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Biological Reduction of Sulphates in Purification of Wastes from the Alcohol Industry

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Abstract

Sulphate-reducing bacteria from the genus *Desulfotomaculum ruminis* were applied for biological purification of wastes from the alcohol industry. Optimum conditions were established for conducting the desulfurication process (temperature, pH, sulphates and phosphates concentrations) at which the maximum decrease in COD of 68.5% and sulphate reduction by 84% were achieved.

Keywords: bacteria, *Desulfotomaculum ruminis,* desulfurication, wastes from the alcohol industry

Introduction

Waste products from fermentation lines in the alcohol industry processing starch and molasses are difficult to neutralize, and thus troublesome to deal with [1, 2]. The exact composition of the wastes depends on the raw products used for fermentation, but never can they be released directly into rivers or to the sewage system [3]. The problem of their utilization has been hitherto solved only locally and sporadically [4] and as yet no proposals have been made.

The molasses brew is unsuitable for use in agriculture [2, 4] to fertilize the soil, not only because of the cost of transportation and condensation but because of the chemical composition - it contains compounds which decompose, releasing toxic pollutants. Some of the polluting elements are accumulated in plants, which consequently loose their worth as potential fodder [5]. The recovery of salts from the wastes and their use in production of fodder yeast is simply not economical [2],

The molasses brew leaving the distillation apparatus is a very thin solution which can be used as a source of carbon and energy in the process of desulfurication. In this process the bacteria oxidize organic compounds to carbon dioxide and simple organic acids using waste sulphates as electron acceptors. So desulfurication, proposed for purification of some industrial wastes [6, 7, 8], may also be used to utilize wastes from the alcohol industry.

In the process of desulfurication, the bacteria oxidize organic compounds and use the energy released to support physiological functions. The sulphates play the role of respiratory substrate and are reduced to hydrogen sulphide which can precipitate metals from the wastes or can be biologically oxidized [9].

The reported attempt to use desulfurication to purify alcohol industry wastes was undertaken as a preliminary step for development of the tower method, an alternative to expensive conventional biological methods which require large areas for biological purification plants. The using of the tower method will enable easier control of the parameters of the process and maintenance of the optimum physical and chemical parameters of the homogenized wastes introduced into the tower with the active medium saturated with the bacteria-reducing sulphates, as well as easier separation of the precipitate from purified wastes.

This paper reports preliminary results on the microbiological method of alcohol industry waste purification applied to waste from the plant in Kofaczkowo with the use of bacteria from the genus *Desulfotomaculum ruminis.*

Materials and Methods

Micro-organisms

Desulfotomaculum ruminis bacteria were isolated from the soil at a site near Poznan and grown in anaerobic conditions (helium) in Starkey medium [10] at 37ºC, pH from 6.8 to 7.2, and C/S = 9.3.

Wastes Tested and Kinetics of the Process of Desulfurication

The waste tested was the brew obtained from fermentation of molasses or a mixture of molasses with rye, from the Alco PEGRO plant in Kołaczkowo, near Gniezno. The chemical composition of the waste is given in Table 1.

The raw waste after decantation in a decanter and removal of about 2% of the precipitate was placed into a homogenizing vessel, enriched with the components necessary for optimisation of the process of desulfurication, and its pH was adjusted to 6.8-7.2. In order to obtain the optimum concentration of sulphates established earlier [11], ferrous sulphate was added to the molasses - rye waste in the amount of 7.09 g/dm^3 (2.45 g SO_4^{2-}/dm^3), while to the molasses waste in the amount of 0.86 g SO_4^{2-}/dm^3 (2.49 $FeSO_4$ x $7H_2O$/dm^3). Moreover, because of a low concentration of phosphates, the molasses waste was enriched with an additional 4.80 g K_2HPO_4/dm^3 (2.62 g PO_4^{3-}/dm^3). The corrected wastes in the amount of 15 cm^3, were introduced into reactors of 20 cm^3 capacity, inoculated with 4% vol. of the innoculum taken each time from the active bacteria culture and the reactors were placed in a heater at 37ºC.

The degree of purification was evaluated by COD measurement after completion of desulfurication.

The reaction rate was estimated from measurements of the degree of microbiological reduction of sulphates at certain time intervals. The results presented are mean values from at least three measurements.

Analytical Methods

To measure the current concentration of hydrogen sulphide, it was absorbed in cadmium acetate and then the amount of precipitated CdS was established by the iodometric method [12].

Table 1. Characterization of the alcohol industry wastes studied.

Component	Molasses-rye waste (20% of rye and 80% of molasses)	Molasses waste
COD [mgO_2/dm^3]	46052	71539
pH	3.48	4.15
d [g/cm^3]	1.035	1.029
C [%]	39.40	34.95
N [%]	3.90	4.34
H [%]	5.99	6.19
K [g/dm^3]	25.0	25.0
Ca [g/dm^3]	0.95	0.92
Na [g/dm^3]	0.75	0.90
Mg [g/dm^3]	0.18	0.90
protein [g/dm^3]	7.9	10.1
SO_4^{2-} [g/dm^3]	0.1395	0.4335
PO_4^{3-} [g/dm^3]	1.316	0.106
precipitate (dry mass) [g/dm^3]	21	21

COD - the index indicating the content of organic pollutants - was determined by the closed reflux titrimetric method [13] in which the organic matter is oxidized in an acidic environment (H_2SO_4) under the effect of potassium dichromate at 150°C. The samples were titrated with a named solution of the Mohr salt in the presence of ferroine sulphate.

The concentrations of potassium, calcium, sodium and magnesium were determined by the spectrophotometric method (Beckman DU 640, λ =700 nm) [14].

The concentration of sulphates was determined by the weight method [15], and that of proteins by the Lowry method [16].

Results and Discussion

As follows from the chemical composition of wastes studied (Table 1), the optimum course of desulfurication requires their modification by increasing the concentration of sulphates and phosphates [11, 17]. The preliminary enriched wastes were subjected to microbiological anaerobic desulfurication. In general, the process runs as follows:

$$\underset{\text{org substrate}}{(C, O, N, P)} + \xrightarrow{\text{bacteria}} S^{2-} + CO_2 + COO^- + NH_4^+ PO_4^{3-}$$

According to the results presented in Fig. 1 and Table 2, the degree of reduction of sulphates in the modified molasses waste after the first cycle of desulfurication was 56.97%, while COD decreased by only 6.90%. After the repeated correction of pH, the concentration of sulphates and phosphates was again inoculated with the pure bacteria culture and in the second cycle the concentration of sulphates decreased by 82.75% and COD decreased by 14.82%. The procedure was repeated for the third time and after the third cycle the concentration of sulphates decreased by 80% and COD decreased by 43.48%. Eventually, after the three cycles of desulfurication conducted in static condi-

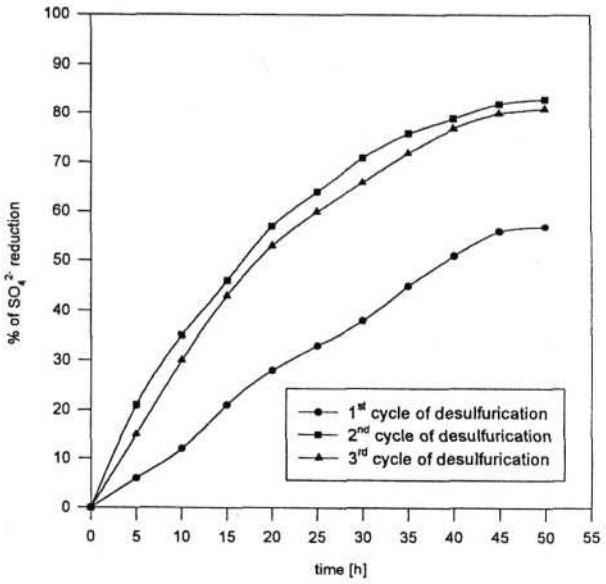

Fig. 1. Kinetic curves illustrating the degree of reduction of sulphates in the process of desulfurication in molasses waste run with the use of *Desulfotomaculm ruminis* bacteria.

Table 2. Results of the studies on the degree of reduction of COD and the concentration of sulphates and phosphates in the process of desulfurication conducted in molasses waste with the use of *Desulfotomaculum ruminis* bacteria.

Parametr	Raw waste	Corrected waste	Waste after 1st cycle of desulfurication	Waste after 2nd cycle of desulfurication	Waste after 3rd cycle of desulfurication	% of reduction
temp. [°C]	–	32-37	32-37	32-37	32-37	–
COD [mgO_2/dm^3]	71539	70936	66044	56258	31798	55.55
SO_4^{2-} [g/dm^3]	0.4335	1.2938	0.5568	0.2232	0.2586	73.24
PO_4^{3-} [g/dm^3]	0.1060	2.7250	1.2830	1.3756	1.3215	51.50
retention time [h]	–	–	50	50	50	–

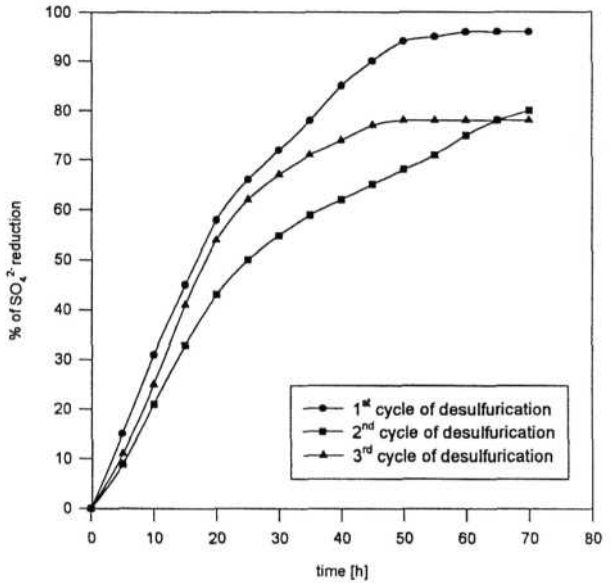

Fig. 2. Kinetic curves illustrating the degree of reduction of sulphates in the process of desulfurication in molasses-rye waste run with the use of *Desulfotomaculm ruminis* bacteria.

tions the concentration of sulphates decreased on average by 73.24%, COD decreased by 55.55%, and the concentration of phosphates decreased by 51.50%.

In the case of the modified molasses-rye waste (Fig.2, Table 3), after the first cycle of desulfurication the degree of reduction of sulphates to sulphides was 95.35%, while COD decreased by 31.11%. After the correction of pH and composition of the waste, in the second cycle of desulfurication the concentration of sulphates decreased by 80.03% and COD decreased by 7.43%. In the third cycle the corresponding values were 76.57% and 45.32%. After the three cycles, the concentration of sulphates decreased on average by 83.98%, COD decreased by 68.47% and the concentration of phosphates was reduced by half.

The results obtained are promising and indicate that the process of desulfurication can be used for purification of alcohol industry wastes. To ensure process efficiency, the chemical composition of the wastes must be modified by the addition of sulphates and phosphates, and its temperature must be kept near 33°C. The wastes left after the process of desulfurication can be further safely utilized; the precipitate left after decantation together with the biomass left

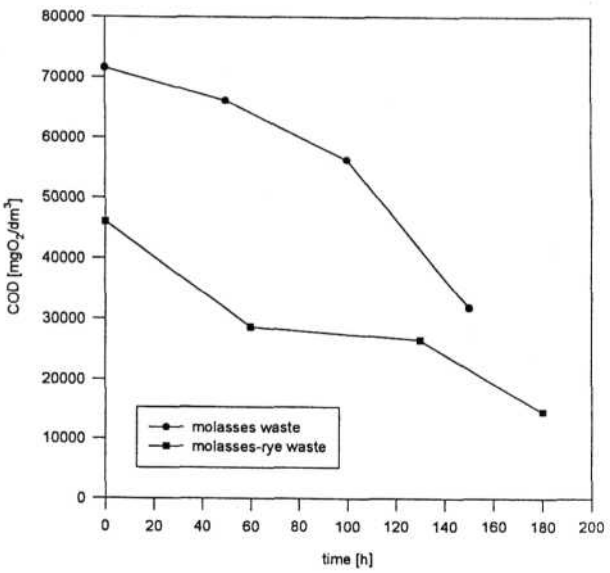

Fig. 3. The degree of reduction of COD in the alcohol industry wastes obtained as a result of desulfurication with the use of *Desulfotomaculm ruminis* bacteria.

Table 3. Results of the studies on the degree of reduction of COD and the concentration of sulphates and phosphates in the process of desulfurication conducted in molasses-rye waste with the use of *Desulfotomaculum ruminis* bacteria.

Parametr	Raw waste	Corrected waste	Waste after 1st cycle of desulfurication	Waste after 2nd cycle of desulfurication	Waste after 3rd cycle of desulfurication	% of reduction
temp. [°C]	–	32-37	32-37	32-37	32-37	–
COD [mgO_2/dm^3]	46052	41640	28687	26555	14520	68.47
SO_4^{2-} [g/dm^3]	0.1395	2.5875	0.1203	0.5166	0.6063	83.98
PO_4^{3-} [g/dm^3]	1.3160	1.3160	1.2139	1.0614	0.6559	50.16
retention time [h]	–	–	60	70	50	–

after desulfurication can be used as components of fertilizers of, e.g. lawns [18]. The hydrogen sulphide can be used for production of metal sulphides (pigments) or, after absorption in acidified solution of ferric sulphate it can be oxidized to elementary sulphur [19]:

$$H_2S + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + H_2SO_4 + S$$

which is easily removable from the solution.
The acidified solution of ferrous sulphate after biooxidation [20]:

can be recycled to oxidize H_2S and then used in the desul-

$$2FeSO_4 + H_2SO_4 + 0.5\ O_2 \xrightarrow{\text{Thiobacillus ferrooxidans}} Fe_2(SO_4)_3 + H_2O$$

furication process [19].

The studies aiming to increase the degree of purification to finally obtain water meeting the standards for municipal use are continued. The solution considered is conduction of the process in a two-stage system: the chemical one (of precipitate formation) and the biological one (based on the tower method) with the active medium containing the sulphate reducing bacteria [17].

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