



Removal of heavy metals and total organic carbon from wastewater using powdered activated carbon

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Abstract. Sources of heavy metals and various micropollutants and their journey into the environment are relatively well studied today. One of the areas where a large proportion of micropollutants end up is wastewater treatment plants (WWTP); therefore, plant operators have become increasingly concerned about how to meet pollution requirements and to reduce pollutant loadings to the environment. This study analyses two possible technological alternatives to remove micropollutants using powdered activated carbon (PAC) by conducting laboratory tests. In the first alternative, a tertiary treatment was conducted with PAC dosed into the treated effluent of the operating WWTP. In the second alternative, PAC was dosed into the bioreactor. The decrease in organic matter and organic micropollutants was measured using the sum parameter total organic carbon (TOC). The tests revealed that for the removal of Cu and TOC the tertiary treatment was more effective, with removal efficiencies of 10.9% and 82.1%, respectively. On the other hand, dosing PAC into the bioreactor had a better removal efficiency for Cr (48.3%), Ni (67.5%), Zn (55.4%), Pb (36.3%), and As (66.7%). As to the removal efficiencies per 1 g of PAC, the highest effect was achieved with the dose of 34 mg/L of PAC dosed into the effluent and 14 mg/L of PAC dosed into the bioreactor. Consequently, the selection of technology requires assessment of the capital costs, operating costs, and sludge treatment technology because dosing PAC into the bioreactor will move all the adsorbed hazardous compounds into the sludge phase, thereby making an immediate use of the sludge complicated.

Key words: heavy metals removal, TOC removal, tertiary wastewater treatment, micropollutant adsorption.

INTRODUCTION

Micropollutants, such as heavy metals, pharmaceutical residues, herbicides, pesticides, and other organic compounds, are causing increasing problems in the environment. Heavy metals are released into the environment through various initial sources, such as cosmetic products, roofing materials, brake pads of vehicles, water pipes, and industrial wastewater, among others. Hazardous compounds are mainly transported by water and air [1]. Various organic pollutants, such as pharmaceutical residues, pesticides, herbicides, and residues of cleaning

agents, have been monitored for these pollutants in the hydrological cycle. After reaching the environment, heavy metals and many organic compounds accumulate in microorganisms, plants, and animals, and then reach humans via the food chain [2]. This has led to a need to remove these compounds at treatment plants in order to prevent them from entering the environment and our food chain [3].

Of heavy metals Cu and Zn show the highest concentrations in wastewater, as these metals are widely used for corrosion protection in roofing materials and various road barriers [4]. In addition, Cu and Zn can also be found in many cosmetic products, PVC stabilizers, various alloys, water softeners, medicines, and paints [5–7]. Looking at

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the results of two different studies, Ong et al. found that heavy metals can be ranked as follows according to their toxic properties: $Cd > Cu > Zn > Cr > Pb$, where Cd has the largest effect and Pb has the smallest effect; or, $Cd > Cr > Cu > Pb > Zn$, where the effect of Zn is the smallest [2].

There are approximately 3000 different active pharmaceutical ingredients and more than 300 pesticides and biocidal products commercially available [8,9]. These compounds can end up in wastewater treatment plants (WWTPs) via human metabolism, washing of fruits, improper handling, or by being carried along with stormwater. Ordinary treatment plants only remove some of these compounds, while a large proportion either degrades partially or accumulates in sludge [10–12]. Although micropollutants in the influent of WWTPs are in very low concentrations (nano- and micrograms per litre), various studies have shown that they nevertheless affect living organisms. Especially as a result of combined factors – many of these compounds are designed to be biologically active, have resistant molecules to ensure their effect, and are not readily degradable – they accumulate and are released into the cycling of substances in the same way as heavy metals [10,13]. Because the monitoring of individual organic micropollutants is complicated and expensive, the sum parameters total

organic carbon (TOC) or dissolved organic carbon (DOC) are increasingly used to measure these compounds [9,14].

For the removal of heavy metals, ion-exchange methods, electro dialysis, coagulation, membrane filtration, biosorption, and adsorption are widely used [3,6,15]. For the removal of organic micropollutants, mainly adsorption and advanced oxidation processes are used [9,16,17]. However, in the wastewater treatment process it is important to look at all the hazardous compounds in their entirety in order to find the optimal technical solution for the removal of both heavy metals and other micropollutants. Table 1 compares several treatment processes for removing various micropollutants.

Each of the technologies has its advantages and disadvantages. For example, advanced oxidation processes oxidize most of the active pharmaceutical ingredients, but it is not guaranteed that the oxidation process will be completed to CO_2 , i.e. a risk remains that intermediate products having an unknown effect are produced [23,24]. Biosorption also has disadvantages because a prerequisite for this process is that the substances to be removed cannot be toxic and the removal takes place through sludge, which does not allow for later reuse of the sludge [22,25]. The coagulation of heavy metals works efficiently for removing specific heavy metals, but

Table 1. Advantages (+) and disadvantages (–) of various technological solutions for removing micropollutants [3,9,14,18–22]. PAC – powdered activated carbon, GAC – granular activated carbon

Technology		Heavy metals		Organic micropollutants
Advanced oxidation process (O_3 , H_2O_2)	–	Does not remove heavy metals	+, –	Oxidizes organic compounds, but produces intermediate products with unknown effects
Advanced oxidation process (O_3 , H_2O_2) + PAC & GAC	+	Removes heavy metals only in PAC & GAC stage	+	Oxidizes organic compounds. Intermediate products are removed with activated carbon
Adsorption (PAC & GAC)	+	Removes a large proportion of heavy metals, but controlling the process is complicated and expensive	+, –	Removes most organic substances, but problems occur with compounds consisting of large molecules and easily soluble compounds
Coagulation	+, –	Many heavy metals can be removed, but adjusting pH is often necessary. Produces chemical sludge	–	Indirect partial removal by means of sorption
Biosorption (microorganisms)	+	Process is difficult to control, but enables removal of heavy metals from aqueous phase into sludge phase. Produces sludge, which then needs separate treatment, e.g. incineration	+, –	Possible only if no toxic compounds are involved. Direct reuse of sludge is not possible
Electrodialysis	+	Efficiently and widely used in industrial wastewater treatment	–	Does not remove organic substances
Membrane filtration	+, –	Concentrates heavy metals, but requires additional treatment of retentate, e.g. GAC	+, –	Concentrates organic substances, but requires additional treatment of retentate, e.g. GAC

requires that the pH be often changed and neutralized before the effluent can be released into the environment. In addition, the removal is carried out through sludge, which excludes the possibility of immediate reuse of the sludge. Moreover, coagulation is not the best solution to achieve very low concentrations of heavy metals [22]. Membrane filtration removes most of the micropollutants, but leaves a concentrated retentate, which then requires additional treatment, such as with O₃ + powdered activated carbon (PAC) or granular activated carbon (GAC) [22,26].

Table 1 shows that the most reasonable method is to remove micropollutants by applying adsorption. Although adsorption with activated carbon is an equilibrium process, many of the pollutants do not respond to physical adsorption and the resulting relationship between the adsorbent and the adsorbate is often weak; thus, the implementation of this process for each individual WWTP will require a specific preliminary study [27,28]. Besides, whether the treatment plant would require any additional technological solutions depends on the dosing point. For example, applying PAC as a tertiary treatment requires a mixing chamber and post-filtration or a settlement tank. Dosing PAC into the bioreactor increases the proportion of hazardous compounds in the sludge and reduces it in the effluent, so it is likely that the sludge must be incinerated and cannot be easily put back in circulation [29].

The aim of this study was to compare the removal of heavy metals and total organic carbon (TOC) by using PAC, as illustrated by an example of an operating WWTP. The analysis compares two PAC dosing point options, treatment efficiencies, and their advantages and disadvantages.

MATERIALS AND METHODS

The comparison of technologies for the removal of heavy metals and TOC was conducted by using activated sludge and effluent from an operating municipal WWTP. The WWTP has the following process steps: screens, sand traps, pre-precipitation of phosphorus, primary sedimentation tanks, bioreactor, post-precipitation of phosphorus, secondary sedimentation tanks (clarifiers), and anaerobic stabilization of sludge. The basic parameters of the activated sludge process are mixed liquor suspended solids (MLSS) 4200 mg/L, sludge retention time (SRT) 16 days, food-to-mass (F/M) 0.05, and hydraulic retention time (HRT) in the bioreactor 8 h. The average loads received at the WWTP are presented in Table 2.

Two technological options for removing heavy metals and TOC were compared, namely the tertiary treatment of the effluent (after biological treatment) with PAC

Table 2. Average parameters of wastewater ($n = 1820$)

Parameter	mg/L
BOD ₇	190
COD	484
Suspended solids	349
P _{tot}	6.32
N _{tot}	49.64

(Test 1, PAC) and dosing PAC into the bioreactor (Test 2, APAC). The test schemes are presented in Fig. 1. In the first test scheme, the test was conducted using the effluent leaving the clarifier of an operating WWTP, and the effects of different doses and HRT on the removal of the studied substances were compared. In the second test scheme, the test was conducted using a model of a WWTP, which consisted of an anoxic tank, an aerobic tank, and a clarifier. PAC was dosed directly into the anoxic bioreactor and the effects of different doses were compared. For the determination of heavy metals (Zn, Cu, As, Pb, Cr, and Ni), ISO 17294-2:2003 (application of inductively coupled plasma mass spectrometry, ICP-MS) standard was applied, and other parameters were determined by the following Hach Lange standard methods: TOC/DOC LCK 380 (sample was filtrated, 0.45 µm), N_{tot} LCK 238, P_{tot} LCK 348, PO₄ LCK 348, NH₄ LCK 305, NO₂ LCK 341, and NO₃ LCK 339. In addition, the water temperature, pH, and conductivity were registered.

The PAC tests were conducted as batch tests in 1000 mL of effluent, with the addition of 10, 25, 50, and 100 mg/L of PAC followed by mixing in the laboratory reactor at 250 rpm. To study the effect of HRT, samples were taken at intervals of 5, 10, 20, 60, and 90 min. To study the effect of different doses, samples were taken 10 min after dosing the activated carbon; a longer HRT would require a very large mixer, which is not possible with the existing treatment plants. The effluent samples were filtrated through a 10 µm filter that imitated the disc and cloth media filters widely used in the tertiary treatment of wastewater.

The model test was conducted on the model of a WWTP (Fig. 2), where the volume of the anoxic part was 3800 mL, the volume of the aerobic part was 10 800 mL, the HRT of the whole process was adjusted to 8 h, which is the average HRT needed to carry out the biological treatment, and the average MLSS was 4200 mg/L (determined by applying EVS-EN 872 standard). The flow rate of the return activated sludge was 180% compared to the incoming flow rate. Before and after the test, the pH, conductivity, temperature, and the concentrations of Zn, Cu, As, Pb, Cr, Ni, N_{tot}, P_{tot}, PO₄, NH₄, and TOC were determined.

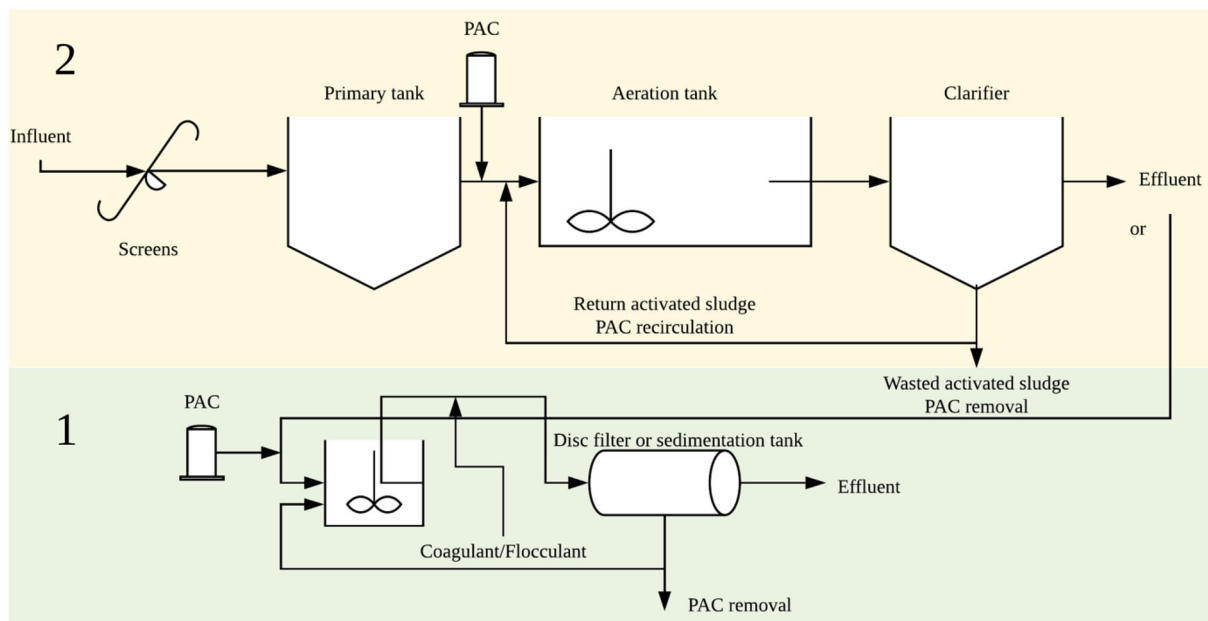


Fig. 1. Schemas of the conducted tests. In Test 2 (APAC), PAC was dosed into the bioreactor. In Test 1 (PAC), PAC was dosed into the effluent taken from the clarifier.

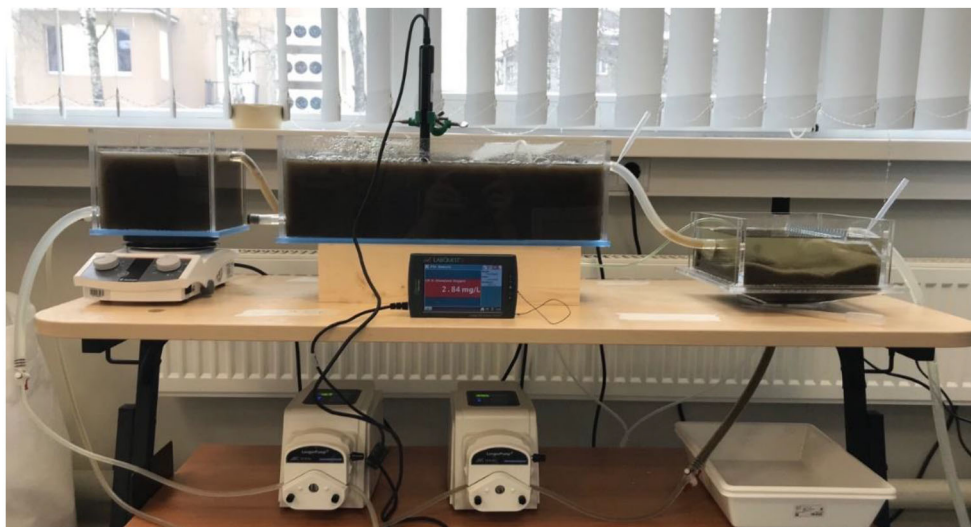


Fig. 2. Model test design. The wastewater treatment scheme consisted of an anoxic tank, aerobic tank, and a clarifier. PAC was dosed into the anoxic tank at concentrations of 10, 25, 50, and 100 mg/L in different tests.

The analysis could not take account of the heavy metals already present in the activated sludge, which also cannot be taken into account in actual WWTPs. However, it was beneficial to determine how PAC affected the adsorption of heavy metals and the equilibrium processes, that is, to analyse how the heavy metals, TOC, and PAC dose were related.

RESULTS AND DISCUSSION

In Test 1, PAC was dosed into the effluent of an operating WWTP in different concentrations in order to determine the optimal PAC dose for the removal of heavy metals and TOC. The HRT chosen for the process was 10 min because after that the equilibrium concentration was

achieved for most of the heavy metals. At the beginning of the test, the pH of the water was 7.22. The higher the PAC dose added, the higher the pH of the test reactor; at 100 mg/L of PAC, the final pH was 7.5, i.e. PAC reduced the acidity of the water. The conductivity of the water before the test was 1200 $\mu\text{S}/\text{cm}$, and at the highest dose of PAC, the equilibrium value reached 1191 $\mu\text{S}/\text{cm}$, i.e. the adsorption did not have a significant effect on conductivity. The results of Test 1 are presented in Fig. 3 and of Test 2 in Fig. 4.

As for Cr, the initial concentration was 0.86 $\mu\text{g}/\text{L}$ and the PAC concentrations dosed were 10, 25, 50, and 100 mg/L. The treatment efficiency increased linearly as the PAC dose increased: at 10 mg/L of PAC, 1.2% of the Cr was removed, and at 100 mg/L of PAC, 25.6% of the Cr was removed. The initial concentration of Cu was 9.25 $\mu\text{g}/\text{L}$ and the removal efficiencies of PAC doses were 15.7%, 54.6%, 62.2%, and 54.6%, respectively. That is, the maximum Cu removal of the equilibrium system was achieved at 50 mg/L of PAC, and the

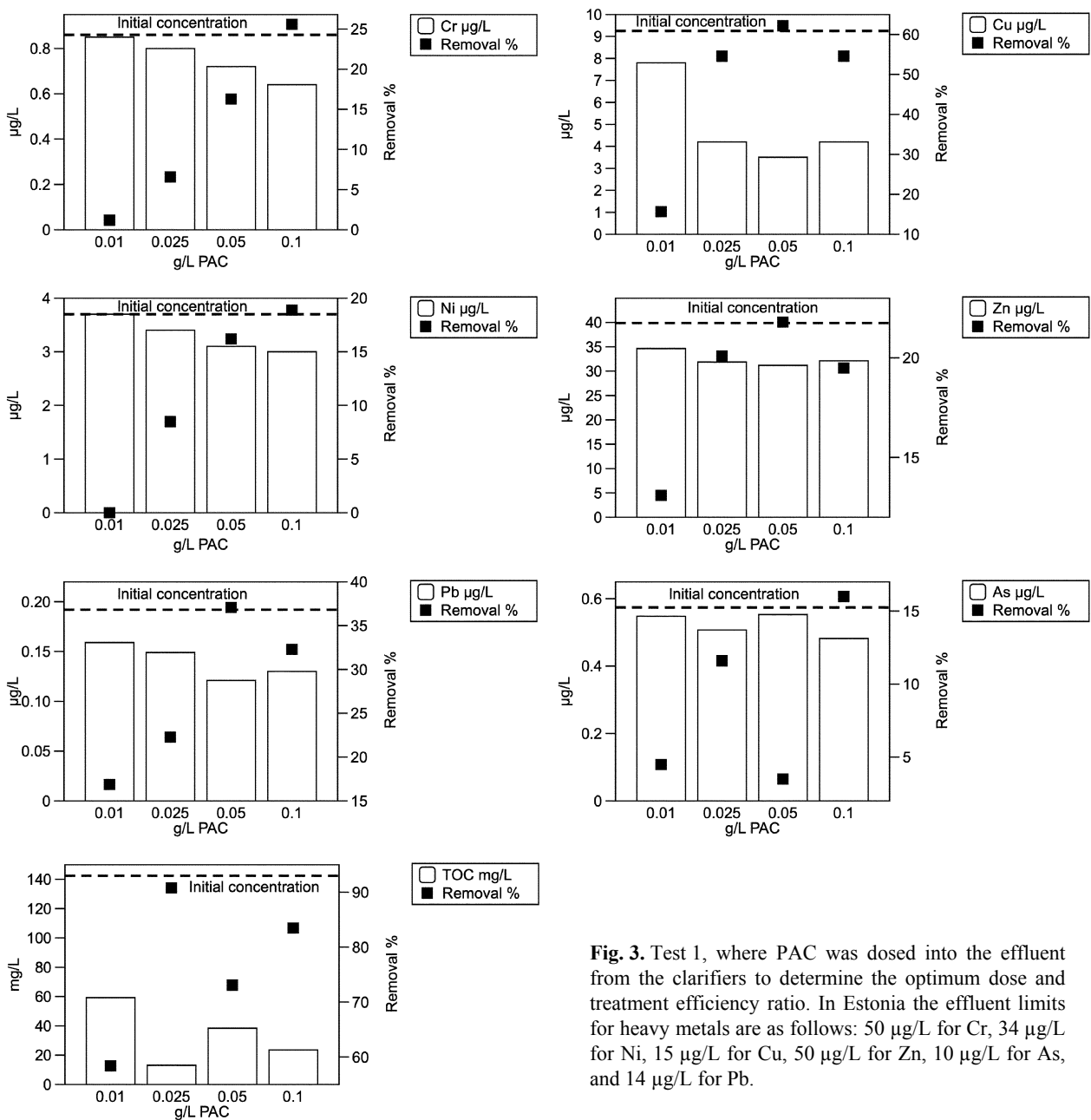


Fig. 3. Test 1, where PAC was dosed into the effluent from the clarifiers to determine the optimum dose and treatment efficiency ratio. In Estonia the effluent limits for heavy metals are as follows: 50 $\mu\text{g}/\text{L}$ for Cr, 34 $\mu\text{g}/\text{L}$ for Ni, 15 $\mu\text{g}/\text{L}$ for Cu, 50 $\mu\text{g}/\text{L}$ for Zn, 10 $\mu\text{g}/\text{L}$ for As, and 14 $\mu\text{g}/\text{L}$ for Pb.

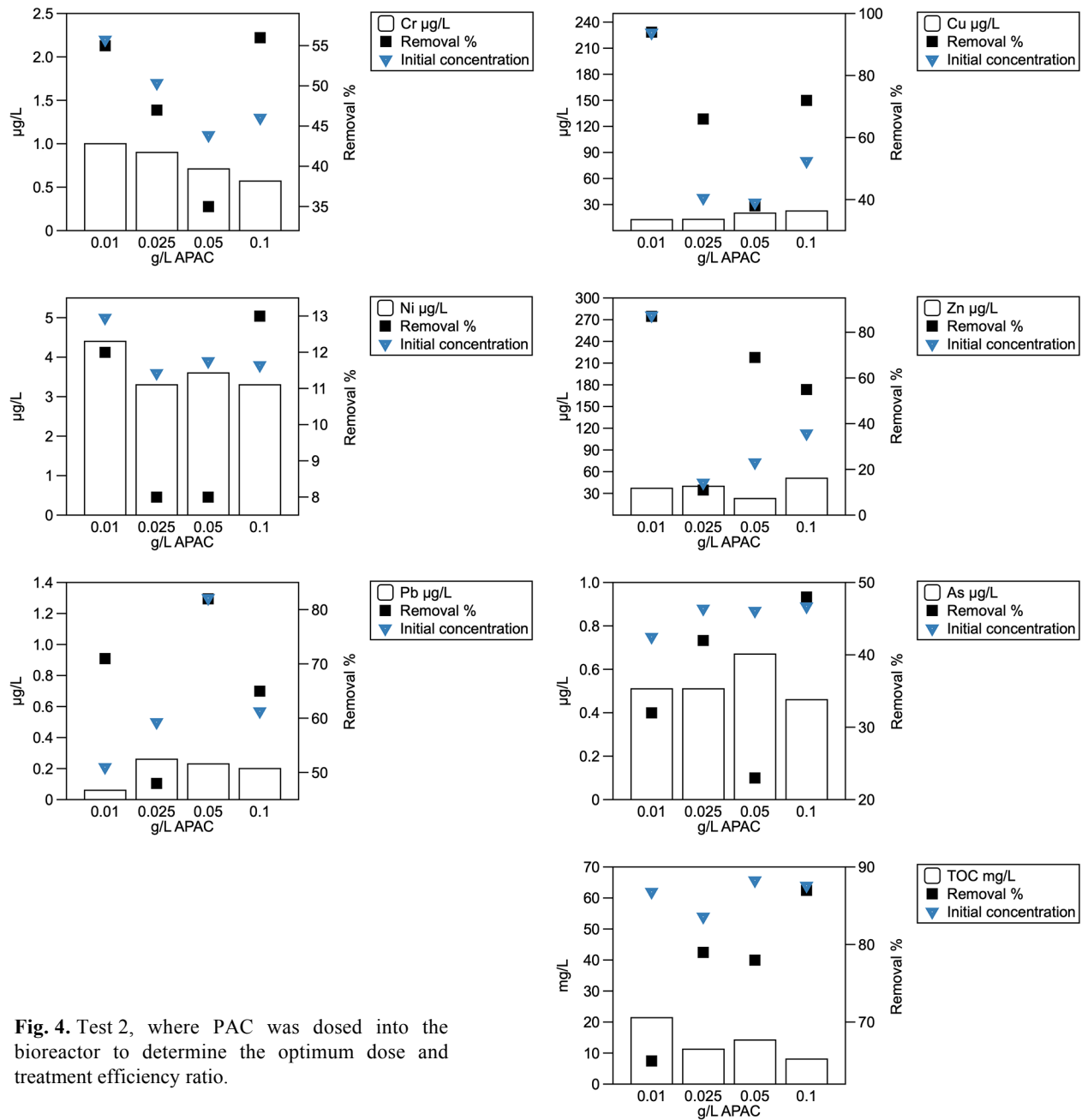


Fig. 4. Test 2, where PAC was dosed into the bioreactor to determine the optimum dose and treatment efficiency ratio.

removal efficiency started to decrease again when dosing 100 mg/L of PAC. Similar dynamics of removal also occurred for Zn, where the maximum adsorption of 21.8% was achieved at 50 mg/L of PAC, and further increase in dosing did not increase the removal efficiency. The optimal response to adsorption (maximum removal >30%) was achieved for Cu, Pb, and TOC, where the highest treatment efficiencies were 62.2%, 37.1%, and 90.8%, respectively (Fig. 3). However, Cr, Ni, Zn, and As did not respond to the adsorption process so well:

their maximum treatment efficiencies were 25.6%, 18.9%, 21.8%, and 16%, respectively. In the case of TOC, the most effective dose of PAC was 25 mg/L, at which the removal efficiency was 90.8%. For Cu, Zn, and Pb, the most effective dose was 50 mg/L of PAC, and for Cr, Ni, and As, the most effective dose was 100 mg/L of PAC.

Ong and co-authors found in their batch tests conducted with synthetic wastewater, at initial heavy metal concentrations one thousand times higher, and

with an HRT 30 times longer than that in this study, that the optimal responses to PAC adsorption were achieved for Cu, Ni, and Zn, and that poor responses were observed for Cd and Cr [2]. The difference in the adsorption of heavy metals compared to that in this study was likely due to the additional compounds, which also adsorb and reduce the specific adsorption of heavy metals. A study conducted by Karnib and co-workers found that the efficiency of adsorption at low concentrations of heavy metals (30 mg/L) was ranked as Ni (90%), Cd (86%), Zn (83.6%), Pb (83%), and Cr (50.6%) [30]. According

to the results of our study, the same ranking was Ni > As > Zn > Cr > Cu > Pb. For a better comparison of the removal efficiencies, Fig. 5 presents the mass removed per 1 g of PAC (Qe).

In Test 2, the pH in the bioreactor before dosing with PAC was 7.32, and the conductivity was on average 1534 μS/cm. The pH in the bioreactor rose and the conductivity decreased as the PAC doses increased. At the maximum PAC dose of 100 mg/L, the pH rose to 7.49 and conductivity fell to 1194 μS/cm. The decrease in the parameters was due to the absorption with PAC as

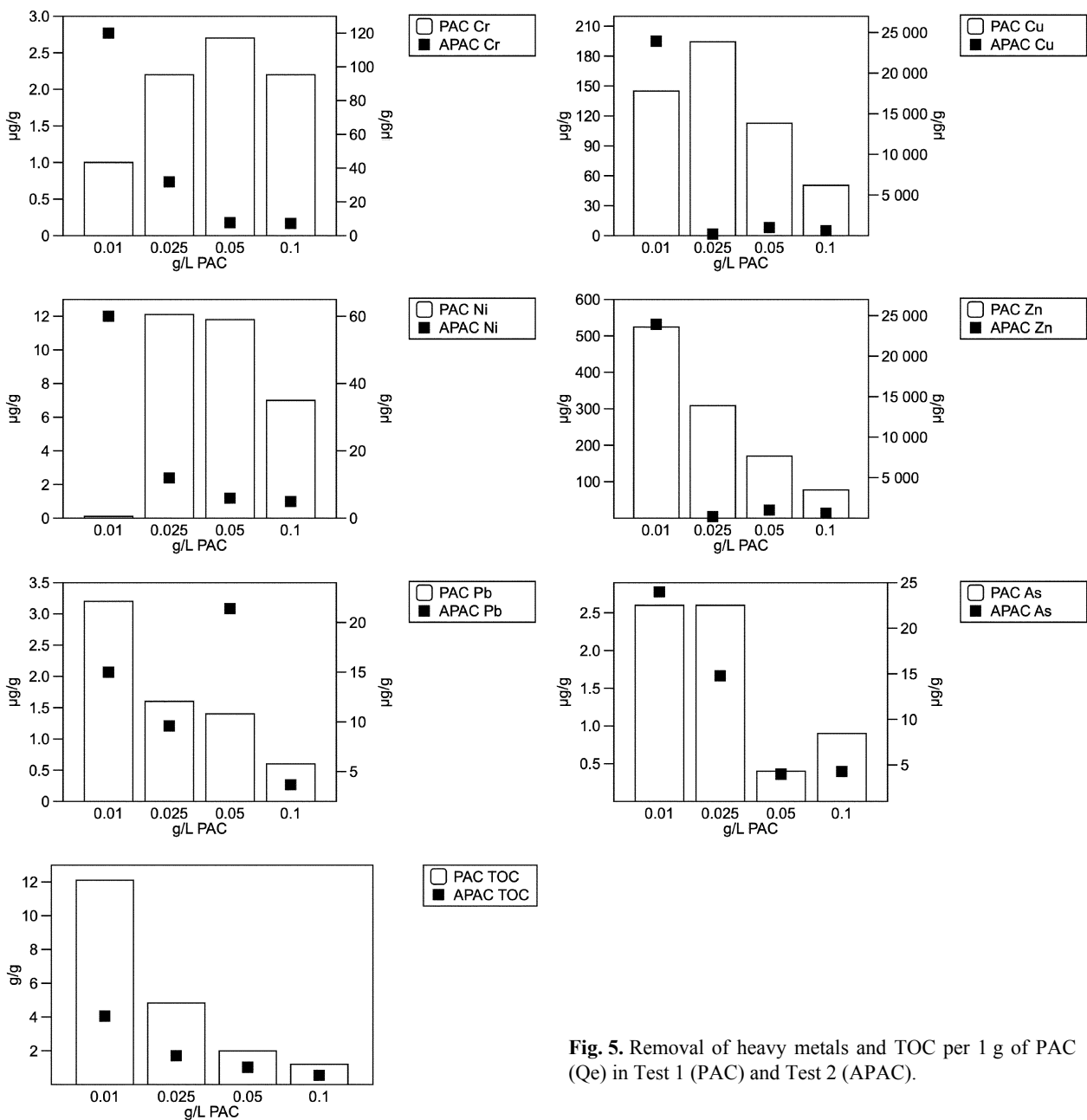


Fig. 5. Removal of heavy metals and TOC per 1 g of PAC (Qe) in Test 1 (PAC) and Test 2 (APAC).

well as the sorption by biomass, which was not studied individually. However, the sorption by biomass can be explained by the comparison of Test 1 and Test 2, the results of which are presented separately in Fig. 5.

As to the removal efficiencies and the initial and final concentrations of Cr, it was found that the smallest PAC dose (10 mg/L) removed 55% of the Cr, and increasing the PAC dose did not improve the treatment efficiency, instead it worsened. As for Cu, the initial concentration in the first series of tests was very high in comparison to that in the other series, but with the PAC dose of 10 mg/L, a removal efficiency of 94% was achieved. Optimal responses to the APAC process were achieved for Cr, Cu, Zn, Pb, As, and TOC, where the maximum removal efficiencies were 55%, 94%, 87%, 82%, 48%, and 87%, respectively. Biological processes enhanced TOC removal, where heterotrophic microorganisms used the readily degradable dissolved organic matter in their vital functions [10,31]. The removal of Ni in these tests was poorer compared to the other parameters, with a respective removal efficiency of 13%. The average treatment values for Test 1 and Test 2 are presented in Table 3.

As can be deduced from Table 3, in terms of the removal efficiency, the two different technological concepts for the removal of Cu, Ni, and TOC proved to be similar, with approximately the same efficiency $\pm 15\%$ achieved for each. At the same time, the differences in the removal of Cr, Zn, Pb, and As were larger; the APAC process proved to be more effective, with removal efficiencies more than 2 times greater than those of the PAC process. This may have resulted from biosorption or sorption, where these specific heavy metals were adsorbed on the PAC surface and also by biomass [15,22]. Wang and co-workers [32] conducted a similar test on the sequencing batch reactor pilot device using wastewater from a chemical industry to study the removal of TOC with PAC. They found that PAC alone removed 38% of the TOC and that the APAC scheme resulted in 68% removal efficiency, which suggested that the remaining 32% of the organic compounds did not respond to adsorption and were not readily biodegradable due to their molecular characteristics. Before any additional removal of TOC, advanced oxidation of wastewater would be required [9,10,32].

To compare the tests with different initial concentrations and to identify the most effective dosing point

and dose of PAC, the removal of heavy metals ($\mu\text{g/g}$) and TOC (mg/g) per 1 g of PAC was identified. The results are presented in Fig. 5. The greatest removal of Cr per 1 g of PAC was achieved at 50 mg/L of PAC in Test 1 and at 10 mg/L of PAC in Test 2, with the removal of 2.7 $\mu\text{g/g}$ and 120 $\mu\text{g/g}$, respectively. For Cu, the most effective dose in Test 1 proved to be 25 mg/L of PAC and in Test 2, 10 mg/L of PAC, which was similar to Cr. In the tests by Ong and co-workers conducted in synthetic wastewater, the following Q_e -s were found: Cu 61 mg/g, Cd 22 mg/g, Zn 29 mg/g, Ni 33 mg/g, and Cr 10 mg/g [2]. The large difference between the tests conducted with synthetic wastewater and actual wastewater indicates that the compounds contained in the wastewater reduce the adsorption efficiency of heavy metals and that the adsorption capability depends on the concentration of the compounds found in the wastewater. The tests with synthetic wastewater have shown that higher concentrations of heavy metals can reduce the specific adsorption [2,33].

The results for TOC differed from those for heavy metals. In Test 1, the most effective PAC dose was 10 mg/L, with a respective TOC removal of 12 096 mg/g. In Test 2, where the same PAC dose proved to be the most effective, the achieved removal was 4060 mg/g. In a study conducted by Margot and co-workers, 10 mg/L was also the most effective dose for removing organic matter; the authors indicated that a higher dose would increase the treatment efficiency by a small degree, but given the increasing operating costs, it would not be justified [10]. The comparison of the two tests showed that a higher removal per 1 g of PAC was achieved in Test 2, except for TOC. The higher removal efficiency most likely resulted from the additional sorption by biomass, which increased the removal of heavy metals, and from the longer HRT of the process [2,32,34]. In terms of correlation, similar responses to adsorption in both tests were observed for As and TOC, but for the other parameters the same correlation was not found.

Based on the tests conducted, which took into account the PAC dose and Q_e , the most effective doses of PAC to remove the studied parameters are presented in Table 4. The data analysis also took into account the rationality aspect, where a 50% increase in the PAC dose was not justified in order to increase the removal efficiency by a small amount, such as a 2.7% increase in the removal of Ni.

Table 3. Average treatment efficiencies in Test 1 and Test 2 (%)

	Cr	Cu	Ni	Zn	Pb	As	TOC
Test 1 PAC	12.4	10.9	46.8	18.6	8.9	27.2	82.1
Test 2 APAC	48.3	10.3	67.5	55.4	36.3	66.7	77.6

Table 4. The most effective PAC dose (mg/L) depending on the dosing point

	Cr	Cu	Ni	Zn	Pb	As	TOC
Test 1 PAC	50	25	50	25	50	25	10
Test 2 APAC	10	10	10	10	10	25	25

In Test 1, the most effective PAC dose was 34 mg/L as an average, and in Test 2, the most effective dose was 14 mg/L of PAC (cf. Table 4). The higher dose in the tertiary treatment was most likely due to the small concentration of suspended solids and the low sorption, whereas in the case of APAC, the circulation of unreacted PAC in the return activated sludge and the additional sorption by biomass were ensured. Leaving aside the costs of sludge treatment, the first technological solution appears to be more expensive (Test 1) than the second (Test 2) because the necessary PAC dose is higher. In addition, it would require additional equipment to remove PAC [35,36]. For the APAC process, only a PAC dosing unit would need to be added, and PAC would be removed along with the waste activated sludge. Given the current technological level, this solution would require the waste activated sludge to be incinerated because the separate removal of heavy metals and other micropollutants from the sludge is very complicated [18,29]. One of the advantages of the APAC process appears to be the improved nitrification. Several studies have demonstrated that PAC provides a good biofilm carrier for various nitrifying microorganisms, and positive effects have been observed for phosphorus removal [37,38].

CONCLUSIONS

Heavy metals and various organic micropollutants pose a serious problem in the environment. Although the sources of micropollutants are mostly products and production processes, wastewater and stormwater also transfer pollutants. Therefore, a need has arisen to remove these compounds at WWTPs. Various technologies are used, such as coagulation, advanced oxidation processes, and membrane filtration, but the technology most suited for the removal of heavy metals and organic pollutants is treatment with activated carbon.

This study examined the use of PAC at a WWTP and compared the effects of two different dosing points and various PAC doses on the treatment efficiency. In addition, this paper outlines the advantages and disadvantages for each of the solutions. The study revealed that both dosing points were suitable to remove heavy metals and TOC, but in terms of the treatment efficiency, using PAC as a tertiary treatment proved to be more

effective for Cu and TOC. Dosing PAC into the bioreactor, on the other hand, was more effective at removing Cr, Ni, Zn, Pb, and As. The first technology, where PAC was dosed after the clarifier, requires larger investments because a mixing chamber, settlement tank, or post-filtration technology needs to be added, but its advantage is that the hazardous compounds are not released into the wastewater after having been concentrated. The second alternative, where PAC was dosed into the bioreactor, appears to be cheaper and more effective in terms of investments, but PAC, after having been concentrated with hazardous compounds, is removed along with the sludge, which makes the reuse of the sludge in a circular economy extremely complicated.

At a WWTP where the sludge is incinerated, it is reasonable to dose PAC into the bioreactor because it appears to be a more effective and cheaper solution. Phosphorus can also be recovered from the ashes of sludge. If the reuse of sludge immediately after stabilization is desired and the WWTP has enough land to build the necessary equipment, it is reasonable to dose PAC as a tertiary treatment. Possible technological solutions to remove or separate PAC contained in the activated sludge and the factors affecting the adsorption of the compounds need further monitoring.

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REFERENCES

1. Men, C., Liu, R., Xu, F., Wang, Q., Guo, L., and Shen, Z. Pollution characteristics, risk assessment, and source apportionment of heavy metals in road dust in Beijing, China. *Sci. Total Environ.*, 2018, **612**, 138–147.
2. Ong, A. S., Toorisaka, E., Hirata, M., and Hano, T. Adsorption and toxicity of heavy metals on activated sludge. *ScienceAsia*, 2010, **36**, 204–209.
3. Fang, L., Li, L., Qu, Z., Xu, H., Xu, J., and Yan, N. A novel method for the sequential removal and separation of multiple heavy metals from wastewater. *J. Hazard. Mater.*, 2018, **342**, 617–624.
4. Jiang, R., Sun, S., Wang, K., Hou, Z., and Li, X. Impacts of Cu(II) on the kinetics of nitrogen removal during

- the wastewater treatment process. *Ecotoxicol. Environ. Saf.*, 2013, **98**, 54–58.
- Sani, A., Gaya, B. G., and Abubakar, A. F. Determination of some heavy metals in selected cosmetic products sold in kano metropolis, Nigeria. *Toxicol. Rep.*, 2016, **3**, 866–869.
 - Kobielska, A. P., Howarth, J. A., Farha, K. O., and Nayak, S. Metal–organic frameworks for heavy metal removal from water. *Coord. Chem. Rev.*, 2018, **358**, 92–107.
 - González-Acevedo, Z. I., García-Zarate, M. A., Núñez-Zarco, E. A., and Anda-Martín, B. I. Heavy metal sources and anthropogenic enrichment in the environment around the Cerro Prieto Geothermal Field, Mexico. *Geothermics*, 2018, **72**, 170–181.
 - Klatte, S., Schaefer, H-C., and Hempel, M. Pharmaceuticals in the environment – a short review on options to minimize the exposure of humans, animals and ecosystems. *Sustain. Chem. Pharm.*, 2017, **5**, 61–66.
 - Giannakis, S., Gamarra Vives, F. A., Grandjean, D., Magnet, A., De Alencastro, L. F., and Pulgarin, C. Effect of advanced oxidation processes on the micropollutants and the effluent organic matter contained in municipal wastewater previously treated by three different secondary methods. *Water Res.*, 2015, **84**, 295–306.
 - Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L. F., et al. Treatment of micropollutants in municipal wastewater: ozone or powdered activated carbon? *Sci. Total Environ.*, 2013, **461–462**, 480–498.
 - Lillenberg, M. *Residues of Some Pharmaceuticals in Sewage Sludge in Estonia, Their Stability in the Environment and Accumulation into Food Plants via Fertilizing*. Ecoprint, Tartu, 2011.
 - Nei, L., Haiba, E., Kutti, S., and Kipper, K. Sewage sludge compost, microbial activity and pharmaceuticals. *Global J. Adv. Pure Appl. Sci.*, 2014, **3**, 30–37.
 - Katsou, E., Alvarino, T., Malamis, S., Suarez, S., Frison, N., Omil, F., and Fatone, F. Effects of selected pharmaceuticals on nitrogen and phosphorus removal bioprocesses. *Chem. Eng. J.*, 2016, **295**, 509–517.
 - Rattier, M., Reungoat, J., Gernjak, W., and Keller, J. Organic Micropollutant Removal by Biological Activated Carbon Filtration: A Review. Urban Water Security Research Alliance Technical Report No. 53, 2012.
 - Luo, S-L., Yuan, L., Chai, L-Y., Min, X-B., Wang, Y-Y., Fang, Y., and Wang, P. Biosorption behaviors of Cu^{2+} , Zn^{2+} , Cd^{2+} and mixture by waste activated sludge. *Trans. Nonferrous Met. Soc. China*, 2006, **16**, 1431–1435.
 - Köhler, C., Venditti, S., Igos, E., Klepizewski, K., Benetto, E., and Cornelissen, A. Elimination of pharmaceutical residues in biologically pre-treated hospital wastewater using advanced UV irradiation technology: a comparative assessment. *J. Hazard. Mater.*, 2012, **239–240**, 70–77.
 - Chang, E. E., Wan, J-C., Kim, H., Liang, C-H., Dai, Y-D., and Chiang, P-C. Adsorption of selected pharmaceutical compounds onto activated carbon in dilute aqueous solutions exemplified by acetaminophen, diclofenac, and sulfamethoxazole. *Sci. World J.*, 2015, **2015**, 186501.
 - Meinel, F., Ruhl, A. S., Sperlich, A., Zietzschmann, F., and Jekel, M. Pilot-scale investigation of micropollutant removal with granular and powdered activated carbon. *Water Air Soil Pollut.*, 2015, **226**, 1–10.
 - Wu, H., Zhang, A., and Wang, L. Immobilization study of biosorption of heavy metal ions onto activated sludge. *J. Environ. Sci. (China)*, 2004, **16**, 640–645.
 - Chipasa, K. B. Accumulation and fate of selected heavy metals in a biological wastewater treatment system. *Waste Manag.*, 2003, **23**, 135–143.
 - Hammami, A., González, F., Ballester, A., Blázquez, M. L., and Muñoz, J. A. Biosorption of heavy metals by activated sludge and their desorption characteristics. *J. Environ. Manage.*, 2007, **84**, 419–426.
 - Carolin, F., Kumar, P. S., Saravanan, A., Joshiba, G. J., and Naushad, M. Efficient techniques for the removal of toxic heavy metals from aquatic environment: a review. *J. Environ. Chem. Eng.*, 2017, **5**, 2782–2799.
 - Lonappan, L., Brar, S. K., Das, R. K., Verma, M., and Surampalli, R. Y. Diclofenac and its transformation products: environmental occurrence and toxicity – a review. *Environ. Int.*, 2016, **96**, 127–138.
 - Alvarez-Corena, J. R., Bergendahl, J. A., and Hart, F. L. Advanced oxidation of five contaminants in water by UV/TiO₂: reaction kinetics and byproducts identification. *J. Environ. Manage.*, 2016, **181**, 544–551.
 - Wu, Q., Huang, K., Sun, H., Ren, H., Xiang Zhang, X., and Ye, L. Comparison of the impacts of zinc ions and zinc nanoparticles on nitrifying microbial community. *J. Hazard. Mater.*, 2018, **343**, 166–175.
 - Arya, V., Philip, L., and Murty Bhallamudi, S. Performance of suspended and attached growth bioreactors for the removal of cationic and anionic pharmaceuticals. *Chem. Eng. J.*, 2016, **284**, 1295–1307.
 - Sekar, M., Sakthi, V., and Rengaraj, S. Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *J. Colloid Interface Sci.*, 2004, **279**, 307–313.
 - Amuda, O. S., Giwa, A. A., and Bello, I. A. Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochem. Eng. J.*, 2007, **36**, 174–181.
 - Bauhaus-Universität Weimar. *Abwasserbehandlung: Gewässerbelastung, Bemessungsgrundlagen, Mechanische Verfahren und Biologische Verfahren, Reststoffe aus der Abwasserbehandlung, Kleinkläranlagen*. VDG, Weimar, 2014.
 - Karnib, M., Kabbani, A., Holail, H., and Olama, Z. Heavy metals removal using activated carbon, silica and silica activated carbon composite. *Energy Procedia*, 2014, **50**, 113–120.
 - Çeçen, F., Semerci, N., and Geyik, A. G. Inhibition of respiration and distribution of Cd, Pb, Hg, Ag and Cr species in a nitrifying sludge. *J. Hazard. Mater.*, 2010, **178**, 619–627.
 - Wang, D., Hu, Q., Li, M., Wang, C., and Ji, M. Evaluating the removal of organic fraction of commingled chemical industrial wastewater by activated sludge process augmented with powdered activated carbon. *Arab. J. Chem.*, 2016, **9**, S1951–S1961.
 - Baysal, M., Kabbani, A., Holail, H., and Olama, Z. Heavy metals removal using activated carbon, silica and silica activated carbon composite. *Energy Procedia*, 2014, **50**, 113–120.

34. Abdel Salam, O. E., Reiad, N. A., and ElShafei, M. M. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *J. Adv. Res.*, 2011, **2**, 297–303.
35. Assmann, C., Scott, A., and Biller, D. Online total organic carbon (TOC) monitoring for water and wastewater treatment plants processes and operations optimization. *Drink. Water Eng. Sci.*, 2017, **10**, 61–68.
36. Hu, J., Aarts, A., Shang, R., Heijman, B., and Rietveld, L. Integrating powdered activated carbon into wastewater tertiary filter for micro-pollutant removal. *J. Environ. Manage.*, 2016, **177**, 45–52.
37. Hu, J., Shang, R., Deng, H., Heijman, S. G. J., and Rietveld, L. C. Effect of PAC dosage in a pilot-scale PAC-MBR treating micro-polluted surface water. *Bioresour. Technol.*, 2014, **154**, 290–296.
38. Specchia, V. and Gianetto, A. Powdered activated carbon in an activated sludge treatment plant. *Water Res.*, 1984, **18**, 133–137.

Raskmetallide ja kogu orgaanilise süsiniku eemaldamine reoveest pulbrilise aktiivsõe abil

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Raskmetallide ja erinevate mikrosaasteainete allikad ning nende teekond keskkonda on tänapäeval suhteliselt hästi uuritud. Üheks punktiks, mida suur osa mikrosaasteaineid läbib, on reoveepuhastid, seetõttu on üha rohkem puhastikäitajaid mures, kuidas seatud piirnorme täita ja koormust keskkonnale vähendada. Antud uuringus analüüsiti kaht võimalikku tehnoloogilist lahendust mikrosaasteainete eemaldamiseks pulbrilise aktiivsõe (PAC) abil ja tehti vastavad laborikatsed. Esimese lahenduse puhul viidi läbi järelpuhastus, kus PAC doseeriti töötava reoveepuhasti heitvette, ja teise lahenduse puhul bioreaktorisse. Orgaanilise aine ja orgaaniliste mikrosaasteainete vähenemist mõõdeti summaparameetri TOC (kogu orgaaniline süsinik) abil. Katsetes selgus, et kõige efektiivsem on eemaldada järelpuhastusega Cu ja TOC, kus eemaldusefektiivsus oli vastavalt 10,9% ning 82,1%. Kuid PAC doseerimine bioreaktorisse andis paremad eemaldusefektiivsused Cr (48,3%), Ni (67,5%), Zn (55,4%), Pb (36,3%) ja As (66,7%) puhul. Arvestades eemaldusefektiivsustega 1 g PAC kohta, leiti, et antud reovee puhul oli kõige efektiivsem esimese doseerimispunkti puhul PAC doos 34 mg/L ja teise puhul 14 mg/L. Sellest tulenevalt on tehnoloogia valikul vaja hinnata investeerimis- ja opereerimiskulusid ning reoveesette töötlemistehnoloogiat, sest PAC doseerimine bioreaktorisse viib kõik adsorbeerunud ohtlikud ühendid settefaasi, mis muudab selle kohese taaskasutamise keeruliseks.