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The Use of Natural Mineral Sorbents (Zeolite, Bentonite, Halloysite) for Decolorization of Corn-sugar Beet Molasse's Vinasse

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1. Introduction

The molasse's vinasse (beet and cane) is one of the most difficult to neutralize wastewater because it has a low pH, high temperature, dark brown color and contains large amounts of ash (ash) and dissolved organic and inorganic substances (Pant and Adholeya 2007). The molasse's vinasse is a dark brown, viscous liquid with a characteristic, pungent and unpleasant odor and acidity (pH 3.5) (Wagh and Nemade 2015). It is wastewater with a high biological oxygen demand (BOD_5) of 45-100 g/dm^3 and chemical oxygen demand (COD) of 90-210 g/dm^3 (Mane et al. 2006).

The presence of three groups of colored compounds, i.e., melanoidins, hexose alkaline degradation products (HADP) and sucrose caramelization products (Bharagava and Chandra 2010, Chandra et al. 2008, Mane et al. 2006) give the color of the vinasse. The caramel and melanoidins are responsible for 80% for the color of beet juice, and thus the sugar beet molasse vinasse (Coca et al. 2004, Satyawali and Balakrishnan 2007). The antioxidant properties of these compounds cause the vinasse to be toxic to many microorganisms associated with wastewater treatment and the aquatic environment (Sirianuntapiboon et al. 2004). The utilization of the vinasse by pouring on the arable fields is dangerous for plant vegetation. It reduces soil alkalinity and reduces the availability of manganese, inhibiting seed germination. It also affects the quality of groundwater, causing a change in their physicochemical properties. The high COD value of the vinasse and the high content of total nitrogen and phosphate in vinasse may, in turn, lead to the eutrophication of natural waters (Mohana et al. 2009).

Color compounds must be removed from the vinasse before it is discharged into the natural environment (Onyango et al. 2011), because it may cause a decrease in the activity of plant photosynthesis (Pazouki et al. 2008). Color compounds are resistant to conventional biological treatment methods ((aerobic and anaerobic), anaerobic digestion, anaerobic lagoon, activated sludge process), which do not allow complete removal of the color from the waste stream (Yadav and Chandra 2018). During these processes, there may even be an increase in color due to the repolymerization of melanoidins (Pena et al. 2003). Conventional vinasse purification methods achieve melanoidin degradation by about 6-7%. It is, therefore, necessary to apply an additional decolorization process for molasse vinasse. Physicochemical methods are often used for this purpose (Mohana et al. 2009). To remove the colorants from the vinasse there are used different methods with different success: adsorption (Ojijo et al. 2010), coagulation (Liang et al. 2009), UV/H_2O_2 oxidation (Dwyer and Lant 2008; Reis et al. 2019), electrochemical methods (Kobya and Delipinar 2008), ozonation (Coca et al. 2007), membrane techniques (Apollo et al. 2014, Satyawali and Balakrishnan 2008), reverse osmosis (Silva et al. 2019) and evaporation (Liakos and Lazaridis 2016).

Among the physicochemical methods for decolorization and removal of organic pollutants, adsorption on activated carbon is very often used due to its actively developed surface, microporous structure, high adsorption capacity and a high degree of surface reactivity (Satyawali and Balakrishnan 2007). Both commercially available activated carbon, as well as specially prepared types such as those made from sugar cane expeller, were used in the research (Onyango et al. 2011). The use of activated carbon to remove color compounds from vinasse is expensive due to the high price of the sorbent itself and the necessary reagents (Coca et al. 2005). Therefore, there is a need for further research to develop materials that will be efficient, cheap and effective in decolorizing the vinasse (Onyango et al. 2011).

Previous studies on decolorization in most cases concerned mainly sugar cane molasse's vinasse (Pant and Adholeya 2007). There are few references to the decolorization of sugar beet molasse's vinasse with the use of natural sorbents (Krzywonos and Szymańska 2011). There is no study on the use of these sorbents for the decolorization of corn-sugar beet molasse's vinasse (CBMV).

The work aimed to remove color compounds from corn-sugar beet molasse's vinasse with the use of five natural mineral sorbents (two types of halloysite (PJC and KR), two types of zeolite differing in grain thickness and bentonite).

2. Materials and methods

2.1. Decoction and natural sorbents

The corn-sugar beet molasse vinasse (CBMV) was from the Ruskie Piaski distillery, located in the Nielisz commune in the Lublin Voivodeship (Poland). The specificity of ethanol production technology in the Ruskie Piaski distillery consists of using sugar beet molasses and corn as raw materials.

Before use, the vinasse was filtered on paper filters to separate the solids. The supernatant was stored at 20°C.

Five natural mineral sorbents were used in the research: active halloysite KR 0-1 mm with gray color, bulk density 0,65 kg/m^3, pH = 5 to 6, (Intermark, Gliwice, Poland); halloysite PJC 0-1 mm with gray color, bulk density 0.80 kg/m^3, pH = 8 (Intermark, Gliwice, Poland); zeolite I (0.0-0.2 mm) and zeolite II (0.2-0.5 mm, gray-green color, volume density 1600-1800 kg/m^3, pH = 11 (Subio Eko, Chałupki, Poland); bentonite (0-0.056 mm) with a white-gray color, bulk density 0.8-1.0 mg/m^3, pH = 10 (Zakłady Górniczo-Metalowe "ZIĘBIEC", Starachowice, Poland).

2.2. The approach of the decolorization process

The sorbents used in the experiments (halloysite KR, halloysite PJC, zeolites I and II, bentonite) before the tests were dried at 105°C. The dose of 10 g of each sorbent was added to 100 cm^3 of vinasse in a 300 cm^3 conical flask. Each experiment was performed in duplicate. The flasks were placed in a Certomat S shaker (B.Braun Biotech International). Samples for analysis were taken every 15 minutes, and the entire experiment runs for 180 minutes at 100 rpm. The samples were centrifuged before analysis (centrifuge 3722L, Fisher Scientific) at 5000 rpm for 5 minutes. The supernatant was frozen (-20°C) and stored in this state for further analysis. The presented results are mean values from replicates.

2.3. Measurement of the decolorization removal

The decolorization removal was measured by the light absorbance at the wavelength λ = 475 nm, using a DR 5000 spectrophotometer (Hach Lange). For measurement, centrifuged and previously diluted vinasse samples were used. Decolorization (D) was calculated according to formula 1:

$$D(\%) = \frac{A_0 - A_t}{A_t} \cdot 100\% \tag{1}$$

where:
A_0 – initial absorbance,
A_t – absorbance at time t.

2.4. Analytical methods

The melanoidins, sucrose caramelization products, and hexose alkaline degradation products (HADP) was determined spectrophotometrically, using the method of Iwanow-Sapronow (Krzywonos et al. 2016; Sapronov 1963). For chemical oxygen demand (COD), total organic carbon content (TOC), total phosphate content was determined spectrophotometrically using the Hach Lange cuvette tests (Anon. 2000). The 5-day biochemical oxygen demand (BOD_5) was determined using a manometric method using the OxiTop kit (WTW). Removal of TOC, BOD_5 and phosphate phosphorus was determined only for the vinasse samples for which the highest decolorization was observed.

The content of glucose, glycerol, the content of organic acids (lactic, tartaric, succinic, pyroglutamic, acetic and isobutyric) was determined by the HPLC method. The Knauer HPLC kit was used, with refractometric and UV/VIS detectors, equipped with a Rezex ROA Organic Acids column (eluent: 2 mM H_2SO_4, flow rate: 0.5 cm^3/min). Tests were carried out at 65°C, at a wavelength of 210 nm.

The content of betaine was determined by high-performance liquid chromatography (HPLC). Knauer HPLC kit with a UV/VIS detector was used for the measurement, equipped with a Venusil SCX column. The eluent was a mixture of 5 mM H_2SO_4 + 5% methanol, and a flow rate was 1 cm^3/min. Analyses were carried out at 30°C, at a wavelength of 206 nm.

3. Results and discussion

The specificity of the ethanol production technology in the Ruskie Piaski distillery, from which the tested vinasse originated, consists of using sugar beet molasses and corn as raw materials. The dark brown vinasse was characterized by [g O_2/dm^3]: chemical oxygen demand (COD) 77.2; glycerol 21.26; lactic acid, 22.2; pyroglutamic acid 6.33; tartaric acid 5.18; succinic acid 10.6; hexose alkaline degradation products (HADP) 10.9; sucrose caramelization products 2.04; melanoidins 1.79 and betaine 25.3. The pH was 4.87, and the density was 22ºBlg.

Figure 1 shows the changes in the degree of color reduction of CBMV depending on the sorbent used.

The highest decolorization of CBMV was obtained for a sample decolorized by bentonite. For this carrier the process took place in two stages. Color removal by more than half (57%) was obtained already after 15 min and remained at this level up to 150 min. Then the decolorization increased to 74% and remained at this level until the end of the process (180 minutes). A similar two-stage process was observed for the decolorized vinasse by halloysite PJC. The reduction rate for this sorbent in the first stage was lower than in the case of bentonite and amounted to almost 50%. In 135 minutes the degree of decolorization increased but was lower than obtained for bentonite (62%). In the case of zeolites I and II, a much lower removal of colored compounds was observed, approx. 15-20% and the equilibrium was obtained after 75 minutes of shaking. When the halloysite KR was used to decolorization of vinasse, the highest decolorization (21%) was observed after 45 min. Unfortunately, in the final phase of this process (last 30 minutes), a significant increase in color was noted.

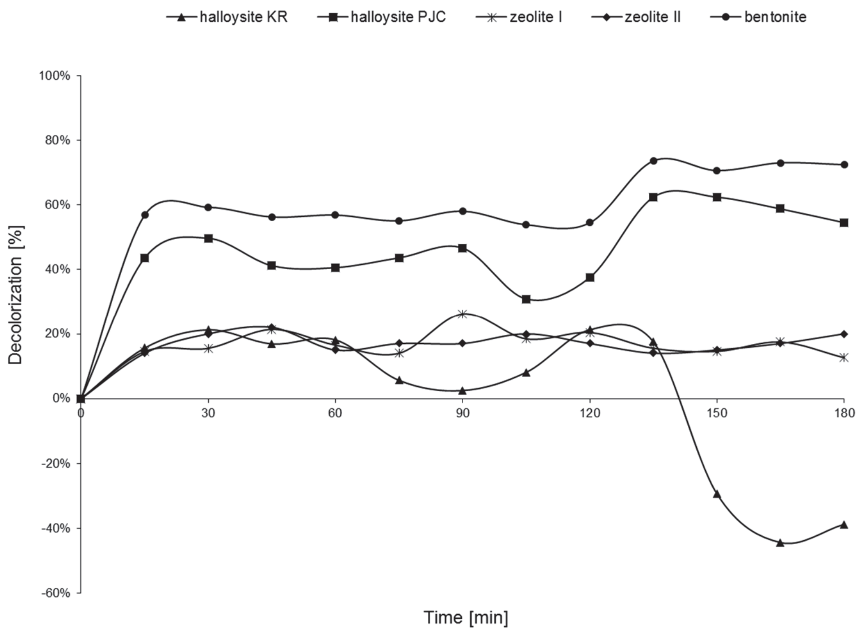

Fig. 1. Decolorization process of corn-sugar beet molasse's vinasse depending on the used sorbent

In a review of existing literature on the subject, no mention was made of the decolorization of corn-sugar beet molasse's vinasse with mineral sorbents.

When the vinasse decolorized with halloysite clay (Krzywonos and Szymańska 2011), after 0.5 hours of the process for a vinasse concentration of 5%, 25%, and 50%, the degree of decolorization was 80%, 98% and 43% respectively, while no decolorization was observed at higher vinasse concentrations. In this study, when the KR and PJC halloysite were used to decolorization corn-sugar beet molasse vinasse, a lower degree of decolorization was obtained (21% and 62% respectively). It should be emphasized that in the presented studies, experiments were carried out on an undiluted (100%) vinasse. Therefore, the used halloysite more effectively decolorized the 100% corn-sugar beet molasses vinasse than sorbents used in the studies of Krzywonos and Szymańska (2011) for decolorization of sugar beet molasses vinasse.

A high initial level of decolorization of the vinasse was observed, similar to the studies of Apollo et al. (2014), in which the natural zeolite was the carrier for the catalyst in the form of titanium dioxide. In the initial phase of the process, particles could be quickly absorbed due to a large amount of free space on the surface of the sorbent. With time, the surface of the sorbent became saturated, and the degree of decolorization stabilized in the following hours of the process. Also in the studies of Prasad and Srivastava (2009) on the use of fly ash for the decolorization of cane vinasse, color removal increased with the increase of the sorbent dose due to the greater availability of the adsorption surface. As in the presented studies, the 50% color reduction was achieved in these studies after only 15 minutes of the process. At a similar dose of sorbent (10 g per 100 cm^3 of vinasse) a degree of color removal of 91% was obtained. However, a 10% dilution of vinasse was used in these studies.

3.1. Content of colored compounds in the experiments

During the experiments, the content of colored compounds (HADP, melanoidins, and sucrose caramelization products) in the samples before and after decolorization of corn-sugar beet molasse's vinasse with the addition of all sorbents was determined (Table 1).

Table 1. The content of colored compounds and pH value of the vinasse before (0 min) and after the decolorization process (180 min) with the use of tested sorbents

		halloysite KR		halloysite PJC		zeolite I		zeolite II		bentonite	
Parameter	Time [min]	0	180	0	180	0	180	0	180	0	180
melanoidins	[g/dm^3]	3.30	3.60	3.22	1.09	3.02	2.21	2.93	2.27	3.31	1.79
HADP*	[g/dm^3]	16.80	22.70	16.50	17.98	16.90	16.20	16.35	15.18	16.86	10.90
caramels	[g/dm^3]	2.11	1.31	2.15	1.63	2.08	1.90	2.05	1.98	2.21	2.04
pH	[-]	4.87	3.55	4.82	5.18	4.87	4.92	4.86	4.93	4.81	5.09

* hexose alkaline degradation products

A slight increase in the content of melanoidins after the decolorization process was observed only for the decolorized vinasse using the KR halloysite.

In other processes, the content of this colored compound decreased (up to 46% for bentonite). On this basis, it can be concluded that this sorbent was the most effective in removing melanoidins from the vinasse.

Analyzing the content of hexose alkaline degradation products, a decrease in their content was observed in the decolorization process of vinasse with zeolite I, zeolite II and with bentonite. The most significant decrease was recorded for the last carrier (by 35%), so also in this case bentonite proved to be the most effective carrier in removing HADP.

In the case of caramels, a drop in their amount was found in the vinasse after the decolorization process in all experiments. The two types of halloysites KR and PJC were more efficient in removing this group of compounds, respectively 38% and 24%.

Unlike in the studies of Krzywonos and Szymańska (2011), where HADP was largely removed, in the presented study the highest removal of melanoidins with bentonite (46%) was observed.

The initial pH of the vinasse (before decolorization) was 4.85 on average. For the vinasse decolorized by halloysite KR, final pH was the lowest and amount to 3.55. The highest final pH of 5.18 was obtained for PJC halloysite decolorized vinasse.

When the halloysite and the activated carbon for decolorization were used, it was found that for the initial pH of 5 (approximately corresponding to the pH of the natural vinasse) the degree of removal of color compounds did not exceed 25% (Krzywonos and Szymańska 2011). In the presented studies, for the initial pH of the vinasse amounting to 4.85, the degree of decolorization was much higher in the case of PJC halloysite (about 50%), and for the halloysite KR, the degree of decolorization was at a similar level (about 18-20%), how in the study of Krzywonos and Szymańska (2011). On the other hand, in the research of Hadavifar et al. (2016) on the decolorization of cane vinasse with the use of, inter alia, granular activated carbon, it was found that the degree of decolorization is strongly dependent on the pH of the vinasse: the higher pH value, the lower the decolorization. When the pH changed from 2 to 10, the degree of color removal decreased from 68% to 31%.

3.2. Degree of removal of chemical oxygen demand (COD)

The chemical oxygen demand was tested for all samples of corn-sugar beet molasses vinasse decolorized using sorbents. The measurements were made for zero time and final samples (Figure 2).

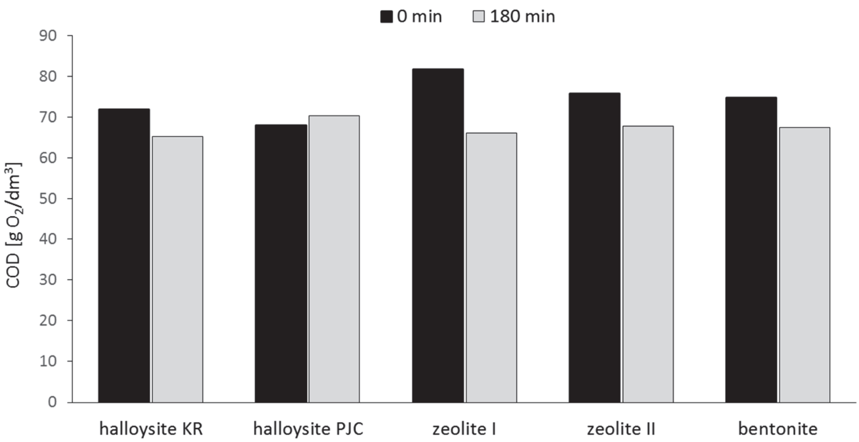

Fig. 2. Chemical oxygen demand for treated CBMV at time 0 and 180 minutes

Only for the decolorized vinasse sample using PJC halloysite, the COD content increased by 3% after three hours of shaking. In other cases, the chemical oxygen demand decreased by about 9-10%. The highest COD removal rate was obtained in the process using zeolite I, and it was 19.2%.

Satyawali and Balakrishnan (2007) obtained a decrease in COD of the vinasse (probably from sugar cane) by 23.6% with the use of active carbon produced from subject bagasse to phosphoric acid. A similar level of removal of COD was also noted in the work of Krzywonos and Łapawa (2012), in which strong alkaline ion exchange resins were used to decolorization sugar beet molasse vinasse. The most substantial removal of COD in undiluted vinasse was achieved using the Dowex 2 resin (23.09%).

The lower level of COD reduction compared to the degree of decolorization may result from the fact that melanoidins present in the vinasse during decolorization are broken down into other organic compounds that also need oxygen for their final degradation (Apollo et al. 2014). It should also be mentioned that in the tests carried out the vinasse was not diluted. Lakshmikanth and Virupakshi (2012) showed that increasing the concentration of the solution reduces color, which results from the higher saturation of the adsorption places.

In the presented studies, the degree of removal of total organic carbon (TOC), five-day biochemical oxygen demand (BOD_5) and phosphate phosphorus were determined only for vinasse samples with the addition of bentonite, in which the highest degree of decolorization was observed. The results obtained during the experiments are presented in Table 2.

Table 2. The content of colored compounds and pH value of the vinasse before (0 min) and after the decolorization process (180 min) with the use of bentonite

Parameter	Unit	Vinasse before decolorization (0 min.)	Vinasse after decolorization (180 min.)
TOC	[g/dm^3]	31.23	33.45
BOD_5	[g O_2/dm^3]	28.00	28.00
Phosphate phosphorus	[mg/dm^3]	513.00	300.00
Succinic acid	[g/dm^3]	13.94	10.81
Lactic acid	[g/dm^3]	22.71	21.56
Pyroglutamic acid	[g/dm^3]	12.61	6.52
Tartaric acid	[g/dm^3]	9.47	9.47
Glycerol	[g/dm^3]	21.26	brak
Glucose	[g/dm^3]	1.87	brak
Betaine	[g/dm^3]	25.30	17.70

Based on the data from table 2, it can be concluded that the decolorization process caused an increase in the total organic carbon content by about 7%. The BOD_5 value for samples before and after decolorization has not changed, from which it can be concluded that sorbents both before and after the decolorization process needed to oxidize organic compounds with the same amount of oxygen.

It can also be seen that the content of phosphate phosphorus was higher for vinasse before decolorization than about decolorized vinasse by about 215 mg/dm^3, and the phosphate phosphorus removal rate is 41%. It can be concluded that as a result of the absorption process, the content of succinic, lactic and pyroglutamic acid decreased. The highest decrease in the content (almost 50%) was noted in the case of pyroglutamic acid of almost 6.1 g/dm^3. The tartaric acid content remained unchanged. Both glycerol and glucose were removed by bentonite absorption. The content of betaine decreased after 180 minutes of shaking with bentonite by about 8 g/dm^3, i.e., by about 30%.

4. Conclusions

The most effective corn-sugar beet molasse's vinasse discoloration was obtained in the process using bentonite and halloysite PJC, respectively 62% and 74% discoloration. Melanoidins and alkaline products of invert degradation were most effectively removed with the participation of bentonite, while the caramels in the presence of halloysites KR and PJC. After the decolorization process, the content of COD and the content of phosphate phosphorus decreased in almost all samples, while the content of TOC increased. The content of individual acids decreased after the decolorization process of the vinasse using bentonite.

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Abstract

The molasse's vinasse, because it contains three groups of color processes in it, i.e., melanoidins, hexose alkaline degradation products, and sucrose caramelization products, is one of the most difficult to treat wastewater. Vinasse is toxic to various microorganisms, harmful to soil, groundwater, and vegetation. The aim of the study was using five natural sorbents: halloysite (PJC and KR), two types of zeolites differing in grain thickness and bentonite.

The highest decolorization (74% and 62%) was obtained in the process with bentonite and halloysite PJC. Melanoidins and hexose alkaline degradation products were removed when KR and PJC were dosed. After decolorization, in almost all experiments COD and phosphate phosphorus contents were reduced. When bentonite was tested, the organic acids were removed.

Keywords:
decolorization, vinasse, mineral sorbents, zeolite, bentonite, halloysite

Zastosowanie naturalnych sorbentów mineralnych (zeolit, bentonit, haloizyt) do usuwania związków barwnych z wywaru kukurydziano-melasowego

Streszczenie

Wywar melasowy, ze względu na zawarte w nim trzy grupy związków barwnych tj. melanoidyn, produktów alkalicznego rozkładu inwertu oraz produktów karmelizacji sacharozy, jest jednym z najtrudniejszych do unieszkodliwienia ścieków. Wywar jest toksyczny dla wielu mikroorganizmów, szkodliwy dla gleby, wód podziemnych i roślinności, dlatego przed odprowadzeniem wywaru do środowiska naturalnego substancje barwne muszą zostać z niego usunięte.

W pracy sprawdzono jak do usuwania związków barwnych z kukurydziano-melasowego wywaru gorzelniczego nadaje się pięć naturalnych sorbentów mineralnych: haloizyty PJC i KR, dwa zeolity różniące się grubością ziarna oraz bentonit.

Najbardziej efektywne odbarwienie (na poziomie 74% i 62%) uzyskano w procesie z zastosowaniem bentonitu oraz haloizytu PJC. Melanoidyny i produkty alkalicznego rozkładu inwertu najskuteczniej zostały usunięte przy udziale bentonitu, natomiast karmele w obecności haloizytów KR oraz PJC. Po procesie dekoloryzacji prawie we wszystkich próbach zmalała zawartość ChZT oraz zawartość fosforu fosforanowego, natomiast wzrosła zawartość ogólnego węgla organicznego. Po procesie dekoloryzacji wywaru z wykorzystaniem bentonitu zmalała również zawartość poszczególnych kwasów.

Słowa kluczowe:
dekoloryzacja, wywar, sorbenty mineralne, zeolit, bentonit, haloizyt