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THE PHARMACEUTICALS REMOVAL BY MEANS OF AOPS

The most recent water environmental research has revealed presence of pharmaceuticals in sewage treatment plants effluents, treated sewage and surface waters, which means that metabolism of medicines in human organism is incomplete. These substances, both in their unchanged forms and as biologically active forms, are present in the environment and influence living organisms. Most pharmaceuticals are characterized with a stable chemical structure and it is impossible to remove them by traditional methods, used in wastewater treatment plants. Thus, the danger of the medicine accumulation during many years seems real. Application of chemical methods is necessary to remove them from the environment. Methods based on Advanced Oxidation Processes (AOPs) use free hydroxyl radicals reacting in nonselective way with many organic substances because of their high normal potential. AOPs consist in chemical and photochemical oxidation processes e.g. oxidation by ozone and hydrogen peroxide, photolysis UV radiation, Fenton or photo – Fenton reactions as well as combinations and modifications of these processes.

Недавние экологические исследования водных ресурсов продемонстрировали наличие фармацевтической продукции в очищенных канализационных, сточных стоках и поверхностных водах, что свидетельствует о неполном метаболизме лекарственных препаратов в человеческом организме. Эти вещества как в своей исходной форме, так и в виде биологически активных форм присутствуют в окружающей среде и воздействуют на живые организмы. Большинство лекарственных препаратов характеризуются стабильной химической структурой и их удаление традиционными методами, используемыми на очистных заводах, невозможно. Накопление лекарственных препаратов в течение многих лет представляет собой реальную угрозу. Необходимо использование химических методов для их извлечения из окружающей среды. Методы, опирающиеся на усовершенствованные процессы окисления (УПО), используют свободные гидроксильные радикалы, неселективно вступающие в реакцию с большим количеством органических веществ благодаря своему высокому стандартному потенциалу. УПО включают в себя химические и фотохимические процессы окисления, например, окисление озоном и пероксидом водорода, фотохимическая диссоциация ультрафиолетовым излучением, реакции Фентона (система "перекись водорода – ион двухвалентного железа") и фотохимическая реакция Фентона, а также комбинации и модификации этих процессов.

Introduction

First information about the presence of pharmaceuticals in the water environment appeared in 1977. This is when Hignite and Azarnoff discovered salicylic acid amounting to 2,8 g/l and clofibric acid amounting to 2,9 g/l in the municipal sewage treatment plant effluent located in Kansas City [1]. The research conducted in Great Britain by Waggott, Watts, Richardson and Brown in the eighties confirmed the presence of the pharmaceuticals in the water environment and contributed to the development of its detection and determination [2]. Due to the scarcity of equipment the exact determination of compounds concentration was impossible. In the ensuing years, more information about the presence of pharmaceuticals was reported especially in the sewage treatment plants, surface waters even in the drinkable water [3]. This issue resulted in science and research projects (Poseidon, Rempharmawater, Eravmis) within the European Union V Framework Programme [4]. These projects have contributed in a substantial way to the development of microanalysis. Due to this fact the determination of substance concentration in ng or μg/l i.e. the concentration in which you can find the pharmaceuticals in the environment,

does not make any problem. The pharmaceuticals have also been examined in terms of their behavior in the sewage treatment process [5]. It turned out that the traditional biological treatment methods do not remove the substances or the removal is insignificant, thus the traditional treatment methods are unsuitable for significant total removal of trace compounds. That is why, more efficient technologies, like advanced oxidation processes or membrane filtration may became more popular.

Pharmaceuticals

Pharmacological compounds undergo total or partial biochemical transformation in the organism. These processes start in the digestive tract, but are more intensive in blood or live tissues. The greatest part of pharmacological compounds is transformed in the liver. The metabolism, depending on the type of the pharmaceutical can vary in its intensity starting from one up to 100 percents [6]. Table presents the percentage amounts of chosen pharmaceuticals, which are excreted from the organism in their original, unchanged form.

Table

The percentage amounts of the pharmaceuticals extracted from the organism in their unchanged forms

Substances	Amount of the compound excreted, %
Ibuprofen	1-10
Sulphamethaxazole	15-20
Ethinoestradiol	50-80
Trimethoprim	Approx. 90
Iopromid	Approx. 100

The excretion usually comes with urine, excrement, but it can also be carried out through skin, mammary glands or lungs [6]. The substance, due to its properties, after it is excreted from the organism into the environment interacts with other, living organisms. The effect of the medicine on the organism has already been examined, however its effects outside the organism are not known. At present, it has been confirmed that the presence of the antibiotics outside living organism causes mutations, and creation of resistant bacterial cultures. Owing to this issue, it will not be possible to treat illnesses caused by these microorganisms by popular, widely applied medicines. This matter constitutes a serious threat to public health. The most common reason for hospital infections are modified, resistant to antibiotics, bacterial forms [7].

Advanced Oxidation Processes (AOPs)

The efficiency of the AOPs results from the increased oxidation pace of the contamination due to the creation of highly reactive hydroxyl radicals (OH^*), which are created from oxidizing compounds added in specific conditions. The great advantage of the hydroxyl radicals is their nonselectivity in relation to organic compounds and high oxidation potential (E = 2,8 V) [8]. In general, the processes of the advanced oxidation can be divided into two groups:

– chemical oxidation without photolysis,

– photochemical oxidation supported by photolysis.

The most common processes included in the first group are as follows:

– ozone oxidation accompanied with high pH (O_3),

– ozone and peroxide hydrogen oxidation (O_3/H_2O_2),

– Fenton's reagent oxidation with low pH (Fe^{2+}/H_2O_2).

The second group, distinguishes among the following photochemical processes:

– ozone oxidation supported by photolysis (O_3/UV),

– peroxide hydrogen supported by photolysis (H_2O_2/UV),

– Fenton's reagent oxidation supported by photolysis with low pH (Fe^{2+}/H_2O_2/UV),

– heterogeneous photocatalysis (TiO_2/UV) [9].

Fenton reaction modification

Two pharmacological compounds have been selected for the purpose of the research-sulphamethaxazole and trimethoprim. Both the substances are widely used, most of all they are applied for urinary, respiratory, alimentary and reproductive system infections

treatment. They are also used in typhus and paratyphus. As one of very few chemotherapeutics, they are effective in prostate gland treatment. Both compounds are applied at the same time, but trimethoprim is used in constant weight ratio and constitutes 20 % of the sulphomethaxazole weight. The advanced oxidation method, applied in order to break their chemical structure, was the modification of the classical Fenton reaction. This method consists in replacing peroxide hydrogen with intensive aeration. The classical Fenton reaction is carried out between peroxide hydrogen and iron ions, on the second level of the oxidation (1), deriving from $FeSO_4$ in the acidic environment (the greatest efficiency in pH = 2.8 [10])

$$Fe^{+2} + H_2O_2 \leftrightarrow Fe^{+3} + OH^- + OH^*. \quad (1)$$

Following the modification consisting in replacing H_2O_2 with intensive aeration, the reaction (1) takes place as a result of the chemical transformation of two-stage transformation based on Fe^{+2} oxidation to Fe^{+3} under the influence of oxygen (2) deriving from compressed air and creating bimolecular hydroxyl radical, which forms peroxide hydrogen when comes into contact with hydrogen ions (3),

$$Fe^{+2} + O_2 \leftrightarrow Fe^{+3} + O_2^{-*}, \quad (2)$$

$$O_2^{-*} + 2H^+ \leftrightarrow H_2O_2 + O_2. \quad (3)$$

It is crucial not to exceed the quantity of iron ions (II). The surplus can cause association initiating the seclusion of the radical chain reaction (5) [11]. Equally important reason for maintaining the concentration of iron ions (II) on certain level is the possibility of shifting the process balance towards the reaction (3), where the excess of the peroxide hydrogen comes into contact with hydroxyl ions as in reaction (4) as a result of which much less reactive dioxide hydroxyl radicals are formed [12]

$$OH^* + H_2O_2 \leftrightarrow H_2O + HO_2^*, \quad (4)$$

$$Fe^{+2} + OH^* \leftrightarrow Fe^{+3} + OH^-. \quad (5)$$

In order to increase the production of hydroxyl radicals the process is supported by UV radiation. The suitable wave length radiation (from 300 nm to 410 nm – this is the range of $[Fe(OH)]^{+2}$ absorption) contributes to the reduction of Fe^{+3} to Fe^{+2} and formation of OH^* (6) [13]. Other source of radicals is the direct UV radiation of H_2O_2 (7), although it is of minor importance in this process, as peroxide hydrogen has worse absorption at this ultraviolet waves lenght

$$[Fe(OH)]^{+2} + h\upsilon \leftrightarrow Fe^{+2} + OH^*, \quad (6)$$

$$H_2O_2 + h\upsilon \leftrightarrow 2OH^*. \quad (7)$$

The copper sulfates $CuSO_4$ is added to the reaction, as cations Cu^{+2} catalyze the reaction. The cooper can react twofold It can be reduced to Cu^+, and then it reacts according to reaction (8) or after forming hydroxide $[Cu(OH)]^+$ becomes influenced by UV radiation (9) [15]

$$Cu^+ + H_2O_2 \rightarrow Cu^{+2} + OH^* + OH^-, \quad (8)$$

$$[Cu(OH)]^+ + h\nu \rightarrow Cu^+ + OH^* + OH^-. \quad (9)$$

Proposed method is cost-effective and more economical than standard Fenton method. There is no need of primary acidification and alkalization of the samples after the process. Moreover expensive hydrogen peroxide is substituted with intensive aeration.

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