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Research Article

THE INFLUENCE OF MOLASSES ON NITROGEN REMOVAL IN WASTEWATER TREATMENT WITH ACTIVATED SLUDGE

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ABSTRACT
The paper presents the efficiency of nitrogen removal from wastewater using molasses as an external carbon source. The study was conducted during the municipal wastewater treatment process in two independent activated sludge chambers of SBR type. One of the chambers contained molasses as the source of easily available organic compounds. The study showed that the use of molasses as the external carbon source during wastewater treatment resulted in a higher efficiency of nitrogen removal than in the reactor where it no support using external carbon source was applied at the same time resulting low level of the COD value in the treated wastewater.

Keywords: removing nitrogen from sewage, external carbon source,, molasses, sewage treatment plant

INTRODUCTION

Providing external sources of carbon to treated water is often necessary to achieve the high efficiency of wastewater treatment plants that have to meet very stringent requirements to reduce nitrogen concentrations. Supporting the biological process of denitrification is achieved by dosing the substances that can be purchased in a form that allows for a direct dosing to the system. The initial stage of activities related to the possibility of using alternative carbon sources in denitrification process is to identify the market for waste products and semi-products from various food industries due to the high COD/N ratio and high content of readily decomposable organic compounds. The post-production wastewater from distillery, brewery, fish industry and waste and semi-finished products such as starch syrup, glucose, molasses, beet pulp, raw spirit or fusible oil are mainly taken into account [Mąkinia i in. 2008; Kalinowska 2006(a, b); Kaszubowska i in. 2011; Mąkinia, Czerwonka 2013].

One of the possible substances to use as an external carbon source is molasses. It is a waste from the food industry containing about 50% of sucrose. Molasses is achieved as a by-product of the sugar industry, used in the distillery industry. It is a ductile brown to dark brown liquid. The substance has a specific odor and sweet-bitter taste. Molasses or hydrolyzed molasses can be used as an aid in the biological treatment of wastewater. The main constituent of molasses, i.e. polysaccharides, contains long chains that prevent from a rapid utilization of this substrate by denitrifying bacteria, so it is recommended that the molasses be subjected to hydrolysis to convert it into simpler compounds such as sucrose, glucose and fructose [Kalinowska 2006b; Najafpour, Shan 2003; Janczukowicz, Rodziewicz 2013]. According to some studies, the efficiency of denitrification using molasses or hydrolyzed molasses exceeds 98%. In the case of the use of hydrolyzed molasses, the efficiency of the process is slightly higher, but costs of hydrolysis are not proportional to the benefits. The difficulty in using molasses as an external carbon source is its high density, which can cause problems with precise dosing of the substance [Kalinowska 2006b; Kulikowska, Dudek 2010; Zhe-Xue Quan i in. 2005].

The study aimed at demonstrating that the use of molasses as an external carbon source in wastewater treatment process has a positive impact on the effectiveness of the removal of nitrogen forms from wastewater and can replace other alternative carbon sources.

METHODS

The study was conducted during the municipal wastewater treatment process in two independent SBR-activated sludge reactors. The active capacity was 10 dm^3, including 6.5 dm^3 was the activated sludge provided by the sewage treatment plant in Białystok, while the remaining quantity originated from the raw mechanically treated wastewater (3.5 dm^3) that were also obtained from the sewage treatment plant in Białystok.

The single cycle of the reactor lasted for 6 hours and included following phases: sewage supply (2 min), mixing (anaerobic) (60 min), aeration (3.5 hrs), sedimentation (1h), and decantation (0.5h). During the aeration phase, the compressed air was fed through the diffuser placed at the bottom of the rector; depending on the operating phase, the amount of air was from 0.1 to 3.0 mg O_2/dm^3, concentration of activated sludge 3.5 kg/m^3, sludge index oscillated within 120–150 cm^3/g, hydraulic load of the chamber was 1.4 m^3/m^3d, whereas the pollution load 0.2 kg COD/m^3d. Molasses, as a source of easily available organic compounds, in an amount of 100 mg/dm^3 wastewater was added into one of the chambers in each cycle, twenty minutes after the sewage pouring.

The collected sewage samples were filtered immediately after the filtration. Each filtrate was subject to determination of the following items in accordance with applicable methodology [Kalinowska 2006a, Kalinowska 2006b, Kaszubowska i in. 2011, Kulikowska, Dudek 2010]:

- COD_{Cr} – dichromate PN-74/C-04578.03,
- BOD_5 – manometric applyingOxiTop Standard system,
- $N\text{-}NH_4$ – spectrophotometryaccording to PN-ISO 7150–1:2002,
- $N\text{-}NO_3$ – spectrophotometryaccording to PN-82/C-04576/08,
- Ntot. – spectrophotometryaccording to PN-EN ISO 6878:2006,
- Ptot. – spectrophotometryaccording to PN-EN ISO 6878:2006.

RESULTS AND DISCUSSION

The results of the R1 reactor wastewater tests without the addition of an external carbon source were included in Table 1, while Table 2 shows the results of wastewater tests from R2 reactor with addition of molasses as external carbon source. Figure 1 shows percentage comparison of nitrogen forms removal in both reactors.

Value of COD in raw wastewater amounted to 530 mgO_2/dm^3, while BOD_5 230 mgO_2/dm^3. Concentration of the total nitrogen in raw sewage was 118 mgN/dm^3, ammonia 51.5 mgN/dm^3 and nitrate 2.6 mgN/dm^3.

Twenty minutes after the reactors filling, some decrease in COD and BOD_5 values were observed – available carbon source were taken by denitrification bacteria. Value of COD in reactor R1 was 268 mgO_2/dm^3,while value of BOD_5 25 mgO_2/dm^3.

In the reactor R2, similar levels were recorded: COD – 259 mgO_2/dm^3, BOD_5– 25 $mgO_2/$

Table 1. Data and test results of wastewater without addition an external carbon source

Reactor R1 – without carbon source							
Parameters	1	2	3	4	5	6	7
	Raw wastewater	Poured wastewater (20 min) after 20 min	Denitrification (20 min) after 40 min	Denitrification (20 min) after 60 min	Nitrification (1.5 h) after 2.5 h	Nitrification (2 h) after 4.5 h	Decantation (0.5h) after6 h
COD [mgO_2/dm^3]	530	268	262	259	254	243	35
BOD_5 [mgO_2/dm^3]	230	25	20	20	15	8	6
Total nitrogen [mgN/dm^3]	118.0	84.0	68.7	55.2	48.1	24.3	14.4
Nitrate NO_3^- [mgN/dm^3]	2.6	3.9	2.4	3.6	4.6	8.6	8.6
Ammonia NH_4^+ [mgN/dm^3]	51.1	58.2	55.3	41.6	33.5	9.7	1.8
Phosphate PO_4 [mgP/dm^3]	18.5	15.2	18	12.8	1.5	1.1	0.8

Table 2. Data and test results of wastewater with addition of molasses as an external carbon source

Reactor R2 – molasses							
Parameters	Dosage of carbon source						
	1	2	3	4	5	6	7
	Raw wastewater	Poured wastewater (20 min) after 20 min	Denitrification (20 min) after 40 min	Denitrification (20 min) after 60 min	Nitrification (1.5 h) after 2.5 h	Nitrification (2 h) after 4.5 h	Decantation (0.5h) after 6 h
COD [mgO_2/dm^3]	530	259	281	268	252	246	28
BOD_5 [mgO_2/dm^3]	230	25	20	15	6	5	4.3
Total nitrogen [mgN/dm^3]	118.0	82.2	64.1	46.2	38.1	12.4	7.1
Nitrate NO_3^- [mgN/dm^3]	2.6	3.6	2.9	2.05	6.9	5.4	4.3
Ammonia NH_4^+ [mgN/dm^3]	51.1	57.9	41.1	33.1	28.9	2.0	1.4
Phosphate PO_4 [mgP/dm^3]	18.5	14.9	15.8	16.3	1.4	1.1	0.7

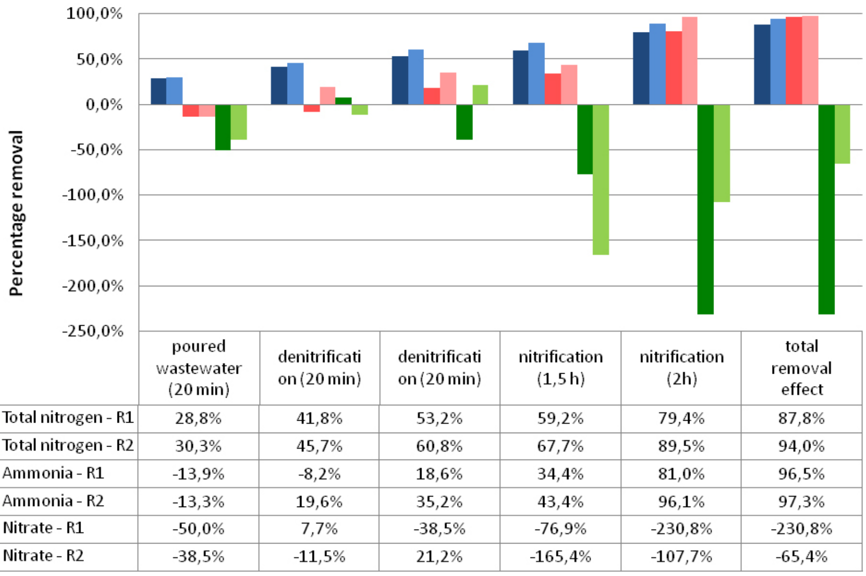

Figure 1. Percentage comparison of nitrogen forms removal in both reactors

dm^3. Content of ammonia in the reactor R1 was 84 mgN/dm^3, in reactor R2 – 82.2 mgN/dm^3. The concentration of nitrates slightly increased and in the reactor R1 was 3.9 mgN/dm^3, while in the reactor R2 – 3.6 mgN/dm^3. There was also an increase in ammonium nitrogen in the reactor R1 to 58.2 mgN /dm^3 and in the reactor R2 to 57.9 mgN /dm^3.

Then molasses as the external carbon source was added into the reactor R2 and after 20 minutes of denitrification process, subsequent samples were collected. In the R1 reactor, where the wastewater treatment process proceeded without support of the external carbon source, a further slight decrease in COD (262 mgO_2/dm^3) and BOD_5 (20 mgO_2/dm^3) was noted. Introducing the carbon source in a form of molasses caused the increase in COD value in the reactor R2 by 22 mgO_2/dm^3 up to 281 mgO_2/dm^3. The BOD value in the reactor R2 was the same as in the R1 reactor (20 mgO_2/dm^3). There was a decrease in the total nitrogen concentration in the R1 reactor to 68.7 mgN/dm^3. In the R2 reactor the overall nitrogen concentration also decreased and amounted to 64.1 mgN/dm^3. In the case of nitrates in the R1 reactor a lower concentration was noted than in the molasses reactor – the concentration in R1 was 2.4 mgN/dm^3 and the concentration in R2 2.9 mgN/dm^3. Concentration of ammonia slightly decreased in R1 to 55.3 mgN/dm^3. In the R2 reactor, a significant decrease in ammonium nitrogen was observed to 41.1 mgN/dm^3. Difference of the ammonia concentrations at that control point between the reactor without carbon source R1 and the molasses reactor R2 amounted 14.2 mgN/dm^3.

After subsequent 20 minutes of anaerobic process of wastewater treatment, further slight decrease in COD in the reactor R1 was found (259 mgO_2/dm^3), value of BOD_5 remained intact (20 mgO_2/dm^3). In the reactor with added molasses, COD was also reduced to 268 mgO_2/dm^3, while BOD5 was 15 mgO_2/dm^3. A clear difference in the concentration of nitrogen forms between the reactors was noted. Concentration of the total nitrogen still decreased reaching 55.2 mgN/dm^3 in reactor R1. In the reactor R2, the total nitrogen concentration was 46.2 mgN/dm^3 what gives a difference of 9 mgN/dm^3 of the total nitrogen concentration between the reactors. The nitrate concentration in the reactor R1 increased to 3.6 mgN/dm^3. In the reactor R2 the situation was reversed – the nitrate concentration was reduced to 2.05 mgN/dm^3 – probably the addition of molasses influences positively the removal of nitrates by denitrifying bacteria. The ammonia level decreased in R1 to 41.6 mgN/dm^3, while in R2 to 33.1 mgN/dm^3. Difference of the ammonia concentrations at that control point between reactor without carbon source R1 and with molasses R2 amounted to 8.5 mgN/dm^3.

Another samples were collected after 1.5 hours of wastewater aeration. Value of COD in the reactor R1 was 254 mgO_2/dm^3, while BOD_5 15 mgO_2/dm^3. In the rector R2 with molasses the COD value was similar – 252 mgO_2/dm_3. The BOD5 value in reactor R2 was 6 $mgO2/dm^3$. There was still a difference in the concentration of nitrogen forms between the reactors. The total nitrogen concentration in the R1 reactor was 48.1 mgN/dm^3. In the R2 reactor, the total nitrogen concentration was 38.1 mgN/dm^3. The total nitrogen concentration difference between reactor R1 and R2 was 10 mgN/dm^3. The concentration of nitrates in the R1 reactor has increased to 4.6 mg/dm^3 – the reason is that the denitrification process is stopped by supplying oxygen to the reactors. In reactor R2 also increased nitrate concentration, but in this reactor was higher value – concentration was 6.9 mgN/dm^3 Content of ammonia decreased in the reactor R1 to 33.5 mgN/dm^3, whereas in R2 to 28.9 mgN/dm^3. Difference in the ammonia concentrations at that control point between reactor without carbon source (R1) and that with molasses (R2) amounted to 4.6 mgN/dm^3.

Subsequent samples were collected after another 2 hours of wastewater aeration. The COD value in the R1 reactor was 243 mgO_2/dm^3, BOD – 8 mgO_2/dm^3. In the reactor with molasses the COD values were close to the value of the reactor R1 – 246 mgO_2/dm^3, while BOD_5 was 5 mgO_2/dm^3. Concentration of the total nitrogen in reactor R1 was determined as 24.3 mgN/dm^3. For reactor R2, concentration of total nitrogen was 12.4mgN/dm^3. Difference in the total nitrogen between both reactors amounted to 11.9 mgN/dm^3. The concentration of nitrates in reactor R1 increased again to 8.6 mg $/dm^3$. In the reactor R2 the situation was reversed – the nitrate concentration decreased to 5.4 mg/dm^3. A long duration of wastewater aeration resulted in a significant lowering the ammonia concentration in both reactors as compared to the previous control point. In R1, concentration of this nitrogen form was 9.7 mgN/dm^3, whereas in reactor R2 only 2 mgN/dm^3. Difference in the ammonia concentration between reactor without carbon source R1 and that with molasses R2 was 7.7 mgN/dm^3.

Value of COD in treated wastewater from reactor R1 after decantation process amounted to 35 mgO_2/dm^3, while value of BOD_5 was 6 mgO_2/dm^3. Despite of adding the external carbon source, the COD value in treated sewage with molasses addition amounted to 28 mgO_2/dm^3, and BOD_5 4.3 mgO_2/dm^3. These are lower numbers than in reactor R1, where no additional carbon source was used. Concentration of the total nitrogen in treated wastewater from reactor R1 amounted to14.4 mgN/dm^3, ammonia 1.8 mgN/dm^3, and nitrates 8.6 mgN/dm^3.Treatment of wastewater in reactor R1 caused the removal of total nitrogen in 87.8% and ammonia in 96.5%. In the case of reactor with molasses addition, concentration of the total nitrogen in treated wastewater was 7.1 mgN/dm^3, ammonia – 1.4 mgN/dm^3 and nitrate – 4.3 mgN/dm^3. Treating the sewage in reactor R2 resulted in the removal of total nitrogen in 94% while ammonia in 97.3%. The use of molasses in R2 reactor has resulted in a higher efficiency of the wastewater treatment process than in R1 reactor, where no external carbon source was applied. Despite of the increase in the final nitrate concentration in reactors R1 and R2, the reactor with external carbon source addition contained lower nitrate concentration by 4.3 mgN/dm^3.

CONCLUSIONS

1. The use of molasses as an external source of carbon during wastewater treatment has resulted in a higher removal efficiency of nitrogen forms – the percentage of total nitrogen removal from sewage was higher by 6%, while for

ammoniacal nitrogen by 0.8% with low COD content in the purified wastewater.
2. Despite of the increase in nitrate concentration in sewage treated in both reactors, the use of molasses has resulted in a decrease in the concentration of nitrates in purified wastewater by 4.3 mgN/dm^{3}as compared to reactor without supply the external carbon source.
3. Molasses as a waste product can provide better alternative to other expensive sources of carbon.

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