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Application of membrane and natural coagulants for stillage purification

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ABSTRACT

Wastewater that remains after bioethanol production (stillage) is a major problem from the viewpoint of environmental protection. Besides the large volume, stillage contains high amounts of organic matter, suspended solids, dead yeast cells and their metabolites, so it should not be disposed in the recipient without previous treatment. In this work the possibility of usage of microfiltration for stillage purification was investigated. Also, the application of natural coagulants was investigated, in order to increase the efficiency of microfiltration for stillage treatment. Results obtained after microfiltration showed chemical oxygen demand (COD) reduction of 35% while the combined use of natural coagulants and microfiltration achieved 50% of COD reduction compared to the initial value. Many published works confirmed the activity of natural coagulants on model water but just few of them investigated the activity of natural coagulants in real samples of waters and wastewaters, which makes this paper significant.

Keywords: Microfiltration; Natural coagulants; Distillery wastewater

1. Introduction

In recent years biofuels have been attracting worldwide attention of scientists, industrialists and governments of many countries. Such attention is mainly motivated by several factors: (1) the increasing demand for limited non-renewable energy resources [1,2], and recognition that the global reserves of these resources are exhausting faster than previously predicted [3], (2) the rising oil prices, (3) concern about fuel emissions (i.e. greenhouse gasses) which lead to many environmentally negative effects [4], (4) the requirements of the Kyoto Protocol, (5) the rural sector development [2], and (6) the necessity to reduce imported oil reliance, and thus save economical and political independence [5], and reduce trade deficits. Bioethanol, both a clean and renewable combustible, is believed to be a good alternative to replace oil and expected to play a more significant role in the future [6–9]. Although the energy equivalent of bioethanol is much lower than that of petroleum, the bioethanol combustion is more efficient and cleaner because of the oxygen content [8,10]. As a consequence, the emission of toxic substances is reduced [11]. Bioethanol production worldwide has strongly increased since the oil crises in the 70s of the twentieth century

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[12,13], and in the last years it is the main biofuel used in the world. The worldwide prognoses are the further increase of the production and consumption of bioethanol.

Stillage is a main liquid waste generated during bioethanol production, whose characteristics are highly variable and dependent on feedstocks and various aspects of the bioethanol production process. Distillery wastewaters are extremely polluted—they have high biological oxygen demand (BOD), chemical oxygen demand (COD) and high BOD/COD ratio, and they also contain inorganic substances such as potassium, phosphates, nitrogen, calcium and sulphates. Pollution caused by them is one of the most critical environmental issues. High COD and high nutrient content of the effluent may result in eutrophication of natural waters, while inappropriate disposal of effluent on the soil affects the groundwater quality by altering its physico-chemical properties and leading to significant levels of soil pollution and acidification. Dark brown polymers, called melanoidins, which are constituents of molasses distillery wastewaters are toxic to aquatic organisms and many microorganisms since they have antioxidant properties. The highly coloured compounds of this wastewater block out sunlight penetration in rivers, lakes or lagoons, hence decreasing both photosynthetic activity and dissolved oxygen concentration and affecting aquatic life [14].

Different treatment approaches, based on biological and various physico-chemical methods, have been introduced for the treatment of stillage. Some of them are: a combination of anaerobic and aerobic biological treatment, fungal, bacterial and algal treatment, adsorption, coagulation and flocculation and oxidation processes, nanofiltration, reverse osmosis, ultrasound and different combinations of these methods.

As costs of wastewater treatment are getting higher it is necessary to develop new techniques, or combinations of techniques for wastewater purification, that will allow their reuse and recycling of valuable matters that can be found in waste flows.

Stillage treatment usually consists of suspended solids removal with decanter or centrifuge followed by anaerobic and aerobic treatments. Although the biological treatment process has several advantages such as an easy access and a large scale operation, the major drawbacks of the process are its high energy consumption (30% of the total energy), high labour costs, and large variations of the treatment efficiency with the change in the raw materials used for the ethanol fermentation [15]. Coagulation and flocculation are also commonly used methods of removing particulates and organic matter from wastewaters. They are usually conducted by adding chemicals such as salts of aluminium and iron and polyelectrolytes. This way the remaining sludge cannot be used as an addition to fertilizers or feed, since it contains high concentrations of coagulants and flocculants, which are potentially harmful on human and animal health [16–19].

Natural coagulants, which are intensively investigated in the last decades, are considered as non harmful and efficient, and besides, the resulting biodegradable sludge can be simply anaerobically treated and disposed in the nature without any adverse influence [20–24].

Membrane processes offer an additional possibility to improve the quality of treated wastewater, and to achieve effluent discharge limits. In this work the possibility of application of coagulation by natural coagulant extracted from the common bean and crossflow microfiltration as a combined treatment process for stillage purification was investigated.

2. Materials and methods

2.1. Natural coagulant preparation

Natural coagulant was obtained in the following way: common bean seeds were ground and sieved through the sieve with pore size of 0.4 mm. An amount of a 50 g/L of the smaller fraction was suspended in distiled water. This suspension was stirred 10 min on a magnetic stirrer in order to extract active coagulant. After that, the suspension was filtered through the filter paper Macherey-Nagel MN 651/120. Obtained filtrate was stored in a refrigerator at +4°C, and used as a natural coagulant.

2.2. Coagulation tests and coagulation process

At first, in order to determine the optimal pH of stillage and the optimal dose of coagulant for coagulation process, coagulation tests were performed. The coagulation activity was assessed by jar test using wastewater obtained after bioethanol production. pH values of wastewater were adjusted to 6 or 9 by adding 33% NaOH just before performing coagulation tests. Jar tests were carried out by adding different amounts of extract to 200 mL of wastewater. After fast stirring at 200 rpm for 1 min in order to disperse the coagulant, it was continued with slower stirring at 60 rpm for 30 min in order to promote the flocculation of the suspended and colloidal particles present in the wastewater, and after that systems were left for 1 h for sedimentation. The same coagulation test was conducted with no coagulant as a blank. After sedimentation for 1 h, residual COD was determined in upper clarified liquid and coagulation activity was calculated.

$$\text{Coagulation activity (CA) (\%)} = (\text{COD}_b - \text{COD}_s) \times 100/\text{COD}_b \quad (1)$$

where COD_b and COD_s are the COD of the blank and the sample, respectively.

When optimal pH and coagulant dose were determined, two coagulation experiments followed by microfiltration, were performed. In the first experiment, pH of stillage was adjusted to optimal by adding 33% NaOH, and optimal dose of coagulant was added to 600 mL of stillage. After fast stirring at 200 rpm for 1 min, it was continued with slower stirring at 60 rpm for 30 min. Immediately after that, microfiltration of stillage was carried out. In the second coagulation experiment, after adjusting of pH of stillage to optimal value by adding 33% NaOH, optimal dose of coagulant was added to the stillage, and the same procedure of stirring was accomplished. After that the system was left for 1 h and sedimentation and microfiltration were carried out with the upper clarified liquid.

2.3. Analytical methods

Stillage and permeate samples obtained after microfiltration of stillage, microfiltration of stillage after addition of coagulant and microfiltration of clarified liquid after coagulation and sedimentation were analysed for dry matter, ash, organic dry matter, suspended solids, COD and total nitrogen according to Standard Methods [25].

2.4. Microfiltration experiment

The experiments were carried out in a laboratory cross-flow microfiltration unit (Fig. 1). The feed was circulated by a peristaltic pump (ISMATEC, Switzerland), in condition of complete recirculation of the fluid. The feed suspension was concentrated to volume concentration factor of 1.88. The permeate was constantly drained away from the system, collected and analysed. The transmembrane pressure difference was adjusted by the regulation valve. The inlet and outlet pressures of the membrane module were measured by two pressure gauges. The average of these two pressure values gave the value of transmembrane pressure as the outside of the membrane is vented to the atmosphere. The membrane module used was a MembraloxTM 1T1-70 module (SCT, Bazet, France). The single channel ceramic membrane used had a nominal pore size 200 nm (TAMI Deutschland) with the length of 250 mm and inner/external diameter of 6/10 mm. The useful membrane surface was $4.33 \times 10^{-3}\,m^2$. The membrane was cleaned according to the recommendation of the manufacturer before each experiment; the cleaning sequence was a classical acid–base one. All experiments were carried out at the room temperature (25°C).

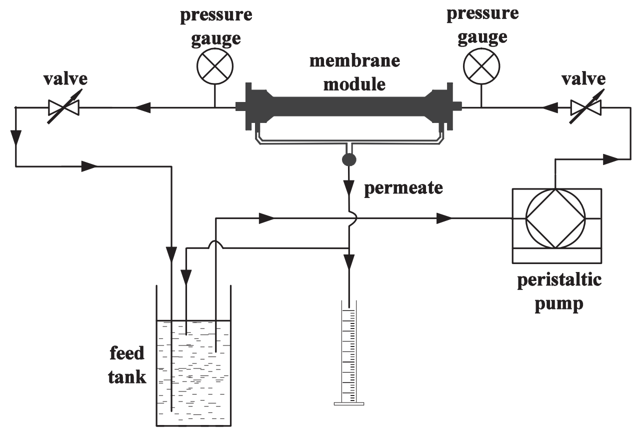

Fig. 1. Scheme of laboratory apparatus for cross-flow microfiltration [26].

3. Results and discussion

3.1. Stillage characteristics and direct microfiltration treatment

Analyses of stillage were conducted immediately after it was brought from the factory. Results of analyses are presented in Table 1. As can be seen from Table 1, stillage had high COD value. Dry matter and total nitrogen content were also high. About 29% of

Table 1
Results of analyses of stillage and permeate

Parameter	Stillage	Permeate
Dry matter (mg/L)	63,700	52,362
Ash (mg/L)	9,640	16,637
Organic dry matter (mg/L)	54,060	35,725
% of organic dry matter ($\%_{DM}$)	85	68
Suspended solids (mg/L)	18,340	–
Ash of suspended solids (mg/L)	1,165	–
Organic dry matter of suspended solids (mg/L)	17,175	–
% of organic dry matter of suspended solids (%)	94	–
COD (mgO_2/L)	102,000	65,964
Total nitrogen (mg/L)	2,866	1,480

dry matter was in form of suspended solids. Based on presented results it can be concluded that stillage was highly polluted. Further in the experiment stillage was passed through the membrane for microfiltration. Obtained permeate was also analysed (Table 1).

Based on these results it can be said that COD in the permeate was decreased compared to initial value in the stillage. Removal efficiency was about 35%. Dry matter content was lower by about 18%, and total nitrogen content by about 48%. Suspended solids were completely removed from the stillage.

3.2. Coagulation tests

Coagulation tests were performed in order to determine the optimal pH of stillage and the optimal coagulant dose. pH values 6 and 9 were chosen to perform coagulation tests. Applied coagulant doses were: 0.5, 2, 5, 10, 20 and 30 mL/L. Calculated coagulation activities (CA) are presented in Table 2.

Considering the results presented in Table 2, it can be concluded that pH 6 was inappropriate for coagulation since coagulation activity was negative at almost all applied doses of the coagulant. This means that COD was higher in treated samples than in blank. The explanation for this is that, at this pH, the coagulant, which is of organic nature, remained in upper phase and hence increased the COD. pH 9 showed as more appropriate for coagulation. The highest CA was achieved at applied coagulant dose of 30 mL/L, but considering the fact that just a little bit lower CA was obtained at significantly lower coagulant dose (10 mL/L), this dose was chosen for further experiments.

3.3. Coagulation and microfiltration

In the second part of the experiment the combined use of the natural coagulant and microfiltration was investigated. At first, microfiltration of stillage, with added optimal dose of coagulant at optimal pH, was done. Results of the analyses of the obtained permeate are presented in Table 3.

Table 2
CA of common bean extract at pH 6 and 9

Coagulant dose (mL/L)	CA (%) at	
	pH 6	pH 9
0.5	−2.11	0.79
2	1.41	8.90
5	−3.29	3.94
10	−0.70	16.14
20	−1.88	16.54
30	0.47	18.11

Table 3
Results of the analyses of the permeate obtained after microfiltration of stillage with added optimal dose of coagulant, with no sedimentation before microfiltration

Parameter	Stillage	Permeate
Dry matter (mg/L)	63,700	52,025
Ash (mg/L)	9,640	18,850
Organic dry matter (mg/L)	54,060	33,175
% of organic dry matter ($\%_{DM}$)	85	64
Suspended solids (mg/L)	18,340	–
Ash of suspended solids (mg/L)	1,165	–
Organic dry matter of suspended solids (mg/L)	17,175	–
% of organic dry matter of suspended solids (%)	94	–
COD (mgO_2/L)	102,000	66,924
Total nitrogen (mg/L)	2,866	1,505

As can be seen from the presented results removal efficiency of COD, dry matter and total nitrogen was similar to the efficiency of microfiltration of the stillage without the addition of coagulant.

After that microfiltration of the clarified liquid obtained after coagulation and sedimentation was carried out. Permeate was analysed and results are shown in Table 4.

As can be seen from Table 4, COD value was lower by about 50% compared to initial value in the stillage. Dry matter content was lower by about 25%. Total nitrogen content also decreased compared to the stillage; removal efficiency was about 52%.

Table 4
Results of analyses of permeate obtained after microfiltration of stillage with added optimal dose of coagulant, with sedimentation before microfiltration

Parameter	Stillage	Permeate
Dry matter (mg/L)	63,700	47,500
Ash (mg/L)	9,640	17,500
Organic dry matter (mg/L)	54,060	30,000
% of organic dry matter ($\%_{DM}$)	85	63
Suspended solids (mg/L)	18,340	–
Ash of suspended solids (mg/L)	1,165	–
Organic dry matter of suspended solids (mg/L)	17,175	–
% of organic dry matter of suspended solids (%)	94	–
COD (mgO_2/L)	102,000	51,090
Total nitrogen (mg/L)	2,866	1,365

4. Conclusions

Based on performed experiments and presented results it can be concluded that using of natural coagulants for improving the efficiency of microfiltration of stillage was satisfactory. Reduction degree of COD, total nitrogen and dry matter was higher with the application of natural coagulants and sedimentation as a pretreatment for microfiltration, compared to direct microfiltration of stillage. Also it can be said that the addition of natural coagulants in the stillage (without sedimentation) and its microfiltration did not give significant results. Considering a pore size of microfiltration membrane, it cannot be expected to remove all organic pollution from wastewater, but it can be reduced significantly.

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