

57 (2016) 1176–1183 January



Characteristics of reject waters and condensates generated during drying of sewage sludge from selected wastewater treatment plants

Beata Karwowska*, Elżbieta Sperczyńska, Ewa Wiśniowska

Faculty of Environmental Engineering and Biotechnology, Department of Chemistry, Water and Wastewater Technology, Częstochowa University of Technology, Dąbrowskiego 69, 42 200 Częstochowa, Poland, Tel. +48 343250491; Fax: +48 343250496; email: bkarwowska@is.pcz.czest.pl (B. Karwowska)

Received 9 September 2014; Accepted 6 November 2014

ABSTRACT

The aim of the investigation was to evaluate the levels of BOD, chemical oxygen demand, biogen compounds (e.g. ammonium nitrogen, phosphates) and the heavy metals (Zn, Cu, Ni, Cd, and Pb) content in supernatants, and condensates generated during sewage sludge drying and reject waters, compared to the concentrations in raw wastewater from selected WWTP in southern Poland. It was stated that when compared to raw wastewater, other liquids were highly polluted with ammonium nitrogen. Reject waters and condensates were not highly polluted with phosphates in contrast to supernatants. The most abundant heavy metal in all samples was zinc, followed by nickel. Copper and lead concentrations were similar but lower than that of zinc. Cadmium concentration was at a very low level. Considering the potential loads of heavy metals, which may be discharged with condensates and supernatants to the head of WWTP, they can be at the level of maximum 2% of the total load. It indicates that one-time effect of these liquids on heavy metals loads discharged into an activated sludge chamber is negligible, however, when accumulated in wastewater treatment, they pose a risk for biological processes.

Keywords: Heavy metals; Supernatants; Condensates; Wastewater

1. Introduction

Methane digestion is one of the commonly used processes of sewage sludge stabilization, both in Poland and European Union [1]. Digested sludge is dewatered before further management processes (e.g. drying, agricultural use). The process generates supernatants, which are usually recycled into influent. This practice significantly increases loads of nutrients (especially nitrogen compounds) in wastewater incoming to an activated sludge chamber. Recycled supernatant can account even for 40% of nitrogen load into the head of wastewater treatment plant, while hydraulic loads contribute about 5–10% of inflow [2]. Data on supernatants properties given by individual researchers are usually focused on the problems of nutrients concentrations. Concentrations of ammonium nitrogen in supernatants vary from about 100 to more than 1,000 mg N-NH₄⁴ L⁻¹, but according to Hill and

Presented at the 12th Scientific Conference on Microcontaminants in Human Environment 25–27 September 2014, Czestochowa, Poland

1944-3994/1944-3986 © 2014 Balaban Desalination Publications. All rights reserved.

^{*}Corresponding author.

Khan [2] are usually in the range of 500–1,500 mg N-NH₄⁺ L⁻¹. Supernatants are usually alkaline [3]; chemical oxygen demand (COD) and BOD values are usually high compared to raw wastewater [4–8]. The results obtained by Cydzik-Kwiatkowska et al. [5] indicate that supernatants are moderately biodegradable under aerobic conditions (BOD₅/COD = 0.4). According to the data of Oleszkiewicz et al. [8], organics in supernatant are not well biodegradable since, about 70% of biodegradable organic compounds are broke down during methane digestion. Load of biodegradable organic compounds in supernatants can support the denitrification process.

Data concerning sodium and potassium concentration in supernatants are within the range of 79 mg Na L^{-1} and 27–195 mg K L^{-1} [3,7], respectively. Supernatants are also polluted with phosphates; the observed concentrations of these compounds are usually higher than 60 mg $PO_4^{3-}L^{-1}$. According to Oleszkiewicz et al. [8], concentrations of orthophosphates in supernatants are within the range of $60-210 \text{ mg PO}_4^{3-} \text{ L}^{-1}$, but sometimes they are higher, e.g. in the study conducted by Qiao et al. [4], concentration of phosphates in a supernatant was at an average level of $410 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ (supernatant separated after thermal conditioning of sludge). In the studies by Piaskowski and Ćwikałowska [9], it was stated that orthophosphates concentration in a liquid phase of a supernatant was equal to 119 mg $PO_4^{3-}L^{-1}$, whereas, in the supernatant containing suspended solids, it is 630 mg $PO_4^{3-}L^{-1}$.

High concentrations of N and P compounds in supernatants are undesirable and affect negative treatment of influents in a wastewater treatment plant. Because of this, most research works on supernatants are focused on the problems connected with nutrients removal or effect on the activated sludge process. In the meantime, it is also important to evaluate the concentrations of inorganic and organic micropollutants in supernatants because, they can act as inhibitors of aerobic and anaerobic processes in wastewater treatment plants. Research works on micropollutants concentrations in supernatants have been rarely done up till now. Włodarczyk-Makuła evaluated concentrations of selected polycyclic aromatic hydrocarbons in supernatants [10]. In terms of heavy metals, some research works were done under the effects of treatment processes on heavy metals release to the supernatants [11– 13]. According to the result obtained by Kamal Gad [12], concentrations of heavy metals in supernatants were in the range of 0.0014 (for Cr (VI)) to 0.0204 mg L^{-1} (for Ni) at pH equal to 6.9. In research carried out by Janosz-Rajczyk and Wiśniowska [13], the concentrations were in the range of 0.0034 (in the case of Hg) to 0.998 mg L^{-1} (data concerning Zn). The data on micropollutants

concentrations in supernatants are insufficient. Taking condensates from sewage sludge drying into consideration, it should be emphasized that the research works on them are few and far between. The given data only indicate that condensates from sewage sludge drying contain high quantities of organic compounds, but they are not suitable for biodegradation (BOD₅/COD = 0.2). They also contain high quantities of nitrogen compounds (C/N is about 8), but low concentrations of phosphorus [14,15]. Condensates from middle temperature dryer devices are less concentrated than those from high temperatures ones [14,15].

The aim of the present investigation was to compare concentration of selected macro and micropollutants (heavy metals) in supernatants, condensates from sewage sludge drying, reject waters, and wastewater from two WWTP in southern Poland. The WWTPs differed with the influent flow and the technology of sewage sludge drying. Based on the results, the threat for aerobic and anaerobic biological processes resulting from heavy metals presence was evaluated.

2. Materials and methods

2.1. Sampling procedure

Samples of raw wastewater (influent), supernatants from filter press dewatering, condensates from sewage sludge drying, and reject waters (mixtures of supernatants and condensates—this waste liquid is recycled into the influent) were taken three times from two wastewater treatment plants in southern Poland— WWTP in Częstochowa (WWTP H) and WWTP in Ruda Śląska (WWTP M). The letter "H" in WWTP H is connected with the fact that in the plant, high temperature drying technology is used. "M" in WWTP M means medium temperature technology.

WWTP H is a plant in which wastewater is treated up to a tertiary level. It treats municipal wastewater, and the inflow to the plant is approximately $43,000 \text{ m}^3 \text{ d}^{-1}$. The raw sludge and excess activated sludge are stabilized in two-stage methane digestion process. The first step is mesophilic methane digestion (35°C) in closed digestive chambers; the second step is digestion in open digestive chambers. Digested sludge is dewatered mechanically with filter presses and then dried (to about 90-95% of d.m.) by indirect drying technology. The heating medium is oil of temperature equal to 220-280°C (high temperature drying). The fumes from the drying process have temperature of about 120-150°C; they are condensed in condensers, mixed with supernatants obtained during filter pressing, and as a mixture recycled to the head of WWTP.

WWTP M treats up to $10,000 \text{ m}^3 \text{ d}^{-1}$ of wastewater. It is mechanical-biological WWTP with BNR removal. Uniquely excess sludge (it is not anaerobically fermented) undergoes dewatering; the process is carried out with filter presses (generated supernatants are recycled to the inflow). The sludge is dried directly with hot air (temperature 100°C —medium temperature drying). Air from a drying device is next cooled; during the process, part of steam generates condensates which are recycled to the sewage system in WWTP (the volume of condensate generated daily is negligible compared to the volume of supernatant and raw wastewater). The remaining cooled air is directed to biofilters.

2.2. Analytical methods

In the unfiltered samples of the liquids taken from wastewater treatment plants, the following physicochemical parameters were determined: pH potentiometrically, alkalinity—with titration method, ammonium nitrogen-with Nessler method, orthophosphates-with a molybdenum blue method, and COD-by a standard dichromate method. All analyses were done according to standard methods [16]. BOD₅ was analyzed with OxiTop[®] measurement system. COD and BOD₅ were also determined in samples filtered through a 0.45 µm filter to evaluate the concentrations of organic compounds in solution. All tests were performed in triplicates.

The total content of selected heavy metals ions (Zn, Cu, Cd, Ni, and Pb) as well as sodium and potassium ions was analyzed in unfiltered samples and the ones filtered through $0.45 \,\mu$ m filter, after concentrated HNO₃ and HCl (1 + 3—aqua regia) digestion. The content of metal ions was detected by an atomic absorption spectrometry method, using a spectrometer novAA 400, Analytic Jena, Germany. In further parts of the study, the term heavy metals is used to name concentration of heavy metal ions.

3. Results and discussion

Physicochemical characteristics of wastewaters, supernatant, condensates, and reject water is presented in Table 1. Raw wastewater from WWTP M (COD within the range 837–850 mg $O_2 L^{-1}$) contained more organic compounds than the ones from WWTP H (COD from 435–518 mg $O_2 L^{-1}$). Influent from WWTP H was more unpredictable than from WWTP M. Based on BOD₅/COD values, it was stated that influent to WWTP M was well biodegradable (BOD₅/COD in the range 0.7–0.8). Influent to WWTP H (with

BOD₅/COD in the range 0.45–0.6) was worse biodegradable, but according to the criteria given by Miksch and Sikora [17], it was still at least moderately biodegradable. BOD₅/COD values observed for WWTP H were typical for municipal wastewater treatment plants [17]. According to the data given by Spellman [18], concentrations of COD in typical wastewater are in the range of 200–500 mg $O_2 L^{-1}$ (although the range observed for municipal influents is between 250 and 1,000 mg $O_2 L^{-1}$ [19]). According to Henze et al., municipal wastewater of total COD higher than 750 mg $O_2 L^{-1}$ must be considered as medium wastewater. The ones of total COD lower than 500 mg $O_2 L^{-1}$ are treated as diluted wastewater [20].

Wastewater from WWTP M contained slightly higher concentrations of ammonium nitrogen and significantly higher concentrations of phosphates than these from WWTP H. Typical ammonium nitrogen concentrations in wastewater are between 12 and 50 mg N-NH₄⁺ L⁻¹ [18]. Wastewater with ammonium concentration lower than 45 mg N-NH₄⁺ L⁻¹ are diluted ones, 45 and above medium, and above 75 mg N-NH₄⁺ L⁻¹ are concentrated ones [20].

Phosphates concentrations were similar in both mixtures of supernatants and condensates. When phosphates concentrations are considered, the contents lower than 10 mg $PO_4^{3-}L^{-1}$ are recognized as typical for diluted wastewater, above 10, but lower than 15 mg $PO_4^{3-}L^{-1}$ for medium, and above 15 as concentrated [20]. According to the classifications given above both wastewater from WWTP H and WWTP M can be classified as medium in terms of the ammonium nitrogen content and concentrated in terms of phosphates concentration.

Concentrations of COD in supernatants from WWTP H were in the range of $356-568 \text{ mg O}_2 \text{ L}^{-1}$ and were similar to the observed in raw wastewater. In supernatants from WWTP M, organic compound contents were significantly lower (COD range between 61 and 79 mg O_2 L⁻¹). The COD values from WWTP M were lower than usually stated in the literature [3,5–8]. Whereas in supernatants from WWTP H, about 60% of COD was present in solution, in supernatants from WWTP M, soluble COD reached over 88%, so was well available for micro-organisms.

Based on BOD_5/COD values, it can be stated that in all collected supernatants both the total and soluble fractions of organic compounds were not suitable for biodegradation ($BOD_5/COD < 0.3$) [17]. This confirms the thesis of Oleszkiewicz et al. [8]. Supernatants from WWTP H and WWTP M differed in terms of ammonium and phosphates concentration, whereas WWTP H supernatants were typical, the other liquids contained low concentrations of biogens. Table 1

			Parameter						
WWTP	Liquid		рН	Alkalinity (mval L^{-1})	$\begin{array}{c} BOD_5 \\ (mg O_2 L^{-1}) \end{array}$	$\begin{array}{c} \text{COD} \\ (\text{mg } \text{O}_2 \text{L}^{-1}) \end{array}$	$\frac{\text{N-NH}_4^+}{(\text{mg N L}^{-1})}$	PO_4^{3-} (mg PO_4^{3-} L^{-1})	
WWTP H	WW	UF F	7.20–7.85	7.2–8.2	200–330 44–92	435–518 97–184	30.28-55.05	6.98–17.54	
	S	UF F	7.82–7.97	60.2–61.3	95–155 45–96	356–568 272–353	612.43–700.9	47.74-64.14	
	RW	UF F	8.91–9.14	6.4–10.1	80–185 48–190	140–309 101–233	80.96-120.4	1.56-4.04	
	С	UF F	8.59–9.16	6.3–9.3	78–215 68–180	305–373 109–259	91.83–154.0	6.30–6.98	
WWTP M	WW	UF F	7.54–7.63	9.0	620–660 300–330	837–850 320–384	54.10-69.15	32.48-39.80	
	S	UF F	7.57–7.62	3.2–3.3	12–21 7	61–79 54–72	0.95–2.32	0.30–0.59	
	RW	UF F	7.70–7.83	3.5–3.7	34–120 12–33	76–504 57–112	10.38–16.00	1.27-4.97	
	С	UF F	6.58–6.61	14. 9–17.5	360–385 260–350	2,304–2,418 2,160–2,237	295.29-342.92	0.52–2.40	

The range of content of selected physicochemical parameters in supernatants, condensates, and wastewater from sludge drying and reject waters from two wastewater treatment plants in southern Poland

Note: WW—wastewater, S—supernatant, C—condensate, RW—reject water, UF—unfiltered sample, F—sample filtered through 0.45 µm filter.

It is quite surprising that condensates from high temperature drying did not contain very high COD contents (up to $373 \text{ mg O}_2 \text{L}^{-1}$). Condensates from WWTP M were more concentrated (COD within the range 2,304–2,418 mg $O_2 L^{-1}$), but the quantities of them generated during sludge treatment are negligible. Supernatants and condensates mixtures from WWTP M are characterized by similar values as mixtures from WWTP H. The reject waters from high temperature drying (they are recycled to the head of WWTP) contained significantly higher concentrations of ammonium nitrogen than the mixtures from medium temperature ones. The results obtained in our study confirm the ones obtained by Roskosch and Otto [15] in terms of low biodegradability and high ammonium concentration.

Concentrations of selected metals (Zn, Cu, Ni, Cd, Pb, K, and Na) in supernatants, condensates, their mixtures with supernatants, and influents from two selected wastewater treatment plants in southern Poland are listed in Table 2. WWTP H is large installation with high temperature drying of sewage sludge. In WWTP M, they use moderate temperature drying devices. It has some influence on the composition of condensates. In general the most abundant heavy metal in the samples was zinc, followed by nickel. Copper and lead concentrations were similar, but lower than zinc. Cadmium concentration was the lowest and it could be concerned as negligible. The total concentration of heavy metals (sum of Zn, Cd, Ni, Cd, and Pb) was in most samples higher in the ones from WWTP H. The average total concentration of all analyzed heavy metals in various types of samples are presented in Figs. 1 (for unfiltered samples) and 2 (for samples filtered through $0.45 \,\mu m$ filter). Unfiltered samples represent concentration of pollutants in a liquid phase and suspended solids, whereas filtered ones represent only concentration in the solution.

As can be seen from Fig. 1, the highest concentrations of heavy metals in unfiltered samples were stated in influent and in condensates for WWTP H. Supernatants from WWTP H contained lower concentrations of heavy metals than both in condensates and raw wastewater and consequently in the mixture of supernatants and condensates, the average heavy metal concentration was lower than in influent and condensate alone. The results presented in Fig. 2 indicate that in influent samples about 55% of heavy metals were present in the solution. In the case of condensates, about 47% of them were present in the solution, and about 53% were bounded to the particles and colloids.

In supernatant samples in which total concentration was lower than in WW and C ones, almost 74% of heavy metals were present in solution, whereas in the case of the mixture of supernatant and

WWTP Liquid Zn WWTP H WW UF 0.37- WWTP H WW UF 0.14- S UF 0.14- 0.27- RW UF 0.14- 0.14- C UF 0.14- 0.14- C UF 0.14- 0.14-	Ni 3-0.09 0.09-0.19 2-0.04 0.08-0.12 3-0.06 0.19-0.20 3-0.04 0.11-0.19	Cd 0.006-0.017 0.003-0.008 0.010 0.017	Pb 0.04_0.10	NIS	
WWTP H WW UF 0.37- S UF 0.14- S UF 0.27- RW UF 0.14- C UF 0.36- C UF 0.36- C UF 0.30-	3-0.09 0.09-0.19 2-0.04 0.08-0.12 3-0.06 0.19-0.20 3-0.04 0.11-0.19	0.006-0.017 0.003-0.008	010 010	ING	К
F 0.14- S UF 0.27- F 0.14- RW UF 0.14- F 0.14- C UF 0.36- F 0.16- C 0.16-	2-0.04 0.08-0.12 3-0.06 0.19-0.20 3-0.04 0.11-0.19	0.003-0.008	0.04-0.17	52.48-53.80	16.21–17.66
S UF 0.27- RW UF 0.14- C UF 0.14- C UF 0.14- F 0.14- F 0.16- F	3-0.06 0.19-0.20 3-0.04 0.11-0.19	0,010,0,017	0.03 - 0.10	50.62 - 56.43	15.42-17.43
F 0.14- RW UF 0.19- F 0.14- C UF 0.36- F 0.10-	3-0.04 0.11-0.19	110-010-010-0	0.03 - 0.11	63,55-64.72	90.82-116.89
RW UF 0.19- C UF 0.14- C UF 0.36- F 0.10-		0.001 - 0.004	0.03 - 0.06	51.23 - 54.48	74.59 - 109.17
F 0.14- С UF 0.36- н	3-0.04 0.11-0.19	0.008 - 0.017	0.03 - 0.12	48.41 - 59.90	15.65 - 16.50
C UF 0.36-	2-0.03 0.09-0.12	0.001 - 0.012	0.03 - 0.18	45.69 - 50.42	14.81 - 15.72
E 010	3-0.10 0.14-0.23	0.009 - 0.017	0.04 - 0.11	41.24–57.53	15.38-16.21
	2-0.03 0.10-0.18	0.004 - 0.005	0.03 - 0.10	39.94–54.26	13.62-15.42
WWTP M WW UF 0.23-	4-0.07 0.05-0.10	0.020 - 0.024	0.12 - 0.22	84.94–99.78	24.20 - 31.75
F 0.20-	4-0.05 0.05-0.07	0.001 - 0.021	0.02 - 0.21	79.68–96.74	19.84 - 27.64
S UF 0.18-	2-0.04 0.06-0.09	0.015 - 0.039	0.13 - 0.21	74.04-690.52	17.52-26.26
F 0.14-	2-0.08 0.05-0.08	0.004 - 0.033	0.06 - 0.19	67.06-68.92	17.34–17.38
RW UNF 0.37-	4-0.17 0.07-0.08	0.018 - 0.032	0.14 - 0.21	46.40-75.22	10.49 - 19.75
F 0.14-	5-0.06 0.06-0.09	0.017 - 0.029	0.04 - 0.21	3.26-73.74	0.43 - 19.47
C UF 0.21-	3-0.04 0.05-0.08	0.010 - 0.022	0.08 - 0.24	5.59 - 71.59	0.58 - 20.13
F 0.15-	2-0.04 0.03-0.09	0.004 - 0.018	0.06 - 0.19	5.21 - 49.54	0.32-12.26

Table 2 The range of content of selected metals in supernatants, condensates, reject waters, and wastewater from two wastewater treatment plants in southern Silesia, mg L⁻¹



Fig. 1. The total concentration of heavy metals in unfiltered samples of wastewater, supernatants, reject waters, as well as condensates taken from WWTP H and WWTP M.



Fig. 2. The total concentration of heavy metals in samples of wastewater, supernatants, reject water, as well as condensates filtered through $0.45\,\mu m$ filter taken from WWTP H and WWTP M.

condensates, it is average 80%. It means that although concentrations of heavy metals in supernatants and the mixtures of supernatants and condensates form WWTP H contained less metal ions, they were in the form which is more bioavailable than in raw wastewater.

In the case of WWTP M, shares of heavy metals in solutions were 70, 83, 62, and 49% for wastewater, condensates, supernatant, and reject waters, respectively. It indicates that opposite to WWTP H the most bioavailable heavy metals were present in raw wastewater, and less available one in supernatants and their mixtures with condensates. As far as the loads of heavy metals possibly discharged with reject waters to the WWTP influent are considered, they can be at the level of about maximum 2%. It means that the effect of these waste liquids on heavy metals loads discharged once into activated sludge chambers is negligible. However, it should be emphasized that continuous discharges of supernatants into the head of

wastewater treatment plan pose a risk of accumulation of these micropollutants in sewage sludge. The order of Zn content in liquids from WWTP H was: WW = C> S > RW and from WWTP M: RW > WW > C > S. What is meaningful, concentrations of Zn in condensates were in the case of both WWTP, higher in condensates than in supernatants, despite the fact that pH of condensates is very high (Table 2). However, in C samples of WWTP H, Zn was mainly present in precipitates and colloids, so, in the form, in which Zn was bioavailable worse. In the C of WWTP M, condensates Tn in solids was at the level similar to S. It indicates that the form of Zn in condensates is dependent on the sludge drying technology.

Concentrations of copper in all liquids from WWTP H and WWTP M were on a similar level and were insignificantly higher for WWTP M samples. Nickel contents in analyzed samples were higher for WWTP H. The order of nickel content in WWTP H and WWTP M samples was: S > C > RW > W and RW> S > WW = C, respectively. As can be seen, also in the case of this metal ions, the contents in condensates in both cases were higher than in supernatants.

The contents order for lead was: WW > C > RW = S for WWTP H and WW = S = RW > C for WWTP M. The cadmium content was in order: S > RW > WW = C and WW > RW > S > C for WWTP H and WWTP M, respectively. Based on the results, there was no clear dependence stated between the metal concentration and the type of a liquid. The metal distribution differed in both studied wastewater treatment plants, and it is not the same for all analyzed metals.

Apart from individual metals concentrations in analyzed liquids, variability of the concentrations is also important. Concentration of Zn and Pb showed the largest variability compared to other heavy metals. Concentrations of heavy metals were more variable in unfiltered samples, which was expected because concentration of metals in sediments and colloids is connected with the characteristics of influent which vary from day to day. On the other hand, the content of metals in the solution, mainly in a water phase of condensates and supernatants is connected with the parameters of processes.

The concentrations of heavy metals obtained in our study were comparable to the results of Janosz– Rajczyk and Wiśniowska [13] for supernatants form WWTP in Częstochowa and to the ones obtained by Kamal Gad [12] in terms of order of magnitude. Differences observed in the case of individual metals are connected with the characteristics of wastewater incoming to WWTP and processes of their treatment.

While comparing the levels of heavy metals in wastewater and other liquids examined in our study

to toxic levels for anaerobic micro-organisms (Table 3), it must be emphasized that they were unable to act as inhibitors of biological anaerobic processes since, the concentrations observed in our study were of order of magnitude lower than having the toxic effects. They can, however, accumulate in sewage sludge and then act toxically.

Evaluating toxic effects for aerobic biological processes (especially activated sludge treatment), it is clear that the concentrations observed in our study are not expected to be toxic to micro-organisms (with the same objection concerning accumulation in sewage sludge). According to the data collected by Coello Oviedo et al. [22], Zn has some toxic effects on activated sludge at concentrations about 3 mg L^{-1} , copper has no toxic effects on activated sludge kinetics even at the concentration of 10 mg L^{-1} , whereas cadmium LD₅₀ value for activated sludge organisms is about 0.31 mg L^{-1} . According to Hartmann et al. [23], toxic effects (50% respiration inhibition) on activated sludge were observed at the following concentrations: cadmiumover 200 mg L⁻¹, copper—about 500 mg L⁻¹, nickel over 4,000 mg L^{-1} , and chromium—over 4 mg L^{-1} , however, the resistance of activated sludge from various WWTP may differ because of some differences in microbial community composition. The results obtained by Sa'idi [24] also confirms that toxic effects on activated sludge are observed at concentrations at least of order magnitude higher than the ones obtained in our study. Our results indicate that individual discharges of supernatants and condensates into the head of WWTP do not contribute to the loads of heavy metals which can affect toxically both aerobic and anaerobic processes of sewage treatment. They, however, may act as toxicants when accumulated in a solid phase.

Soluble metal contents (Na and K) were slightly lower in filtered samples than in not filtered ones. This is the result of their presence rather in liquid than in solid phase. Sodium concentrations were higher in WWTP M samples except for condensates samples in which concentration of Na was higher in WWTP H samples. Potassium concentrations were higher in WWTP H liquids except for influent (WW).

Table 3

Soluble heavy metals concentrations, in $mg L^{-1}$ which act inhibitory to anaerobic fermentation [21]

Heavy metal	Concentration
Cadmium	0.01-0.02
Chromium (VI)	1.0-1.5
Copper	0.5-1.0
Nickel	1.0-2.0
Zinc	0.5–1.0

The order of sodium content in WWTP H and WWTP M samples was: S > WW > RW > C and WW > S > RW > S, respectively. The order of potassium content in WWTP H and WWTP M samples was: S > WW > RW = C and WW > S > RW > C, respectively. As can be seen from the above results, soluble metals concentrations were the highest in influent samples in the case of both WWTP.

4. Conclusions

Based on the results obtained in the study it can be concluded that:

- (1) Condensates and reject waters both from WWTP H and WWTP M differed in terms of physicochemical characteristics from supernatants. It was especially visible in the case of WWTP H. Reject waters and condensates from this WWTP contained lower ammonium concentrations compared to supernatants alone.
- (2) Also phosphates concentration was significantly lower in C and RW from WWTP H (compared to S). Phosphates concentrations in condensates from WWTP H were comparable to the ones observed in raw wastewater; concentrations observed in reject waters from this WWTP were lower than in raw wastewater. It means that discharge of reject waters can increase the ammonium concentration in an influent, but not phosphates.
- (3) Organic compounds present in reject water were in WWTP H moderately biodegradable under aerobic conditions (based on BOD5/ COD ratio).
- (4) In the case of WWTP M, mostly polluted with COD and N-NH4⁺ substratum was condensate, but, the volume of it generated during sludge drying is negligible, so it cannot increase the concentrations of an organic compound and ammonium nitrogen in an influent.
- (5) All examined heavy metals were present in wastewater, condensates, supernatants, and the mixtures of supernatants and condensates. In general the most abundant heavy metal in all samples was zinc, followed by nickel. Copper and lead concentrations were similar, but lower than zinc. Cadmium concentration was at a very low level.
- (6) Considering the potential loads of heavy metals which may be discharged with condensates and supernatants to the head of WWTP, they can be at the level of maximum 2% of the total load. It means that the effect of these liquids on

heavy metals loads discharged into activated sludge chamber is negligible when introduced one time. They, however, can accumulate in wastewater sludge and then act toxically on the biological processes.

(7) Concentrations of heavy metals in all examined liquids were at least of one order of magnitude lower than toxic for anaerobic and aerobic processes. It means that presence of heavy metals in supernatants and condensates does not increase toxicity of influent to biological treatment processes in WWTP, when discharged one time.

Acknowledgment

This work was supported by the Częstochowa University of Technology project BS–PB –402–301/11.

References

- M. Cimochowicz-Rybicka, Minimization of sewage sludge production–European trends and selected technologies, in: Proceedings of a Polish-Swedish-Ukrainian seminar, Research and Application of New Technologies in Wastewater Treatment and Municipal Solid Waste Disposal in Ukraine, Sweden and Poland, Ukraine, 2012, pp. 99–107.
 C.B. Hill, E. Khan, A comparative study of immobi-
- [2] C.B. Hill, E. Khan, A comparative study of immobilized nitrifying and co-immobilized nitrifying and denitrifying bacteria for ammonia removal from sludge digester supernatant, Water Air Soil Pollut. 195 (2008) 23–33.
- [3] S. Gao, W. Walker, R. Dahlgren, J. Bold, Simultaneous sorption of Cd, Cu, Ni, Zn, Pb, and Cr on soils treated with sewage sludge supernatant, Water Air Soil Pollut. 93 (1997) 331–345.
- [4] W. Qiao, C. Peng, W. Wang, Z. Zhang, Biogas production from supernatant of hydrothermally treated municipal sludge by upflow anaerobic sludge blanket reactor, Bioresour. Technol. 102 (2011) 9904–9911.
- [5] A. Cydzik-Kwiatkowska, P. Rusanowska, M. Zielińska, K. Bernat, I. Wojnowska-Baryła, Structure of nitrogenconverting communities induced by hydraulic retention time and COD/N ratio in constantly aerated granular sludge reactors treating digester supernatant, Bioresour. Technol. 154 (2014) 162–170.
- [6] K. Bernat, D. Kulikowska, M. Zielińska, A. Cydzik-Kwiatkowska, I. Wojnowska-Baryła, The treatment of anaerobic digester supernatant by combined partial ammonium oxidation and denitrification, Desalin. Water Treat. 37(1–3) (2012) 223–229.
- [7] J. Suschka, S. Popławski, Ammonia removal from digester sludge supernatant, in: E. Plaza, E. Levlin, B. Hultman (Eds.), Integration and Optimisation of Urban Sanitation Systems, TRITA-LWR.REPORT 3007, Report No 11, Stockholm, 2004, pp. 113–120.
- [8] J.A. Oleszkiewicz, G. Bujoczek, J. Barnard, Sludge processing from biological nitrogen and phosphorus removal WWTP, in: Proceedings of LEMPROJEKT

Seminar on Design and Operation of Wastewater Plants, Kraków, 2000, pp. 191–225 (in Polish).

- [9] K. Piaskowski, M. Ćwikałowska, Profile of orthophosphates concentration changes during sewage and sludge treatment, Annu. Environ. Prot. 9 (2007) 183– 197 (in Polish).
- [10] M. Włodarczyk-Makuła, PAHs balance in solid and liquid phase of sewage sludge during fermentation process, J Environ. Sci. Health A 43 (2008) 1602–1609.
- [11] G. Zhang, J. Yang, H. Liu, J. Zhang, Sludge ozonation: Disintegration, supernatant changes and mechanisms, Bioresour. Technol. 100 (2009) 1505–1509.
- [12] M. Kamal Gad, Sewage sludge thickening and stabilisation using ECO NADMIC HMR, ECO NADIC 3S as alkaline additives for reuse in agriculture and soil fertilizing, in: International Conference on Chemical, Agricultural and Medical Sciences (CAMS-2014), Turkey, 2014, pp. 49–91.
- [13] M. Janosz-Rajczyk, E. Wiśniowska, Leaching of organic and inorganic micropollutants from chemically stabilized sewage—Sludge OFMSW mixtures, Chem. Pap. 59 (2005) 453–457.
- [14] Y. Wang, F. Wang, M. Ji, Characteristics of emitted odor and discharged condensate water of sludge thermal drying project in Shenzen Nanshan thermal power plant, Adv. Mater. Res. 777 (2013) 127–132.
- [15] A. Roskosch, S. Otto (Eds.), Technical Guide on the Treatment and Recycling Techniques for Sludge from Municipal Wastewater Treatment with references to Best Available Techniques (BAT), Federal Environmental Agency, Germany, 2014.
- [16] L.S. Clesceri, A.E. Greenberg, A.D. Eaton (Eds.), Standard Methods for the Examination of Water and Wastewater, twentieth ed., American Public Health Association/Water Environment Federation, Washington, DC, 1998.
- [17] K. Miksch, J. Sikora, Wastewater Technology, PWN, Wasaw, 2010 (in Polish).
- [18] F.R. Spellman, Spellman's Standard Handbook for Wastewater Operators. CRC Press, Boca Raton, FL, 2009.
- [19] J. Drinan, F. Spellman, Water and Wastewater Treatment; A Guide for Nonengineering Professional. CRC Press, Boca Raton, FL, 2013.
- [20] M. Henze, M. van Loosdrecht, G. Ekama, D. Brdjanovic, Biological Wastewater Treatment, IWA Publishing, London, 2008.
- [21] N.A. Mignone, Biological Inhibition/Toxicity Control in Municipal Anaerobic Digestion Facilities, Alabama Water and Pollution Control Association, 2005. Available from: http://www.awpca.net/Biological%20Inhi bition.pdf.
- [22] M.D. Coello Oviedo, D. Sales Márquez, J.M. Quiroga Alonso, Toxic effects of metals on microbial activity in the activated sludge process, Chem. Biochem. Eng. Q. 16 (2002) 139–144.
- [23] S. Hartmann, H. Skrobankova, J. Drozdova, Inhibition of activated sludge respiration by heavy metals, recent advances in environment, energy, ecosystem and development, in: Proceedings of the 2013 International Conference on Environment, Energy, Ecosystems and Development (EEEAD 2013), Italy, 2013, pp. 231–435.
- [24] M. Sa'idi, Experimental studies on effect of heavy metals presence in industrial wastewater on biological treatment, Int. J. Environ. Sci. 1 (2010) 666–676.