Effect of Inorganic Coagulants on the Characteristics in Anaerobic Digested Distillery Stillage Valorization †

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Abstract: The aim of the study was to determine the possibility of using coagulation for treatment of anaerobically digested distillery stillage. Post-fermentation sludge from waste product of bioethanol production is usually drained. Then, condensed sediments are directed as a fertilizer for arable fields. The remaining liquid phase due to the high content of organic compounds cannot be discharged to environment. The study used inorganic salts of iron and aluminum as coagulants to treatment liquid fraction obtained after methane fermentation of distillery stillage. In valorization process, the reduction of organic compounds and suspended solids was not sufficient. The highest doses of coagulants reduced COD concentration of about 80% and lower the pH of the solution. However, the dose 10 mL/L is not economically profitable and due to concentration of aluminum or iron it is too harmful for environment.

Keywords: coagulation; anaerobic leachate; distillery stillage

1. Introduction

Depleting fossil fuel resources have increased interest in renewable sources of energy. The most popular among biofuels is bioethanol. In 2015, the bioethanol global production reached the level of 98 billion liters. Distillery stillage is the main waste product of bioethanol production. Inappropriate disposal of the stillage leads to pollution of soil, surface- and ground-waters. The bioethanol production sector faces noticeable challenges, as awareness regarding the environmental impacts caused by the uncontrolled disposal of stillage grows.

Approximately 13 L of stillage per every L of bioethanol is produced in the bioethanol process. [1]. Distillery stillage is characterized by complex composition, high BODs values and low pH value, its disposal is a serious environmental problem [2]. Depending on the raw material used to produce bioethanol, concentration of COD of stillage ranges from 10 g O2/L [3,4] to more than 100 g O2/L [5]. They also contain substances such as potassium, phosphates, nitrogen, calcium and sulphates [6,7]. The stillage has relatively low sugar content, mainly glucose, but on the other hand, it contains residues of degraded yeast cells, so it could be considered a good nitrogen source [8].

Since stillage contains many valuable ingredients, it is used as fodder, as a base for further microbiological production (for example biogas), as a fertilizer, etc. [9]. The stillage can be processed as a whole or it is screened or centrifuged to produce thin stillage and wet distillers’ grain. Separation of wastewaters to tin and concentrated fractions gives new possibilities of their uses [10].

Coagulation and flocculation are the essential processes used for the removal of particulates and organic matter from wastewaters, and are usually conducted by adding chemicals such as salts of aluminum and iron and polyelectrolytes. Coagulation is a chemical process that involves
neutralization of charge whereas flocculation is a physical process and does not involve neutralization of charge. Coagulation itself results in the formation of floc but flocculation is required to help the floc further aggregate and settle.

The proposed solution for management of post-fermentation effluent from fermentation tank with distillery stillage is to use coagulation. Post-fermentation sludge from biogas plants is usually drained. Then, condensed sediments are directed as a fertilizer for arable fields. The remaining liquid phase due to the high content of organic compounds cannot be discharged to environment. The study used inorganic salts of iron and aluminum as coagulants to treatment liquid fraction obtained after methane fermentation of distillery stillage.

2. Material and Methods

The study involved the use of liquid leachate from drainage of post-fermentation sludge. The characteristic of anaerobic digested distillery stillage is presented in Table 1. Four kinds of coagulants with commercial names of PIX 111—iron (III) chloride solution ((Fe) 13.4 ± 0.6%, (Fe²⁺) max 0.3%), PIX 123—iron (III) sulfate solution ((Fe) 12.6 ± 0.3%, (Fe²⁺) max 0.7%), PAX 16—aluminum polychloride solution (Al₂O₃ 16%) and PAX XL 19H—aluminium polychloride solution (Al₂O₃ 23.6%) were used. The coagulant dosage ranged from 25 to 400 μL/L. Anaerobic digested distillery stillage samples were stirred with coagulants at 400 rpm for 1 min, then the mixing speed was reduced to 80 rpm for 5 min for flocculation. The sedimentation phase lasted 30 min.

| Indicator      | Unit       | Value     |
|----------------|------------|-----------|
| pH             |            | 7.8       |
| COD            | mg O₂/L    | 8365 ± 23 |
| Total nitrogen | mg Ntot/L  | 1688 ± 88 |
| Total phosphorus| mg P-PO₄/L| 192 ± 13  |
| Total solids   | mg/L       | 7115 ± 102|

COD concentrations were measured with cuvette testes (Hach Lange USA, Loveland, CO, USA) and spectrophotometer UV/VIS (DR 5000). The pH was measured with multiparameter (Hach Lange HQ 440D).

3. Results and Discussion

Usually higher COD removal was achieved with aluminum-contained coagulants. However, the highest COD reduction was achieved with the use of the coagulant PIX 111 in a dose of 300 μL/L (Figure 1). The COD concentration in valorized solution reached 5527 ± 106.82 mg O₂/L. As valorization process ensured only 34% reduction in COD, in the subsequent studies higher coagulant doses were used, ranged from 0.8 mL/L to 10 mL/L of digestate.

![Figure 1. Efficiency of COD removal by coagulation with PIX 111, PIX 123, PAX 16, PAX 19H in the dose ranged from 25–400 μL/L.](image-url)
Using PIX 111 with a dose of 10 mL/L, COD concentration in coagulated liquid fraction of digestate of 1480 ± 132.14 mg O₂/L was achieved. In turn, the same dose of PIX 123 and PAX 16 ensured COD reduction to the level of 2000 mg O₂/L (Figure 2.). The lowest COD removal was noted during the coagulation with PAX XL 19H. Despite high efficiency of COD removal with a dose of coagulant of 10 mL/L, the process is economically unprofitable. This dose of coagulant also introduce high amount of aluminum/iron in the obtained sludge.

![Figure 2](image)

**Figure 2.** Efficiency of COD removal by coagulation with PIX 111, PIX 123, PAX 16, PAX XL 19H in the dose ranged from 0.8 to 10 mL/L.

The coagulation of liquid fraction from methane fermentation of distillery stillage influenced on the pH values in the obtained solution. The use of high doses of inorganic coagulants resulted in a significant decrease in pH of the valorized digestate (Figure 3).

![Figure 3](image)

**Figure 3.** pH during coagulation in the doses of coagulants from 25 to 400 μL/L.

The use of the coagulation process appears to be ineffective for treatment of liquid fraction from methane fermentation of distillery stillage. Organic matter removal was low, even at high dosages of coagulants it was not sufficient. Moreover, coagulation generated large amounts of solids difficult to remove via gravity sedimentation. The color of the anaerobic digested distillery stillage was removed slightly.

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