Micropollutants in wastewater and their degradation by ferrates (VI)

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Abstract: In recent years, the occurrence of micropollutants (MPs) in sewage-, surface-, ground- and drinking water, and their removal processes are widely discussed. The content of various chemical organic/inorganic pollutants (pharmaceuticals, drugs, pesticides, hormones, heavy metals etc.) has increased over the years. Most of these compounds are not eliminated or biotransformed in traditional wastewater treatment plants. Several advanced oxidation processes (AOPs) for the removal of resistant micropollutants from water sources have been studied. Ferrate (VI) has aroused interest as an alternative oxidizing agent in drinking water pre-oxidation treatment. Electrochemically prepared potassium ferrate was used to remove the studied organic micropollutants. The effect of ferrate on two widely occurring organic micropollutants in water sources, carbamazepine and caffeine, was investigated. High performance liquid chromatography (HPLC) was used for sample analysis.

Keywords: potassium ferrate, carbamazepine, caffeine, wastewater

Introduction

A wide scale of pharmaceutical compounds has been found in ground waters in the whole Europe (Loos et al., 2010). Although MPs are mostly present in very small (almost undetectable) concentrations (ng·L^{-1}), their existence in aquatic systems is connected with various detrimental effects in organisms such as genotoxicity, mutagenicity, and estrogenicity (Baronti et al., 2000). Continuously increasing consumption of pharmaceuticals causes accumulation of these drugs and their metabolites in environment. Several studies have shown that wastewater from treatment plants (WWTPs) in Europe contains a variety of micropollutants (Das et al., 2017; Munz et al., 2017; Falås et al., 2016; Luo et al., 2014; Loos et al., 2013; Rivera-Utrilla et al., 2013). MPs most commonly detected in higher concentrations are for example metformin, irbesartan, carbamazepine, iopromide, ibuprofen, diclofenac, caffeine, diartizoate, etc. (concentrations of these compounds in the effluent from WWTPs are above several hundreds of ng·L^{-1}) (Das et al., 2017). This work is focused on the degradation of carbamazepine and caffeine in water by an oxidizing agent, ferrate.

Carbamazepine (CBZ) is an anticonvulsant (Fig. 1a) used to treat epilepsy, seizures and neuropathic pain. It is also used to treat bipolar disorder and schizophrenia. It stimulates nerve impulses that cause seizures and pain. Caffeine (Fig. 1b) is the most widely consumed psychoactive substance on the planet. It stimulates the central nervous system and also certain parts of the autonomic nervous system (Mirossay, 2009; Zhang et al., 2008). Caffeine reversibly blocks the action of adenosine on its receptor and thus prevents the onset of drowsiness induced by adenosine. This stimulant is legal and unregulated in all parts of the world and more than 80 % of the world's population use caffeine in some form (Mumin et al., 2006; Nawrot et al., 2013).
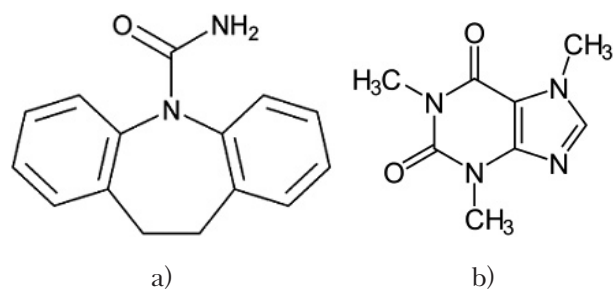
Fig. 1. Structural formula of carbamazepine (a) and caffeine (b).

These two compounds belong to the top detected pollutants in EU wastewater treatment plants (WWTP) effluents in the last decades. In 2010, the frequency of caffeine occurrence was the second

highest (82.9 %) and the highest observed concentration reached 454 ng·L^{-1} (average concentration of 9 ng·L^{-1}) (Loos et al., 2010). In the same study, the frequency of carbamazepine occurrence was 42.1 %, maximum concentration reached 390 ng·L^{-1} and the average concentration was 12 ng·L^{-1}. Only three years later, the same authors repeated the monitoring of the micropollutants in WWTPs effluents in EU (Loos et al., 2013). A significant increase of the concentration of these compounds in effluents from WWTPs was detected. Caffeine was detected with the frequency of 93 %, the maximum concentration reached 3002 ng·L^{-1} and the average concentration was 191 ng·L^{-1}. More significant increase was observed for carbamazepine, the frequency of detection was 90 %, maximum observed concentration was 4609 ng·L^{-1} and the average concentration reached 832 ng·L^{-1}. The average concentration of these compounds in WWTP effluents was nearly 20 times higher for caffeine and almost 70 times higher for carbamazepine. The reason for the significant increase of carbamazepine concentration in water is its lower removal efficiency in WWTPs (Luo et al., 2014). While caffeine belongs to "highly removed compounds" (degree of removal >70 %), carbamazepine is in the category "poorly removed pollutants" (degree of removal <40 %). Removal efficiency with standard deviation is only (32.7 ± 17.9) % for carbamazepine while for caffeine it is (88.7 ± 15.9) %. Despite the relatively good removability of caffeine in WWTPs, the removal efficiency is not sufficient to cover the large consumed amounts of caffeine-containing products.

Based on a statistical survey in EU in 2013 (euromonitor.com), average consumption of coffee in Slovakia is approximately 2.5 kg per person per year. According to the Statistical Office of Slovakia (archiv.statistics.sk), the number of inhabitants was about 5,416,000 in 2013, and about 4,411,000 were older than 18 years. That means that the consumption of coffee in Slovakia is higher than 11 thousand tons per year. Moreover, it is important to note that coffee is not the only one caffeine-containing product (tea, cola drinks, chocolate, etc.).

The consumption of carbamazepine has been increasing every year (Loos et al., 2010; Luo et al., 2014). Zhang and Geißen (2010) published information about the sold amounts of carbamazepine. More than 383 tons of CBZ were sold in Europe in 2007; approximately 2.9 tons in Slovakia. They also theoretically calculated the concentration of CBZ in WWTP effluents for 2007; the predicted value for Slovakia was about 1524 ng·L^{-1} (average calculated amount for Europe is about 1797 ng·L^{-1}) (Zhang and Geißen, 2010).

Various treatment processes, especially for the removal of CBZ from wastewater have been tested. Removal processes including coagulation and sedimentation show poor removal efficiency: that with ferric chloride/aluminum sulfate reached the removal efficiency of only (6.3 ± 15.9) % (Suarez et al., 2009), and that with ferric sulfate only up to 10 % (Vieno e al., 2006; Matamoros and Salvadó, 2013). The UV/H$_2$O$_2$ treatment was studied by various research groups (Pereira et al., 2007; Andreozzi et al., 2001; Vogna et al., 2004). The removal efficiency varied from about 5 % (Pereira et al., 2007) to more than 70 % (Vogna et al. 2004) depending on the conditions and treatment times. However, by-products formed in this treatment process are much more toxic than the original substance, for example acridone or acridine (Donner et al., 2013). Also the classic and modified Fenton's reactions (removal efficiency of 20−80 %) (Giannakis et al., 2015; Karpinska et al., 2015) and chlorination (removal efficiency of 5−64 %) (Soufan et al., 2013; Lee and Von Gunten, 2010) were studied. Removal efficiency close to 100 % was obtained by ozonation (Lee et al., 2014). A disadvantage of the ozonation process is the formation of carcinogenic bromides from Br-compounds present in treated waters (Hollender et al., 2009). The effect of ferrate on the CBZ degradation (CBZ concentration of 10 µg·L^{-1} and 100 µg·L^{-1}) was also studied (Zhou and Jiang, 2015). The concentration of added ferrate was (1−5 mg·L^{-1}) at pH = 6−9 and the removal efficiency was nearly 100 %.

Degradation of caffeine was investigated by various AOPs. Removal efficiency of ozonation (Rosal et al., 2009), UV/H$_2$O$_2$, UV/TiO$_2$ or Fenton reaction (Dalmázio et al., 2005) and electro-Fenton processes using a BDD electrode (Ganzenko et al., 2015) were very high, up to 100 %. The above mentioned AOPs do not completely exclude the production of various harmful by-products, similarly as in case of CBZ.

Ferrate (FeO$_4^{2-}$) belongs to the group of AOPs. It acts as an oxidant, disinfectant, and coagulant in water. This compound is also interesting due to its other positive properties such as selective reactivity, relative stability in its salt form (compared to other high valent iron Fe^{IV} and Fe^{V}), and the formation of non-toxic decomposition by-products (Deng et al., 2018; Sharma et al., 2016; Zheng and Deng, 2016). Therefore it is a promising water treatment chemical compound in environmental remediation processes. Many research groups investigated the influence of ferrates on various organic and biological MPs present in WWTP effluents (Rai et al., 2018; Manoli et al., 2017; Kubiňáková et al., 2017; Mackuľak et al., 2016).

In this work, the influence of electrochemically synthesized potassium ferrate on the CBZ and caffeine removal commonly present in WWTP effluents was investigated. The effect of different Fe^{VI} concentrations on CBZ and caffeine degradation was evaluated.

Experimental

Chemicals

$C_{15}H_{12}N_2O$ — carbamazepine (p.a.), purity > 98 %, SIGMA-ALDRICH

$C_8H_{10}N_4O_2$ — caffeine (p.a.), analytical standard, SIGMA-ALDRICH

K_2FeO_4 — potassium ferrate, electrochemically prepared with the final concentration of nearly 80 % (w/w) (Kubiňáková et al., 2015)

Analysis of samples by HPLC

The determination was carried out on a HPLC-PDA device detector (model Young Lin 9100). Mobile phase used for the analysis was methanol/water, the ratio of these two phases was gradually changed during the analysis, from the initial value (φ_r = 1 : 9) to the final value (φ_r = 9 : 1) 16 minutes before the end of the analysis. The column used was a Grace Smart TM, RP-18, (Grace, USA) with the length of 150 mm, inner diameter of 4.6 mm at the mobile phase flow rate of 1 ml·min^{-1}; PDA detector wavelengths were: 222 nm, 254 nm, 320 nm, and 380 nm.

Results and discussion

Carbamazepine

Basic solution of CBZ with the concentration of 10 mg·L^{-1} was prepared by dissolving an appropriate amount of the compound in distilled water. The solution was stored at the temperature of 5 °C. Four different ferrate solution concentrations: (0.1, 0.5, 1, 5) mg·L^{-1}, were considered for the investigation of the CBZ degradation capability. Appropriate amounts of powder potassium ferrate were added to 100 mL of the CBZ solutions. After mixing and waiting for half an hour, the samples were analyzed by HPLC.

Changes of pH were measured every 10 minutes during the first 30 minutes, until the reaction of ferrate was complete (Fig. 2). pH was measured with a digital pH meter pH Testr 30 (Helago, Czech Republic). Acidobasic properties of the solutions did not vary significantly during the treatment. pH values decreased with the increasing dose of ferrate added to the CBZ solution. The highest pH values (of about 7) were reached for the highest concentration of added ferrates, 5 mg·L^{-1}.

The samples were analyzed with HPLC after completing the reaction of ferrate (disappearing of the violet color of the solutions). Retention time was used as a qualitative variable to identify CBZ in the chromatograms. The size of the under-curve-area (peak area) on the chromatogram was the quantitative parameter. Removal efficiency (η) of ferrate for CBZ was calculated according to Eq. 1, where A_0 is the initial under-curve-area of the basic solution and A_i is the peak area of the remaining CBZ in the treated sample.

$$\eta = \frac{A_0 - A_i}{A_0} \cdot 100 \ \%$$ (1)

A comparison of individual chromatograms allowed identifying some trends in the structure
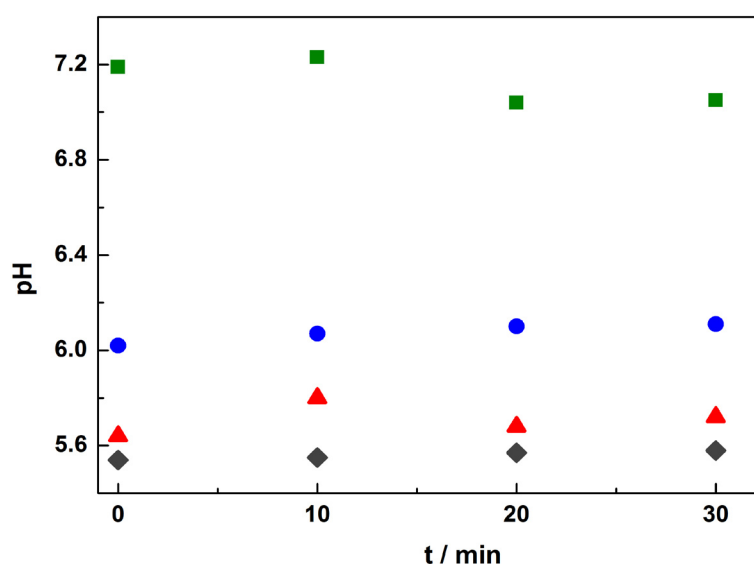
Fig. 2. Dependence of the CBZ solution pH after various additions of ferrate in time. Ferrate concentrations: ♦ 0.1 mg·L^{-1}, ▲ 0.5 mg·L^{-1}, ● 1 mg·L^{-1}, ■ 5 mg·L^{-1}.

of the CBZ degradation product. Application of ferrate results in peaks on the chromatograms with lower retention time, which means that more polar (hydrophilic) compounds than CBZ are formed. In Fig. 3 and Fig. 4, two examples of chromatograms are provided: for basic solution (Fig. 3) and for solution with the highest concentration (5 mg·L^{-1}) of ferrates (Fig. 4). Channel lines represent specific wavelengths. Generally, data detected at the wavelength of 220 nm (Channel 1; the most sensible wavelength for CBZ) were used for the evaluation and calculation of the removal efficiency. The chromatogram in Fig. 3 contains one dominant peak for CBZ at the retention time of 12.40 minutes. The chromatogram in Fig. 4 has a more pronounced peak at the retention time of 1.58 minutes and it also contains more peaks at lower retention times than that in Fig. 3. Ammonia removal from the

amide group is likely in case of CBZ. Increasing of the CBZ hydrophilicity oxidation should lead to the removal of residues in a subsequent technological step (for example activated sludge) and thus more effective CBZ removal from wastewater.

Values of the CBZ peak area obtained from the HPLC analysis were evaluated and the results are summarized in Tab. 1. The highest removal efficiency of 29 % was found for the application of 0.5 mg·L^{-1} and 5 mg·L^{-1} of potassium ferrate. pH values for these concentrations are still in slightly acidic area. The lowest concentration of ferrate was not sufficient to provide the degradation despite of the most acidic environment.

Caffeine
Basic solution of caffeine (concentration of 10 mg·L^{-1}) was prepared and stored in the same

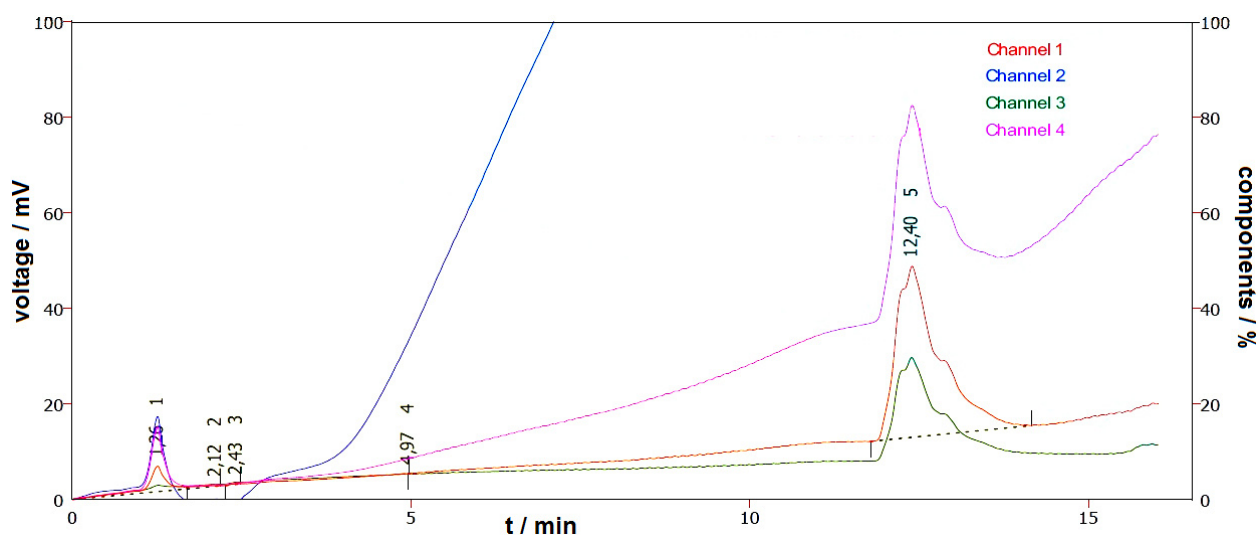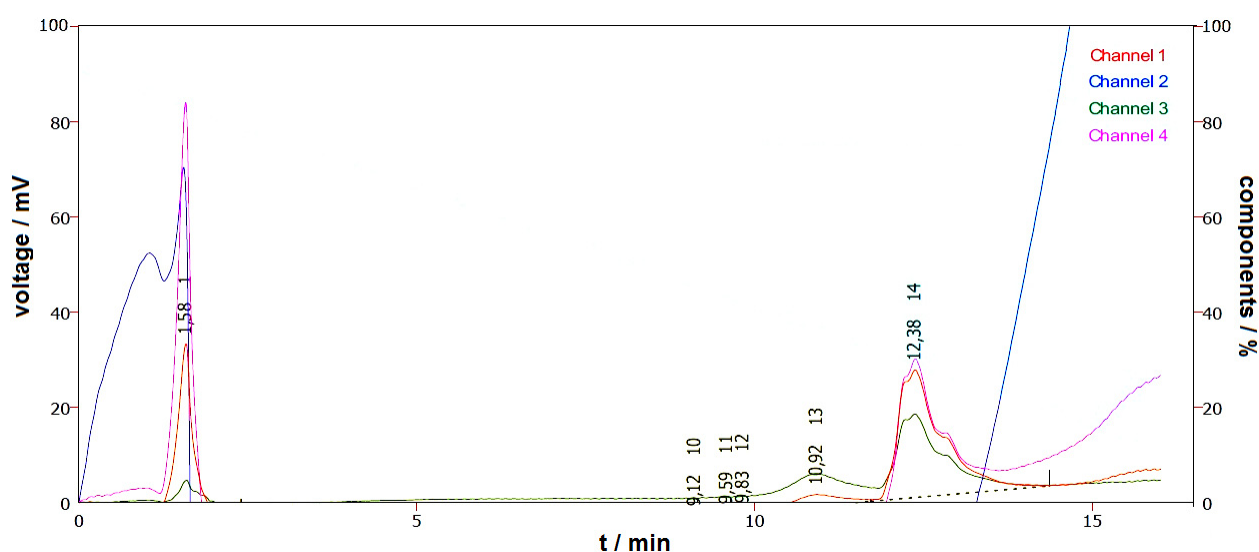**Fig. 3.** Chromatograms of basic CBZ solution (10 mg·L^{-1}).

Fig. 4. Chromatograms of CBZ solutions and its degradation products for the ferrate concentration of 5 mg·L^{-1}.

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Tab. 1. Results for the application of different ferrate concentration to CBZ solutions; concentrations of added ferrates ($c(Fe^{VI})$), retention time for detected CBZ peak (t_R), pH of solutions, removal efficiency (η).

| $c(Fe^{VI})/(mg \cdot L^{-1})$	t_R / min	pH	$\eta/\%$
0.0	12.40	5.55	–
0.1	12.40	5.58	22.7
0.5	12.39	5.72	28,9
1.0	12.37	6.11	13.8
5.0	12.38	7.05	29,1

way as that of CBZ. Six different ferrates concentrations (0.1, 0.5, 1, 3, 5, and 7) mg·L⁻¹ were added to

100 mL of the basic caffeine solutions. Before the HPLC analysis, pH (30 minutes/every 10 minutes) was measured immediately after the application of ferrates (Fig. 5). pH for individual solutions was increased very softly within the reaction time; a more pronounced increase of pH was observed for higher concentration of ferrate in the basic solution. The highest pH values (of about 8) were reached for the highest addition of ferrates (7 mg·L⁻¹).

Subsequently, the samples were analyzed by HPLC. A peak for caffeine in the chromatogram in the standard solution of caffeine (basic solution, c = 10 mg·L⁻¹) was detected at the retention time of 13.33 min (Channel 1 in Fig. 6). It has been shown that the most effective ferrate concentrations for caffeine degradation are (0.5 and 1.0) mg·L⁻¹ (Fig. 7),
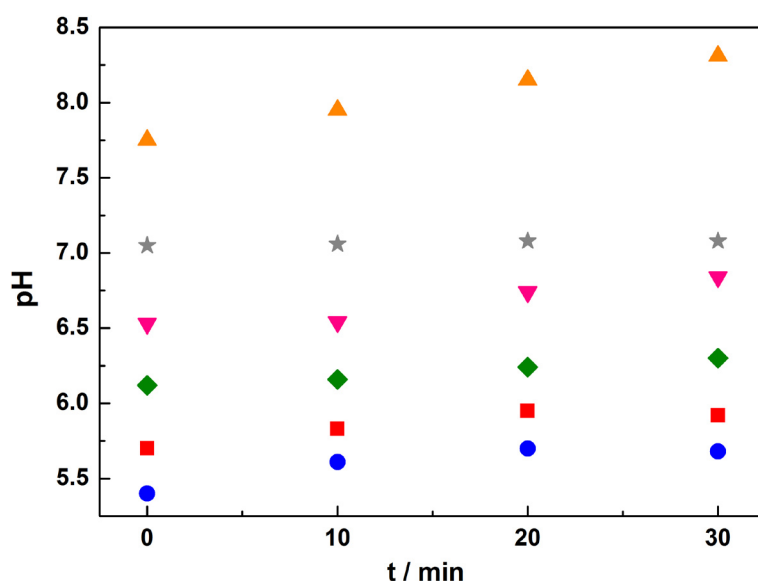
Fig. 5. Dependence of caffeine solution pH after different additions of ferrate in time. Ferrate concentrations: ● 0.1 mg·L⁻¹, ■ 0.5 mg·L⁻¹, ◆ 1 mg·L⁻¹, ▼ 3 mg·L⁻¹, ★ 5 mg·L⁻¹, ▲ 7 mg·L⁻¹.
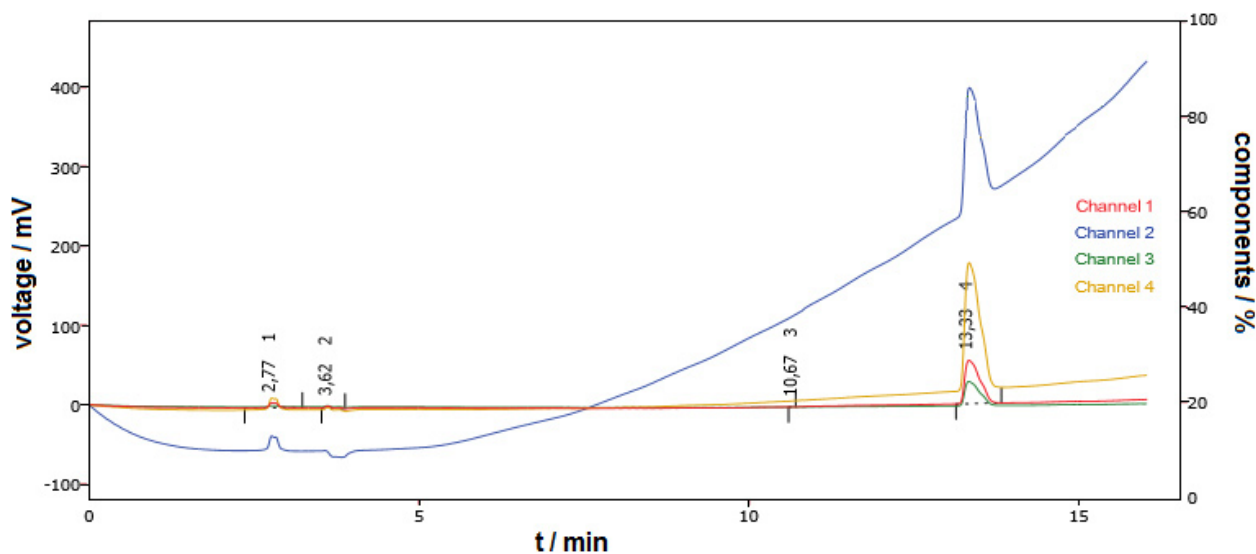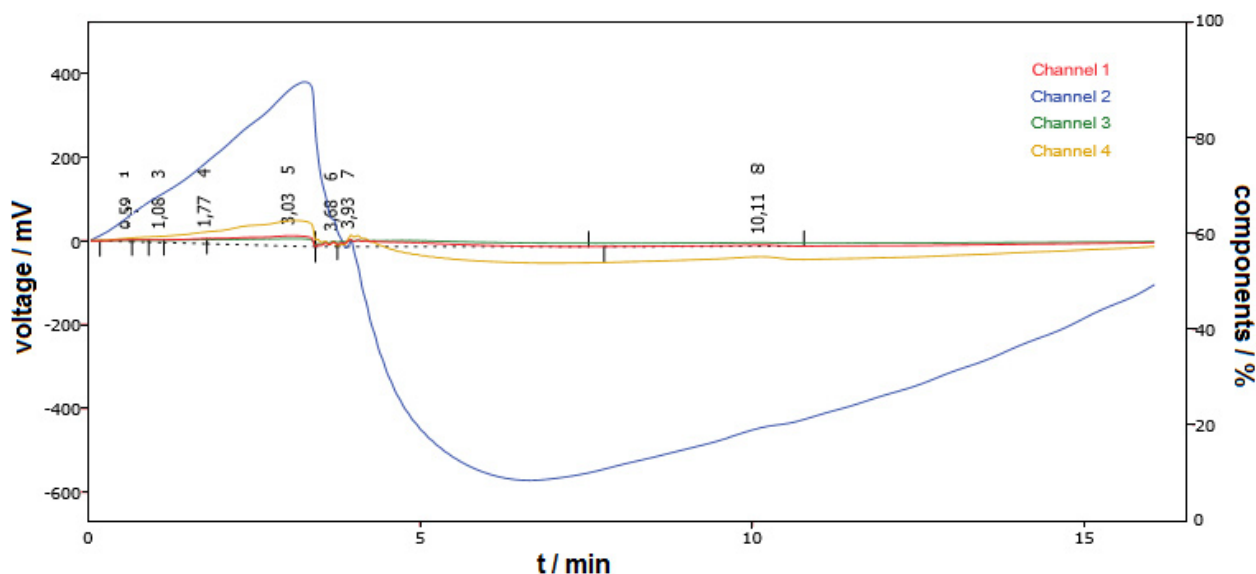

Fig. 6. Chromatograms of the basic solution of caffeine (10 mg·L⁻¹).

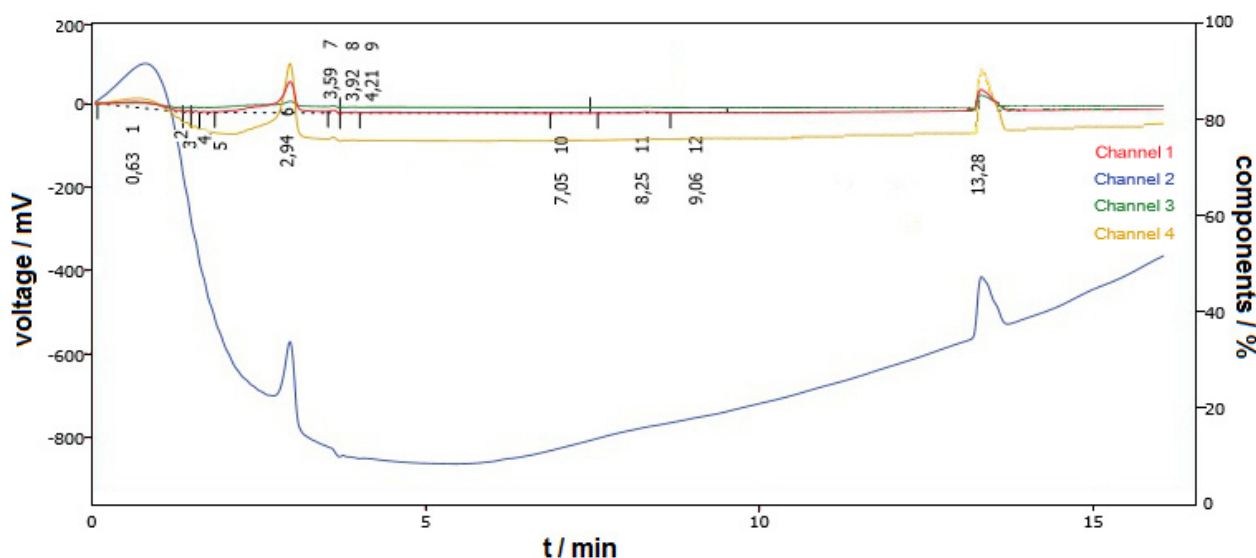**Fig. 7.** Chromatograms of caffeine solutions and its degradation products for the ferrate concentration of 1 mg·L⁻¹.

Fig. 8. Chromatograms of caffeine solutions and its degradation products for the ferrate concentration of 7 mg·L⁻¹.

Tab. 2. Results for the application of different ferrate concentrations to caffeine solutions; concentrations of added ferrates ($c(Fe^{VI})$), retention time for detected caffeine peak (t_R), pH of solutions, removal efficiency (η).

$c(Fe^{VI})/(mg·L^{-1})$	t_R/min	pH	$\eta/\%$
0.0	13.33	5.39	–
0.1	12.88	5.92	–
0.5	–	5.68	100
1.0	–	6.30	100
3.0	13.29	6.84	1.3
5.0	13.21	7.08	4.5
7.0	13.28	8.31	7.9

which result in complete degradation of caffeine in water solution.

The lowest concentration of ferrate (0.1 mg·L⁻¹) has proven to be insufficient for caffeine degradation despite the acidic pH. Low ferrate concentration only slightly altered the caffeine structure which was observed at lower retention time than the considered standard (Tab. 2). Higher ferrate concentration increases the pH, which has a negative effect on the removal efficiency. Even at a relatively high ferrate concentration (3—7 mg·L⁻¹), almost no caffeine degradation was observed (Fig. 8). Increasing pH to a neutral and alkaline value caused significant reduction of the removal efficiency and ferrate (strong oxidizing agent

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especially in acidic environment) is not capable to degrade caffeine.

The influence of ferrate on the caffeine structure was observed only on the side chains in neutral and slightly alkaline environment. Degradation products which could be identified were acetic acid (retention time of about 3.2 min), formic acid (retention time of about 2.9 min). Retention times between 3.5—3.6 minutes are characteristic for amines and below 2.3 minutes for ketones. Exact structures of the species cannot be determined by HPLC analysis.

Conclusions

Efficiencies of potassium ferrate oxidation process on the degradation of carbamazepine and caffeine in aqueous solutions were investigated. pH dependencies of CBZ and caffeine solutions with different additions of ferrate on time were also studied. The removal efficiency for both studied micropollutants was strongly dependent on the solution pH. Acidic environment ensured higher oxidation power of the ferrates; neutral and alkaline environment decreased the removal efficiency even at higher ferrate concentrations. Removal efficiency for CBZ in solution was only about 30 %. Similarly, removal efficiencies were measured at relatively low concentrations of added ferrate ($0.5\ mg \cdot L^{-1}$) in solution with pH < 6 and also at the concentration 10 times higher ($5\ mg \cdot L^{-1}$) in solutions with pH of about 7. The removal efficiency for caffeine reached 100 % at two relatively low concentrations of added ferrates (0.5 and $1.0\ mg \cdot L^{-1}$), pH of the solutions were below 6.3. Degradation of caffeine from water containing higher amounts of other compounds (real effluent from WWTP) was about 76 % with the application of $0.5\ mg \cdot L^{-1}$ of ferrate. Toxicity assessment of the degradation products and by-products of CBZ and caffeine, and consequential confirmation of the results are required.

Application of ferrates in wastewater strongly depends on its pH and their concentrations. pH of the effluent from WWTP is about 7—8 and its decreasing has no reason because of the huge volume flows (approximately 43 000 m³ per day). However, ferrate can be applied in the water post-treatment step for the effluent from hospital facilities or facilities with higher drug use. Volume flows of water from hospital effluents (average facility) are more than 210 times lower than from average WWTP. Based on a simple economical calculation, costs of CBZ removal in case of hospital facilities can be more than 70 times lower than in a WWTP per year (in case of caffeine it can be even higher).

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