

## FATE OF PPCPS IN SEQUENCING BATCH REACTOR (SBR)

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### Abstract

In this study, the main objective was to investigate the possibilities of the removal PPCPs (pharmaceuticals and personal care products) in the SBRs at the sludge ages of 20 and 10 days and at the two different temperatures 10°C and 20°C. The pharmaceuticals and personal care products can appear in the aquatic environment in several ways: via urine and faeces, by direct use of manure as fertilizer and also by inappropriate storage of the mentioned products. The obtained results showed, that the highest removal was gained for acidic compounds (ibuprofen, ketoprofen and naproxen). At the sludge age 20 d ibuprofen was degraded in above 90%, but at the sludge age 10 d, it was removed at the same level only at the temperature of 20°C. Moreover, it can be stated, that removal of some PPCPs shows strong correlation with sludge age. The following compounds showed higher removal at the longer sludge age: iopromide, DAMI, ibuprofen, bezafibrate, ketoprofen and pentoxifyllin. Furthermore, at the sludge age 10 d the emphatic correlation temperature – removal is observed for ibuprofen, ketoprofen and bezafibrate.

### Streszczenie

Głównym celem pracy było przeprowadzenie badań dotyczących możliwości usuwania substancji farmaceutycznych ze ścieków przy użyciu reaktora typu SBR o różnych wiekach osadu czynnego (10 i 20 d) w temperaturze 10°C i 20°C. Największą podatność na degradację uzyskano dla ibuprofenu, ketoprofenu i naproxenu. Przy wieku osadu równym 20 d usunięcie ibuprofenu przekraczało 90% w obu badanych temperaturach, natomiast przy wieku osadu równym 10 d, ten sam poziom usunięcia otrzymano w temperaturze 20°C. Stwierdzono, że usunięcie niektórych badanych substancji farmaceutycznych (iopromid, DAMI, ibuprofen, bezafibrat, ketoprofen i pentoksyfyllina) jest zależne od wieku osadu. Dodatkowo, przy wieku osadu 10 d wykazano zależność między eliminacją substancji farmaceutycznych (ibuprofen, ketoprofen, i bezafibrat) a temperaturą prowadzenia procesu.

Keywords: Pharmaceuticals and personal care products (PPCPs); SBR; Sludge age; Temperature; Removal.

## 1. INTRODUCTION

Pharmaceuticals and personal care products (PPCPs) are widely used all over the world. After consumption, metabolites of pharmaceuticals and unmetabolised PPCPs are excreted by human body via urine and faeces. In such way they enter the wastewater and then they are transported to the wastewater treatment plant (WWTP). If PPCPs are not completely removed, small amounts (from 0.013 µg/L in case of ketoprofen to 22.0 µg/L in case of carbamazepine, detected in treated wastewater) can enter the environment. The same pathways of the contamination can be caused by the veterinary medication. The other way of the environment contamination is direct use of the manure as a fertilizer at the agricultural lands and then by the leakage the PPCPs can reach the ground water. Additionally, direct contamination of the environment can be caused by inappropriate storage of the pharmaceuticals and by the leakage from the sewage system.

Therefore, in the aquatic environment a wide range of the pharmaceuticals and personal care products can be found. They characterize different chemical properties as well as different area of application, for example bezafibrate and gemfibrozil represent lipid regulator, diclofenac, ibuprofen, indomethacin, naproxen and ketoprofen belong to the analgesic and antiphlogistic medicines, carbamazepine is an antiepileptic drug, sulfamethoxazole and roxithromycin are antibiotics, iopromide is a X-ray contrast media agent, AHTN (tonalide) and HHCB (galaxolide) are the representatives of the musks. The residues of the pharmaceuticals are suspected to cause serious situations, that common diseases could not be treated with known medicines. It was estimated, that more than 70% of bacteria are resistant to at least one antibiotic [1].

The research concerning occurrence pharmaceuticals and personal care products (PPCPs) in environment were performed in the USA and in some countries in Europe, for example in Germany, Switzerland and Denmark [1, 2, 3]. In Poland till now there was no research on this topic and the only data, which could be obtained, comprised the amounts of the sold pharmaceuticals. In order to improve knowledge concerning the possibilities of the removal of the PPCPs by the activated sludge process, the laboratory scale experiments were set up. SBRs (Sequencing Batch Reactor) were chosen to conduct the research, because of their advantages compared to the continuous systems of the activated sludge, for example higher flexibility in responding to changes in the

wastewater influent, possibility to work with higher loads, what effects in compact dimensions of the installations. SBR technology proves to be a good alternative for municipal sewage plants and can help to save investment costs.

In this paper, the main objective was to investigate the possibilities of the removal PPCPs in the SBRs at the sludge ages of 20 and 10 days and at the two different temperatures 10°C and 20°C.

## 2. MATERIAL AND METHODS

For the purpose of this study two SBRs of the volume 45 L were started up. The SBRs operated in 8-hour cycles (0.75 h – filling up in anoxic/anaerobic conditions, 5.25 h – aeration, 0.75 h – sedimentation and decantation, 1 h – outflow, 0.25 h – stoppage and the next cycle beginning). They were installed at the WWTP in Zabrze, which was built in 1998 and nowadays treat 70% of the wastewater, which is produced in the city. The mean flow rate is equal to 63 000 m<sup>3</sup>/d.

SBRs were fed with real wastewater after mechanical treatment (grid, sand chambers). The real wastewater was introduced to the averaged tank and next the sewage was dosed by the peristaltic pumps into the SBRs. In the same way the effluent was sucked out. The experiments were performed at the temperature 10°C and 20°C, which reflect the range of the temperature at the WWTP. At the temperatures of 10°C and 20°C the SBRs with the two different sludge age (20 and 10 days) in parallel were operated.

Excess biomass was withdrawn from the SBRs on the daily basis, as to maintain sludge age. Before the investigations the activated sludge was adapted to the proper sludge age in time no shorter than three sludge ages. The operating conditions are shown in the table 1.

**Table 1.**  
Operation conditions of the SBRs

Parameter	Unit	SBR1	SBR2	SBR3	SBR4
	Value				
Reactor volume	L	45	45	45	45
Flow rate	L/d	90	90	90	90
Sludge age	d	10	20	10	20
Temperature	°C	10	10	20	20
Sludge concentration	g/L	5	6.2	5.3	6.3

**Table 2.**  
The average results of the routine analyses

Parameter	Unit	SBR1	SBR2	SBR3	SBR4
Value					
Influent					
COD	mgO <sub>2</sub> /L	446	446	560	560
Kjeldahl nitrogen	mgN/L	60	60	96	96
Ammonia nitrogen	mgNH <sub>4</sub> <sup>+</sup> -N/L	43	43	44	44
Nitrate nitrogen	mgNO <sub>3</sub> <sup>-</sup> -N/L	1.1	1.1	0.6	0.6
P total	mgP/L	13	13	18	18
Effluent					
COD	mgO <sub>2</sub> /L	67	53	50	49
Kjeldahl nitrogen	mgN/L	9	8	10	13
Ammonia nitrogen	mgNH <sub>4</sub> <sup>+</sup> -N/L	8	7	1	3
Nitrate nitrogen	mgNO <sub>3</sub> <sup>-</sup> -N/L	9	10	29	27
P total	mgP/L	1.5	1.3	0.8	0.3

**Table 3.**  
Occurrence of the PPCPs in the influent to the WWTP

PPCPs	Detected	Not detected
Analgesic,	ibuprofen, naproxen, ketoprofen,	fenoprofen, prophiphenazon
antiphlogistic	diclofenac, indomethacin, pentoxifyllin	phenazon,
Antibiotic	sulfamethoxazole	sulfamethazin, roxithromycin
Antiepileptic	carbamazepine	-
Lipid regulator	bezafibrate, gemfibrozil, etofibrat	clofibrac acid (metabolite)
Musk	galaxolide	tonalide
Psychiatric drug	-	diazepam
X-ray contrast	iopromide, iopamidol, iomeprol,	-
media	ditrizoate, iohexol, DAMI	

The samples were taken from influent, effluent and mixed liquor at least three times a week. The average results are shown in the table 2.

The pH was measured with portable WTW pH-meter, dissolved oxygen and temperature with portable WTW DO-meter, COD was measured by means of dichromate method, Kjeldahl nitrogen and ammonia nitrogen were determined by means of Kjeltect System 1026 Tecator, nitrite and nitrate nitrogen were determined colorimetrically. These routine analyses were performed in the laboratory at Silesian University of Technology, Environmental Biotechnology Department. The PPCPs analyses were performed by Johannes Gutenberg University of Mainz, ESWE – Institute in Germany. Samples for analysis were filtrated, frozen and stored in dark-glass bottles at -18°C. Frozen samples were transported to the ESWE – Institute in Germany and next the PPCPs were determined and quantified by liq-

uid chromatography tandem mass spectrometry (LC-MS-MS) or gas chromatography mass spectrometry (GC-MS) after solid-phase extraction (SPE) as described by Ternes (1998) [4] and Hirsch et al. (1999) [1].

### 3. RESULTS AND DISCUSSION

During the research the routine analyzes were performed in order to check the efficiency of the wastewater treatment in the SBRs. All results met the Polish standards, therefore, it should be assumed, that the process of the wastewater treatment proceeded in the proper way.

In the influent to WWTP in Zabrze 17 out of 27 analyzed PPCPs were found, and they belonged to five groups (Tab. 3). The highest concentration was detected in case of iopromide; it was equal 27 µg/L.

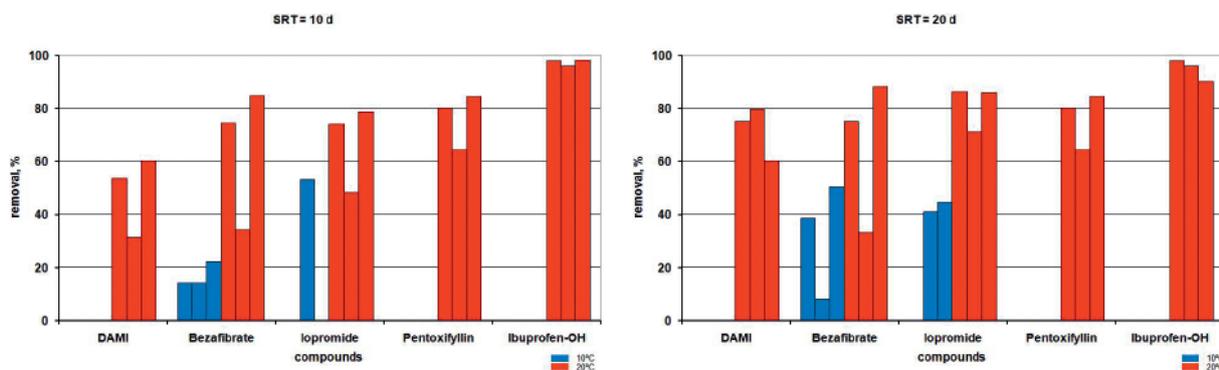


Figure 1. The PPCPs, which were removed more effectively at the temperature 20°C

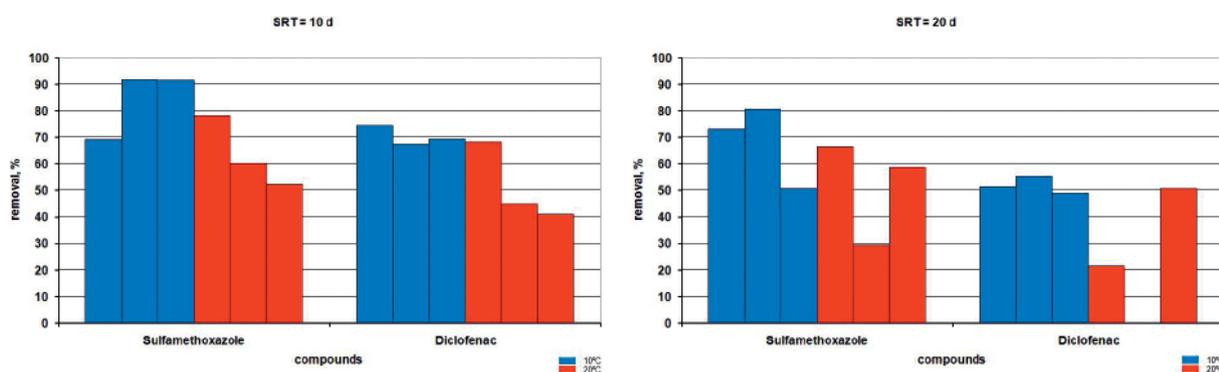


Figure 2. The PPCPs which were removed more effectively at the temperature 10°C

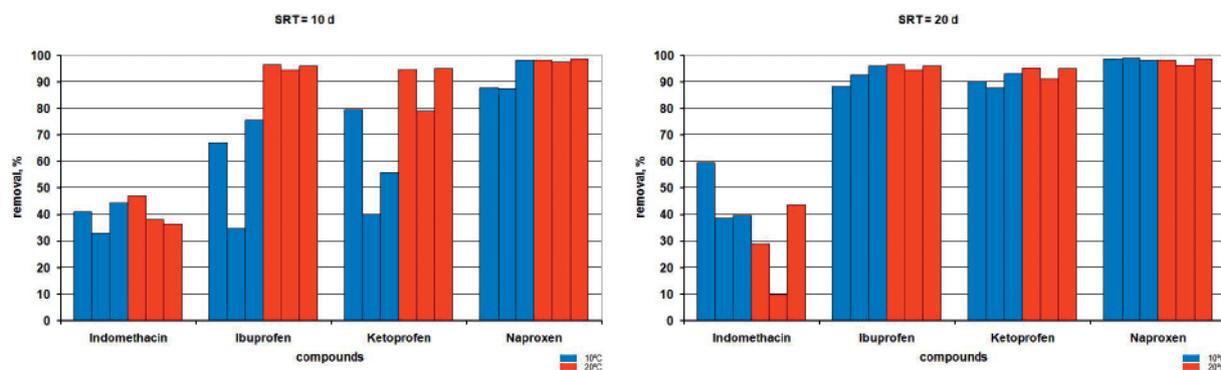
It can be explained by the high number of the hospitals in the city.

The concentration of the chosen PPCPs in the SBR – effluents varied in a dependency to the sludge age and temperature during the wastewater treatment process. The removal of five PPCPs: DAMI, bezafibrate, iopromide, pentoxifyllin and ibuprofen-OH was only significant at the temperature 20°C at the both examined sludge ages. At the sludge age 10 d, the lowest removal was noticed for DAMI, about 50%, the highest – for ibuprofen-OH above 95%. Furthermore, increase of the sludge age to 20 d caused rise of the removal mentioned above group of the PPCPs. The average removal of the DAMI, bezafibrate, iopromide, pentoxifyllin exceeded the value of 70%, the elimination of the ibuprofen-OH remained at the same level (Fig. 1).

The literature data brings some ambiguous information on ibuprofen-OH. On the one hand Buser et al. (1999) [5] observed significant elimination of this compound (above 95%), on the other hand in the research done by Stumpf et al. (1998) [6] the ibupro-

fen-OH concentration was almost the same in the influent and effluent. Concerning bezafibrate, the similar results can be found in the literature, however, the removal of this compound was reported at the level of 95% [7], whereas in SBR experiments it achieved maximum value of 88% at the sludge age 20 d and temperature 20°C.

Sulfamethoxazole also showed high efficiency of removal (Fig. 2). The average removal of this compound at the sludge age 10 d and temperature 10°C exceeded the value of 84%. But in case of sulfamethoxazole, with the increase of the sludge age and temperature, the removal did not rise or remain at the same level. On the contrary, it decreased even to 62,6% at the sludge age 20 d and temperature 20°C. Another PPCP, which showed such behaviour is diclofenac. At the sludge age 10 d and temperature 10°C the removal was around 70%, with sludge age 20 d, went down to about 50% and at the temperature 20°C and the sludge age 20 d, the average removal was equal to 41%. There is no explanation of this state and in the literature such situation was not



**Figure 3.**  
The substances, which were significantly removed at both examined temperatures

mentioned, only removal of the diclofenac was reported. According to the other authors, the diclofenac shows contradictory results. Some authors noticed its removal up to 70% [4, 7], however, the others observed no even slight elimination [8].

Indomethacin, ketoprofen, ibuprofen and naproxen belong to the group of the PPCPs, which were removed at the significant level at both examined temperatures. The average removal of indomethacin at the sludge age 10 d was independent on the temperature. In both temperatures 10°C and 20°C, the average removals of this compound were on the level of 40%. At the sludge age 20 d an insignificant impact of the temperature on the indomethacin removal can be observed (Fig. 3). The highest removal at the sludge age 10 d, above 90% (at both temperatures 10°C and 20°C), was noticed for naproxen. At the temperature 20°C, the removal of ibuprofen and ketoprofen also reached 90%, but at the temperature 10°C it was significantly lower. Nevertheless, with the sludge age of 20 d, the elimination of these substances grew to the 90% (Fig. 3). The high rate of the ibuprofen degradation was reported in the literature by many authors at the level of 95% [5, 6, 7, 8]. According to Drewes et al. (2001) [9] and Heberer (2002) [8], ketoprofen and naproxen were not removed during wastewater treatment, they were always detected in the secondary effluent.

The obtained results showed, that the highest removal was gained for acidic compounds (ibuprofen, ketoprofen and naproxen). At the sludge age 20 d ibuprofen was degraded in above 90%, but at the sludge age 10 d, it was removed at the same level only at the temperature of 20°C. Its main metabolite, ibuprofen-OH, was degraded only at the temperature 20°C. Moreover, it can be stated, that removal of some PPCPs shows strong correlation with sludge

age. The following compounds showed higher removal at the longer sludge age: iopromide, DAMI, ibuprofen, bezafibrate, ketoprofen and pentoxifyllin. There are two exceptions: sulfamethoxazole and diclofenac. Furthermore, at the sludge age 10 d the emphatic correlation temperature – removal is observed for ibuprofen, ketoprofen and bezafibrate.

#### 4. CONCLUSIONS

1. Only 17 out of 27 analyzed PPCPs were detected in the wastewater in Poland.
2. The removal of the iopromide, DAMI, ibuprofen OH, bezafibrate and pentoxifyllin was more significant at temperature 20°C.
3. The following compounds, diclofenac and sulfamethoxazole, were removed more effectively at the temperature 10°C.
4. With sludge age 10 d, the stronger temperature dependence on the removal is shown for some PPCPs.
5. The best results of the biological removal at 10°C and 20°C were noticed for acidic compounds. The removal of such compounds exceeded 90%.
6. The removal of the PPCPs showed dependence on the sludge age.

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