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Section: Water Engineering

Removal of ammonium ions from digested sludge liquors using natural sorbent zeolite

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Abstract

Sludge liquors arising from dewatering of digested sludge by centrifuges or alternative dewatering measures referred to as side-streams. These are recycled back to the head of the works and, depending on their source, can markedly increase the ammonium loading on the wastewater treatment plants. Although forming only a small proportion of the overall volumetric flow, the high concentration of recycled sludge liquors (typically >500 mg/L NH_4^+-N) results in a disproportionate impact. This article is dealing with the use of naturally obtained sorbent – zeolite – as an ion exchange in batch tests procedure for ammonium removal from sludge liquor. The novelty of the research was concentrated on rejected sludge liquor from the centrifugation of digested sludge related to high ammonium nitrogen concentrations. The sludge liquor taken at Vilnius sludge treatment plant after centrifugation of digested sludge. Research study carried out with different zeolite particle sizes of 0.3–0.8 mm; 0.8–1.6 mm; 1.6–2.5 mm; 2.5–3.2 mm in laboratory scaled batch test. Comparison of the results showed that the highest removal of ammonium nitrogen from digested sludge liquor obtained by using 0.3–0.8 mm particle size of zeolite.

Keywords: digested sludge liquors; ammonium nitrogen; zeolite.

Nomenclature

NH_4^+–N – ammonium nitrogen (mg/L).
SS – suspended solids (mg/L).
pH – the molar concentration of hydrogen ions in the solution.
WWTP – wastewater treatment plants
C_0 – initial concentration of suspended solids (mg/L)
C_t – concentration of suspended solids in the analysed layer after t minutes from the start of the sedimentation process (mg/L)

1. Introduction

Recently, requirements for the quality of treated wastewater according to nitrogen compounds have been increasingly tightened [1]. The following nitrogen compounds are produced in wastewater: ammonium nitrogen, organic nitrogen, nitrite and nitrate nitrogen. The totality of the latter nitrogen compounds comprises the total nitrogen. Ammonium ions suppress an activity of microorganisms during the sludge digestion process, therefore, longer digestion duration is necessary [2], [3]. After dewatering of the digested sludge, the sludge liquor produced that is returned to the wastewater treatment plant. There, the concentration of ammonium nitrogen may range from 200 mg/L NH_4^+-N to 1500 mg/L NH_4^+-N [4], [5]. This constitutes approximately 10–20% of the all amount of total nitrogen falling into the biological wastewater treatment process [3], [4], [6]. An increased concentration of nitrogen compounds before wastewater treatment does not always allow assuring the required quality of treated wastewater [7].

One of the ways to reduce the concentration of ammonium nitrogen, and at the same time the concentration of total nitrogen in wastewater – to treat the sludge liquor produced after dewatering of digested sludge, prior to returning it to the wastewater treatment plant. This method would be applied as an additional method of preventing wastewater pollution with ammonium nitrogen. The sludge liquor could be removed by ion exchange and sorption method. Natural sorbents are recommended in the research literature for the treatment of natural water and wastewater [8–11]. Natural zeolite

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distinguishes for a good ion sorption capacity. The advantages of the clinoptilolite are the following: low cost, high selectivity towards the ammonium ions in the presence of other concurrent cations in the wastewaters and wide spreading in nature [12–14]. The removal of the ammonium ions with zeolites is a result of ion exchange and/or adsorption. Both processes are parallel [11], [15], [16].

Due to the advantages listed, it is expedient to investigate the suitability of zeolite to remove ammonium ion from the sludge liquor. After it absorbs ammonium ions, zeolite (clinoptilolite) may subsequently be used as a fertilizer in agriculture [17].

2. Materials and methods

An experimental study was carried out in September-December 2013. Since June 2012, new sludge treatment facilities operate in Vilnius wastewater treatment plant, and a mesophilic sludge digestion has been implemented. The digested sludge is dewatered with centrifuges. While dewatering the digested sludge with centrifuges during the study period (September-December 2013), the sludge liquor – fugate – was produced. During the study 7 samples of the sludge liquor obtained after dewatering the sludge digested in a mesophilic regime were taken at the Vilnius wastewater treatment plant (composite samples of 25L were formed by taking 1 L of the sludge liquor). The samples were taken to the laboratory of the Water management department at VGTU. There, temperature of the delivered sludge liquor samples, pH, NH_4^+–N, also the concentration of suspended solids (SS) were measured. The latter was determined by using a filtering method described in the regulatory document LAND 46-2007 “Water quality. Determination of suspended solids. A Filtering Method Using a Fibreglass Filter”. Vacuum filtering equipment; fibreglass filter with pores of 0.45 μm; drying unit with a temperature of 105 ^{0}C; analytical scales (precision 0.1 mg) were used. The concentration of suspended solids was determined 3 times in each sample. To determine the concentration of ammonium nitrogen, “MerckSpectroquant, 1.00683.0001 Ammoniumtest” test which determination limits are 5.0–150 mg/L NH_4^+–N, and a spectrophotometer “Genesys 10 Vis” (wave length 190–1100 nm) were used. Samples with bigger than 150 mg/L NH_4^+–N were diluted with distilled water (1:10; 1:100 and 1:1000 dilution) and the concentration of ammonium nitrogen was determined accordingly.

Tests for reducing the concentration of ammonium nitrogen using natural zeolite brought from the Ukraine, Sokirnick minefield, have been made. Fractions used – grains of 0.3–0.8 mm; 0.8–1.6 mm; 1.6–2.5 mm; 2.5–3.2 mm in diameter. They were selected using calibrated sieves. Samples of these fractions with a mass of 20, 50, 100 and 200 g were mixed with 1 L of the sludge liquor in an automatic mixer for 30 min at 100 rev/min, and then were left for settling for 30 min; then, the concentration of ammonium nitrogen was determined in the filtered samples. Filtering was done through fibreglass filters with 0.45 μm pores.

A test for reducing the concentration of suspended solids in samples of the sludge liquor has been made in the laboratory. After determining the initial SS concentration, the tested liquor was mixed well and poured into 1-liter cylinders–settlers with a depth of 300 mm. After 20 min of the start of the test, 300 mL of water was siphoned using a bulb and a hose from each of the two cylinders–settlers. The water tested from the first settler was siphoned from a depth of 90 mm, and from the second one – from a depth of 210 mm. SS concentration was determined in the samples taken. This procedure was also repeated in 40, 60, 80 and 100 minutes after the beginning of testing in the remaining cylinders. Precipitation efficiency achieved during the period *t* was calculated according to the formula:

$$E_t = \frac{C_0 - C_t}{C_0} \cdot 100, \% , \quad (1)$$

where: C_0 – initial concentration of suspended solids, mg/L; C_t – concentration of suspended solids in the analysed layer after t minutes from the start of the sedimentation process, mg/L.

To increase the precipitation efficiency, the coagulant – ferric chloride ($FeCl_3 \cdot 6H_2O$) was used. Different quantities of 10% ferric chloride solution were taken: 3 ml, 6 ml and 10 ml. The each amount of reagent was mixed in three 3 L cylinders–settlers with a depth of 300 mm. After 15 minutes, 300 mL of the liquor was siphoned from a depth of 210 mm of the cylinders–setllers containing different reagent doses (3 ml, 6 ml, 10 ml of 10% of $FeCl_3$ $6H_2O$). SS concentration was determined in the samples taken. This procedure was repeated in 30 and 45 minutes after the start of testing.

After reducing the SS concentration in the tested sludge liquor, samples were mixed again with four fractions of zeolite by the method described above, and a test of determining the concentration of ammonium nitrogen was made. Errors consisted of samples taking and measuring tools accuracy errors. After the experimental work, a statistical analysis of the results was prepared by eliminating unreliable values above the 95% confidence interval.

3. Results and discussion

Results of analysis of sludge liquor samples taken during the experiment are presented in Table 1.

According to the data of Table 1 the concentration of ammonium nitrogen in the digested sludge liquor from Vilnius WWTP fluctuated at the interval of 1025–1750 mg/L. These values of the concentration are analogous to values mentioned in references [4], [5]. The pH average value of the sludge liquor is 7.3, so, ammonium ions do not turn to ammonia NH_3

[18]. Figure 1 shows the results obtained after digested sludge liquor mixing with zeolite fractions (100 g and 200 g), as it is indicated in methodology.

Table 1. Characteristics of sludge liquor

Date of taking the sample	Amount of sample (L)	pH*	NH_4^+-N* (mg/L)	SS* (mg/L)	T* (°C)
2013.09.10	25	7.2	1025	845	20
2013.09.17	25	7.0	1010	705	22
2013.10.08	20	7.2	955	720	22
2013.10.25	25	7.4	1240	836	21
2013.11.13	20	7.3	1455	1020	23
2013.11.26	20	7.4	1640	985	22
2013.12.03	25	7,6	1750	1236	20
Average	23	7.3	1296	921	21

Note: * Average value of three measurements is presented

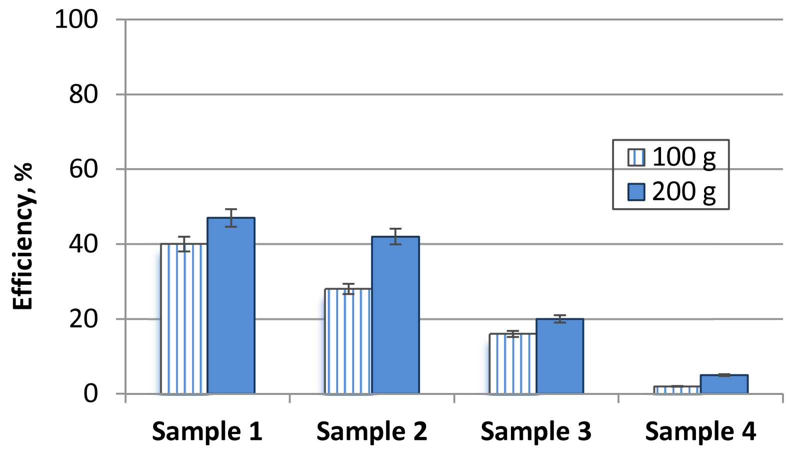

Fig 1. The efficiency of zeolite fractions removing ammonium ions from the samples. Sample 1 – 0.3–08 mm; Sample 2 – 0.8–1.6 mm; Sample 3 – 1.6–2.5 mm; Sample 4 – 2.5–3.2 mm (the initial concentration of ammonium nitrogen – 1240 mg/L).

According to the data of Figure 1 the highest efficiency of removal from digested sludge liquor was obtained using the finest zeolite fractions (0.3–0.8 mm) by its volume of 200 g. Although the efficiency of the removal of ammonium ions reached only 48%. It means that using less volumes of zeolite (20 g and 50 g) is beside the purpose. Such tenuous efficiency can be explained by high initial concentration of ammonium nitrogen (1240 mg/L) and high concentration of SS (836 mg/L) in sludge liquor samples. Floating materials prevent the processes of ammonium ion exchange and adsorption, while they stick and isolate the superficies of zeolite granules. In the further researches the SS quantities in sludge liquor was reducing as it was described in the part of methodology. Table 2 shows the results of the efficiency of SS sedimentation.

Table 2. The SS concentrations and the efficiency of SS removal at different durations of sedimentation (the initial average SS concentration of the samples – 950 mg/L).

Duration of sedimentation, min	h_1 = 90 mm		h_2 = 210 mm	
	C_t, mg/L	E_t, %	C_t, mg/L	E_t, %
20	945	0.5	905	4.7
40	940	1.0	872	8.2
60	932	1.9	820	13.7
80	945	0.5	781	18
100	943	0.7	740	22.1

Investigating the efficiency of SS sedimentation without reagents was reached the efficiency of 1.9% at the depth of 90 mm after 60 minutes and the efficiency of 22% in the depth of 210 mm after 100 minutes (Table 2). Such efficiency of sedimentation is very tenuous. It was noticed that in sludge liquor the process of degradation of organic matter continues and due to gas emission the upper layer of the liquor (90 mm) becomes clear slower than the middle one (210 mm). On purpose to improve the efficiency of SS sedimentation ferrous chloride was used in further experiments (as described in the part of methodology). The results of the efficiency of SS sedimentation using ferrous chloride are given in Table 3.

Table 3. The SS concentrations and the efficiency of SS removal using ferrous chloride (the initial average SS concentration of the samples – 1020 mg/L)

Duration, min	10% $FeCl_3$ 10 mL				10% $FeCl_3$ 6 mL				10% $FeCl_3$ 3 mL			
	h_1 = 90 mm		h_2 = 210 mm		h_1 = 90 mm		h_2 = 210 mm		h_1 = 90 mm		h_2 = 210 mm	
	C_t, mg/L	E_t, %	C_t, mg/L	E_t, %	C_t, mg/L	E_t, %	C_t, mg/L	E_t, %	C_t, mg/L	E_t, %	C_t, mg/L	E_t, %
20	570	44.1	655	35.8	645	36.8	750	26.5	746	26.9	840	17.6
40	225	77.9	386	62.1	595	41.7	610	40.2	538	47.3	675	33.8
60	98	90.4	202	80.2	393	61.5	398	60.9	462	54.7	510	51.0
80	52	94.9	67	93,4	281	72.5	265	74.0	287	71.9	384	62.4
100	30	97.0	45	96.6	105	89.7	156	84.7	120	88.2	245	76.0

According to the data of Table 3 the least efficiency was reached using 3 mL 10% $FeCl_3 \cdot 6H_2O$ at the duration of 100 minutes of sedimentation. The efficiency of 88.5% reached at the depth of 90 mm and 76% – at the depth of 210 mm. The highest efficiency of 97% was reached using reagent dose of 10 mL (Table 3). The SS concentration did not exceed 50 mg/L in the samples. Such sedimentation can be held efficient. So, for the further treatment of the sludge liquor was taken the dose of 10 mL 10% $FeCl_3 \cdot 6H_2O$.

Figure 2 shows the comparison of the efficiency of SS sedimentation (depth – 210 mm).

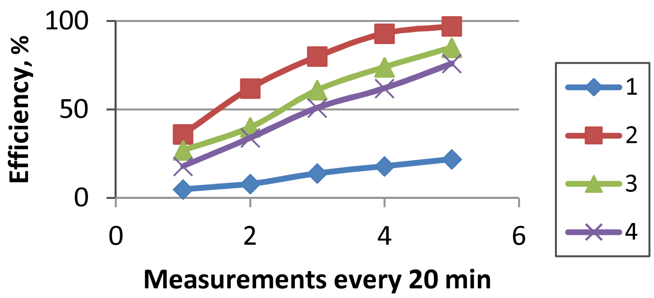

Fig 2. The efficiency of SS sedimentation (depth – 210 mm): 1 – without reagent; 2 – 10 mL ferrous chloride; 3 – 6 mL ferrous chloride; 4 – 3 mL ferrous chloride

Figure 3 shows the results obtained after carrying out the SS sedimentation when the sample of liquor siphoned from the depth of 210 mm of the sediment tank was mixed with zeolite particles in size of 20 g and 50 g.

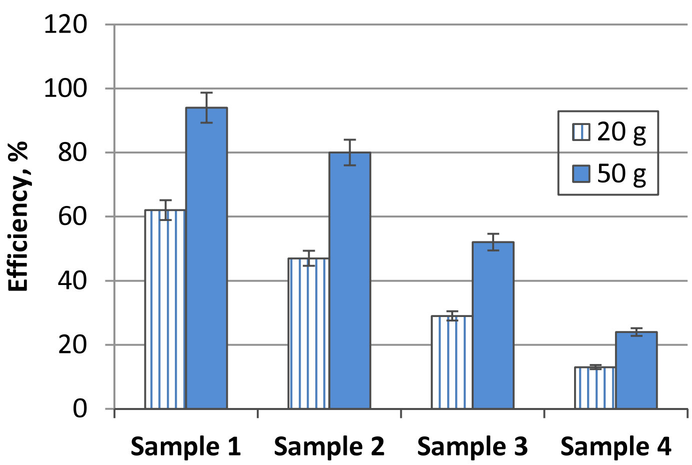

Fig 3. Removal efficiency of zeolite fractions after precipitation: Sample 1 – 0.3–0.8 mm; Sample 2 – 0.8–1.6 mm; Sample 3 – 1.6–2.5 mm; Sample 4 – 2.5–3.2 mm (the initial concentration of ammonium ions – 955 mg/L)

According to Figure 3, a rather efficient removal of ammonium ions from the liquor (94%) was observed using the finest zeolite fraction, when it was taken 50 g of the material per 1-liter liquor. Comparing this with the data given in Figure 1 the efficiency of the ammonium nitrogen removal increased by 46%, though the volume of zeolite fraction particles in size 0.3–

0.8 mm decreased twice. Under the conditions of the experiment, 19 mg of ammonium nitrogen was removed using 1 g of the finest zeolite fraction particles from the sludge liquor. According to references [4] strain of zeolite (MesoLite) can absorb about 50 mg ammonium ions, when the initial concentration of NH_4^+–N in the liquor is about 600 mg/L (more than 95% of ammonium was removed). As this article is dealing with ammonium removal from sludge liquor when the initial concentration of ammonium nitrogen is more than 1000 mg/L, the obtained results showed less efficiency of removal. These results reassert the [11], [12], [19] authors that zeolite during ion exchange and adsorption processes remove ammonium ions from liquor. Vast surface area of sorbing material is needed to carry out these processes and it cannot be isolated from the liquor by SS particles. The same volume of finer zeolite particles covers larger surface area, so, in this case the finest fraction is the most appropriate. It was beside the purpose to take still less particles (less than 0.3 mm) because it is difficult to separate them from treated liquor [9]. To sum up the results of the experiment, the finest zeolite fraction (0.3–0.8 mm) is the most appropriate to decrease ammonium ions concentration in sludge liquor, when the initial concentration of NH_4^+–N fluctuate at the range of 955–1750 mg/L. Therefore, the SS concentration in liquor should be decreased to 50 mg/L or less. The dose of 10 mL of 10% $FeCl_3 \cdot 6H_2O$ reagent per 1 L sludge liquor should be used for SS sedimentation, when the initial SS concentration fluctuates from 705 mg/L to 1240 mg/L. After the treatment of sludge liquor, zeolite with absorbed ammonium ions could be applied in agriculture as fertiliser. According to scientists involved in development of the fertilizer [17] such zeolite (Clinoptilolite) improves quality of soil, as ammonium ions from zeolite are assimilated gradually and are not washed into groundwater. Further investigation should be undertaken in the field of chemical composition of zeolite to assure that ammonium is not washed from zeolite and plants are able to assimilate it gradually.

4. Conclusions

1. It was estimated high concentration of ammonium nitrogen in the digested sludge liquor from Vilnius WWTP (955–1750 mg/L). This result supported the hypothesis that sludge liquor rich with ammonium ions is obtained after dewatering digested sludge and it can influent the quality of effluent by nitrogen compounds.
2. The efficiency of 48% of ammonium nitrogen removal from sludge liquor using zeolite was reached, when the initial ammonium nitrogen concentration was 1240 mg/L and SS concentration – 836 mg/L. The highest efficiency was reached using the finest zeolite fractions (0.3–0.8 mm), when 200 g of it had been mixed with 1 litre of sludge liquor for 30 minutes and left to settle for 30 minutes more.
3. The SS concentration in sludge liquor should be decreased to 50 mg/L or less before ammonium nitrogen is removed from sludge liquor using zeolite. To precipitate SS the dose of about 10 mL of 10% FeCl3. 6H2O per 1 litre of liquor should be taken, when the initial SS concentration fluctuates from 705 mg/L to 1240 mg/L.
4. A rather high removal efficiency of ammonium nitrogen (94%) from sludge liquor processed with ferrous chloride is reached using zeolite fraction in size of 0.3–0.8 mm (the initial concentration of NH4+–N is about 1000 mg/L). The amount of zeolite taken – 50 g per 1 litre and mixed for 30 minutes with 1 litre of sludge liquor and left for 30 more minutes to settle.

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