissolved substances were determined. All the coagulation tests were carried out at a constant ($0.1\,m^3$) volume of waste.

Table 4 provides the results of the coagulation of slaughterhouse wastes by means of a coagulating agent obtained by ultrafiltration and diafiltration as well as klutan. Lignosulphonate coagulant is more efficient than klutan when applied to precipitation of protein and fats, taking into account the load of the liquid left after coagulation and the amount of the precipitated sediment. Thus, at a batch of the coagulating agent amounting to $0.250\ kg/m^3$, the COD of the liquid just above the sediment is $0.310\ kg\ O_2/m^3$ when using a coagulating agent obtained by means of the membrane method, and $0.617\ kg\ O_2/m^3$ when using klutan. The total solids in the liquid above the sediment amounted to $2.03\ kg/m^3$ and $2.34\ kg/m^3$ for the klutan and the lignosulphonate coagulants, respectively, and the amounts of precipitated protein and fat sediments for the coagulants mentioned above were $1.65\ kg/m^3$ and $2.34\ kg/m^3$, respectively. The obtained results, concerning the coagulation of

Table 4

Coagulation of proteins and fats from slaughterhouse wastewaters* with lignosulphonate coagulant obtained by means of membrane processes

Coagulant dose kg of TS**/m^3 of wastes	Chemical oxygen demand		Total solids		Amount of sediment kg/m^3 of wastes
	kg O_2/m^3	Removal efficiency %	kg/m^3	Removal efficiency %	
		Lignosulphonate coagulant			
0.200	0.582	85.3	2.19	38.3	1.76
0.250	0.310	91.5	2.03	42.8	2.34
0.300	0.474	88.0	2.22	37.5	2.10
0.375	0.435	89.0	2.24	36.9	1.78
		Klutan			
0.200	0.646	83.6	2.32	34.6	1.64
0.250	0.617	84.4	2.34	34.1	1.65
0.300	0.557	85.9	2.31	34.9	1.70
0.375	0.609	84.6	2.38	32.9	1.69

*COD of raw wastewater, 3.96 kg O_2/m^3. Total solids of raw wastewater, 3.55 kg/m^3.
**Total solids.

slaughterhouse wastewater, justify the statement that the optimal dose of the lignosulphonate coagulant, calculated for the total solids, is contained in the range from 0.25 to 0.30 kg/m^3.

The results of protein and fat coagulation in slaughterhouse wastes due to application of vanillin lignin dissolved in sodium hydroxide and sodium carbonate solutions have been gathered in tabs. 5 and 6. They lead to the conclusion that vanillin lignin can be used as a coagulating agent for slaughterhouse wastewaters. As to the rate of reducing the COD in the drained off water and the amount of precipitated sediments it shows efficiency a somewhat higher than klutan. The total amount of solids, however, is higher in the case of applying vanillin lignin than when klutan is used. This is due to the larger volume of added lignin solutions and to the fact that vanillin lignin contains more inorganic compounds than klutan. The content of inorganic compounds is, moreover, increased by the sodium hydroxide and sodium carbonate contained in vanillin lignin solutions. It has been found that the optimal doses of coagulating agents to each kg O_2 of COD in raw wastes are: 1) 0.11–0.15 kg of vanillin lignin in sodium hydroxide solution (concentration 0.2 kmol/m^3); 2) 0.200–0.326 kg of vanillin lignin in 4% solution of sodium carbonate.

Table 5

Coagulation of proteins and fats from slaughterhouse wastewaters* with vanillin lignin solution in NaOH

Coagulant dose kg of TS***/m^3 of wastes	Chemical oxygen demand		Total solids		Amount of sediment kg/m^3 of wastes
	kg O_2/m^3	Removal efficiency %	kg/m^3	Removal efficiency %	
0.250	0.705	81.5	2.39	26.2	1.40
0.300	0.684	82.1	2.41	25.7	1.50
0.350	0.642	83.1	2.39	26.2	1.53
0.400	0.580	84.8	2.36	27.3	1.61
Klutan**	0.601	84.2	1.72	47.3	1.61

*COD of raw wastewater 3.81 kg O_2/m^3. Total solids of raw wastewater 3.25 kg/m^3.
**Coagulant dose 0.250 kg/m^3 wastewater.
***Total solids.

Table 6

Coagulation of proteins and fats from slaughterhouse wastewaters* with vanillin lignin solution in Na_2CO_3

Coagulant dose kg of TS***/m^3 of wastes	Chemical oxygen demand		Total solids		Amount of sediment kg/m^3 of wastes
	kg O_2/m^3	Removal efficiency %	kg/m^3	Removal efficiency %	
0.500	1.22	72.5	2.66	29.9	1.55
0.600	0.843	81.0	2.41	36.4	1.96
0.700	0.671	84.9	2.37	37.4	2.06
0.800	0.619	86.0	2.34	38.4	2.32
1.00	0.542	87.8	2.43	36.1	2.73
1.10	0.585	86.8	2.53	33.4	2.45
1.20	0.636	85.6	2.58	32.1	2.38
1.40	0.662	85.1	2.72	28.2	2.31
2.00	0.740	83.3	3.06	19.4	2.62
Klutan**	0.703	84.1	2.00	47.2	1.93

*COD of raw wastewater 4.44 kg O_2/m^3. Total solids of raw wastewater 3.80 kg O_2/m^3.
**Coagulant dose 0.250 kg/m^3 wastewater.
***Total solids.

5. SUMMARY AND CONCLUSIONS

The paper deals with the methods of obtaining lignosulphonate coagulants from raw waste sulphite liquor and vanillin lignin.

The production of a coagulating agent from raw waste sulphite liquors consists in

concentrating them during ultrafiltration and the cleaning of the obtained concentrate by means of diafiltration.

In the case of vanillin lignin investigations have proved that it is an active coagulating agent for slaughterhouse wastes only as a solution. It has been found that the suspension of vanillin lignin in water does not show any coagulating properties. Aqueous solutions of sodium hydroxide and sodium carbonate may be used as solvents of vanillin lignin. The optimal concentrations of the dissolving solutions were sodium hydroxide – 0.2 kmol/m^3 and sodium carbonate – 4 or 5%.

The optimal dose of the coagulating agent obtained from raw waste sulphite liquors amounts to 0.250 kg/m^3 of wastes (calculated for total solids), while the optimal doses of coagulant obtained from vanillin lignin are as follows:

1) coagulant with sodium hydroxide as a solvent – 0.4 kg/m^3 of waste (calculated for total solids), average COD load being about 3.8 to 4.5 kg O_2/m^3,

2) coagulant with sodium carbonate as a solvent – 0.8–1.0 kg/m^3 of waste (calculated for total solids) showing a COD of 3.8 to 4.5 kg/m^3.

For wastes with different loads proportionally higher or lower doses of coagulating agents are to be applied.

The obtained lignosulphonate coagulants show a higher efficiency in precipitating proteins and fats from slaughterhouse wastes in relation to the load of the liquid after coagulation, as well as a higher output of sludge than klutan used for the same purpose.

Taking into consideration the coagulant doses and the efficiency of sewage purification, the most advantageous is the coagulating agent obtained from raw waste sulphite liquors by means of membrane methods. A disadvantage of the coagulating agent obtained from vanillin lignin lies in the large doses (even if compared with klutan) and the troublesome sediment resulting from the dissolving of vanillin lignin in sodium carbonate solution. Nowadays, however, due to economical and technical reasons a more expedient coagulating agent for prompt application to industry seems to be vanillin lignin. The lignosulphonate coagulant obtained from raw waste sulphite liquors may be considered as applicable in future.

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WYKORZYSTANIE ODPADOWYCH LIGNOSULFONIANÓW DO PRODUKCJI KOAGULANTÓW STOSOWANYCH W ODZYSKU BIAŁKA ZE ŚCIEKÓW Z RZEŹNI

Przedstawiono przygotowanie koagulantów lignosulfonianowych i ich zastosowanie w koagulacji ścieków z rzeźni. Koagulanty otrzymano z surowego ługu posiarczynowego za pomocą metod membranowych i z ligniny wanilinowej stosując jej roztwór w wodorotlenku lub węglanie sodu. Koagulanty lignosulfonianowe charakteryzowały się większą wydajnością podczas strącania białek i tłuszczów ze ścieków niż klutan, który jest obecnie stosowany do tego celu.

ИСПОЛЬЗОВАНИЕ ОТХОДНЫХ ЛИГНОСУЛЬФОНАТОВ ДЛЯ ПРОИЗВОДСТВА КОАГУЛЯНТОВ ПРИМЕНЯЕМЫХ В ВОЗВРАТЕ БЕЛКА ИЗ СКОТОБОЙНЫХ СТОКОВ

Представлено подготовление лигносульфоновых коагулянтов и их применение для коагуляции скотобойных стоков. Коагулянты получено из сырового отработанного сульфитного щёлка с помощью мембранных методов, а также из ванилинного лигнина применяя её раствор в гидроокиси или в карбонате натрия. Лигносульфоновые коагулянты характеризуются большей эффективностью во время осажцения белков и жиров из стоков чем клютан применяемый ныне с той целью.