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PARAMATERS OF PRETREATING WASTEWATER POLLUTED WITH CHEMICALS BASED ON MODIFIED FENTON'S REACTION

The pharmaceuticals present in the municipal sewage reach the municipal sewage treatment plants, but most often fail to be completely removed in there. Therefore, in the case where they constitute a substantial part of the sewage stream (hospitals, clinics, pharmacological production plants) their chemical pretreatment seems justifiable. A method based on the modification of Fenton's reaction has been suggested. It consisted in replacing peroxide hydrogen with compressed air and enhancing the reaction by UV rays and copper cations Cu^{+2} as catalysts. All the process parameters have been determined experimentally. The possibility of implementing the method in industry has been taken into consideration, therefore the values of the parameters such as pH and aeration intensity were established on a lower level despite the fact that their higher values were more effective.

1. INTRODUCTION

60–90% of the pharmaceuticals that together with sewage reach the municipal sewage treatment plants are removed, hence about 10–40% penetrate together with the treated sewage into the surface waters [3]. The pharmaceuticals which are biologically active substances interact with living organisms [10]. Due to the fact that a vast number of the pharmaceuticals has got very resistant chemical structures, they will cumulate in the environment over a span of time. Considering their properties they were classified as a refractive compounds, i.e., they cannot be decomposed by means of the traditional biological treatment methods, therefore they are recognized as a new group of contaminants [2], [11]. In order to eliminate the pharmaceuticals from the environment, it seems indispensable to develop the method which would enable their preliminary degradation. To this end, a method of the chemical removal (modified Fenton's reaction) based on taking advantage of high oxidizing properties of the

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hydroxyl radicals OH^\bullet was suggested. The radicals, due to their high oxidizing potential $E^0 = 2.76 \text{ V}$, react in a nonselective way with many chemical substances which have strong molecular structures and cause their infringement.

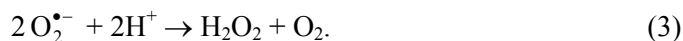
A traditional Fenton's reaction is the following [1]:



Iron in the form of ferrous sulfate(VI) (FeSO_4) reacts with hydrogen peroxide (H_2O_2) and as a result iron is oxidized and generates hydroxyl radical. In the case of modified Fenton's reaction, iron is also supplied in the form of FeSO_4 salt, however hydrogen peroxide was replaced with compressed air, which brings about the following reaction [9]:



When the newly formed radical of the oxygen molecule $\text{O}_2^{\bullet-}$ comes into contact with the hydrogen cation it creates hydrogen peroxide H_2O_2 :



In this way, all the substrates necessary for reaction (1) are formed. Unfortunately, the process is not effective enough. In order to boost its performance, UV radiation and copper ions Cu^{+2} in the form of copper(II) sulfate(IV) salt (CuSO_4) were used as supportive catalysts, i.e., promoter.

Fe^{+3} formed during reaction (2) brings about the formation of ferric hydroxide ($\text{Fe}(\text{OH})_3$). This compound is present in the water solutions in few forms, according to the principle of dissociation in the following stages:



The cation $[\text{Fe}(\text{OH})]^{+2}$ exposed to an appropriate UV wavelength radiation (from 300 to 410 nm) is able to form hydroxyl radicals with simultaneous reduction of its oxidation level [6]:



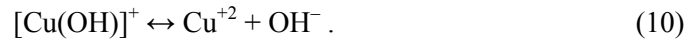
When the UV radiation comes into direct contact with the hydrogen peroxide it can also cause additional formation of hydroxyl radicals [7]:



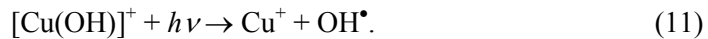
The above mentioned reaction is of minor importance in the process, as the hydro-

gen peroxide is featured by poor absorption in ultraviolet range.

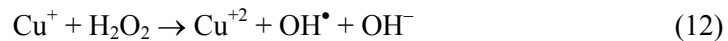
It is presumed that copper cations undergo the same transformation as iron ions. In the water solution, they undergo double dissociation:



When the $[\text{Cu(OH)}]^+$ ion, formed as a result of reaction (9), comes into contact with UV radiation it can produce OH^\bullet radical following the below pattern [8]:



Subsequently, the copper cations Cu^+ can react with H_2O_2 during chemical transformation (11) in the following way:



with simultaneous copper regeneration and generation of the additional hydroxyl radicals.

2. MODIFICATION OF FENTON'S REACTION

2.1. DETAILS OF THE PROCESS

The modification of Fenton's reaction consists in replacing hydrogen peroxide with the compressed air. In order to allow the oxygen to dissolve in the compressed air up to the sufficient amount, a high reactor was used ($h = 50$ cm). In order to boost the efficiency, UV rays of the wavelength $\lambda = 365$ nm were generated by 120 W lamp and copper cations Cu^{+2} in the form of copper(II) sulfate(VI) (CuSO_4) were used as catalyst. Commencing the reaction, the water solution of the pharmaceutical originally acidic was alkalized with 0.1 mol solution of sodium hydroxide (NaOH) to pH 7. Subsequently, suitable amounts of salts, copper and ferrous sulfate(VI) were added. The mixture prepared in this way was aerated. In the case, where the process was supported by the UV radiation, the mixture was poured into a low reactor ($h = 5.5$ cm) in order to enlarge the surface of liquid which was subject to radiation, simultaneously improving the penetration of the radiation. At the same time, the solution was aerated (with lower intensity to prevent foaming and pouring out), which caused its mixing and ensured minimum dose of the oxygen.

The insolation was carried out periodically, alternatively with aeration. After the process was finished the post-reactive mixture was alkalized again with 0.1 mol solu-

tion of hydroxide sodium to pH 7. The scheme of the process is shown in figure 1.

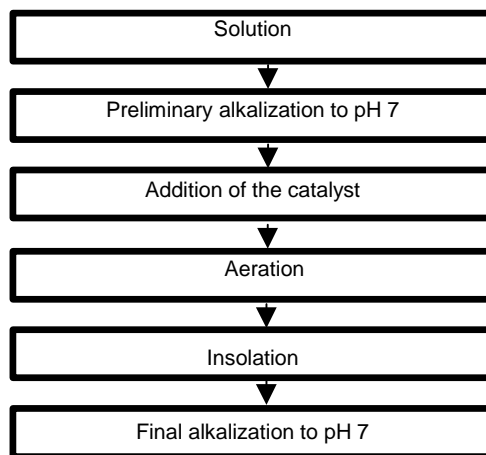


Fig. 1. Scheme of the process

2.2. SELECTION OF THE PARAMETERS

All the parameters of the process were experimentally selected. The chosen criteria were established on the basis of the chemical oxygen demand and the measurements of the concentration of the substance examined. The subject of the research was sulfamethoxazole of original concentration approaching 60 mg/dm^3 . Sulfamethoxazole is a component of the bisseptol solution, an antibacterial medicine, which includes two biologically active compounds, i.e., sulfamethoxazole and trimethoprim, and other organic and inorganic stabilizing substances. The concentration of the sulfamethoxazole was measured by the High Performance Liquid Chromatography HPLC – UVD 340u by Gynkotek. In the process of determination, the acetonitrile with phosphate buffer in the ratio of 30:70 on column RP-18 was used as an eluent. The sulfamethoxazole was detected after 6.5 min, with the wavelength $\lambda = 269 \text{ nm}$. Each time 0.5 dm^3 of the bisseptol solution containing 60 mg/dm^3 of sulfamethoxazole and 160 mg DOC/dm^3 was used. DOC (dissolved organic carbon) analyses were done with TOC-V_{CSH} Shimadzu analyzer. The reaction lasted 2.5 h. Within this time the changes in the solution were observed. The following optimal parameters of the process were determined: concentration of ferrous ions, aeration intensity, concentration of copper ions, insolation time and pH of the solution. All the reactions were repeated three times in order to check the recurrence of the results. Analyses took place at the room temperature, i.e., about $20 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$, at the atmospheric pressure.

The optimal concentration of the ferrous ions was established based on the percentage loss of COD. The experiment has been carried out at the aeration intensity of 400

dm³/h and pH of the solution amounting to 4. The results obtained are presented in figure 2.

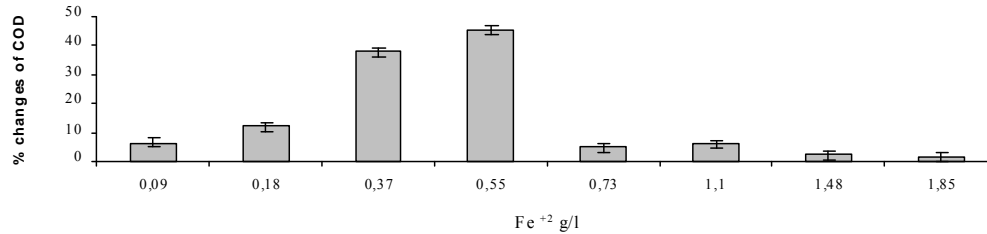


Fig. 2. The percentage changes of COD at different concentration of ferrous ions

The highest percentage removal of the COD was noticed at ferrous ion concentration of 0.55 g per liter of the biseptol solution containing 60 mg of sulfamethoxazole per liter. As a sulfamethoxazole is not a sole organic compound in the biseptol, the optimal dose has been converted into 100 mg DOC of the biseptol. It gave 0.34 g Fe⁺²/100 mg DOC.

The optimal aeration intensity was determined by the percentage loss of COD at 0.55 g/dm³ of ferrous ions and pH of the solution amounting to 4 (figure 3).

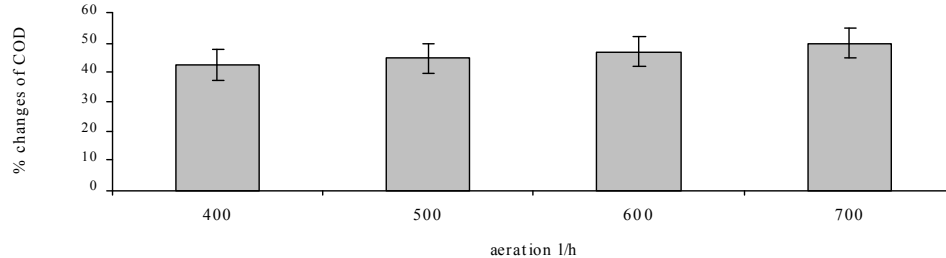


Fig. 3. The percentage changes of COD at different aeration intensity

The diagram proves that an increase the aeration intensity does not improve the efficiency of the process, it can only increase its cost. Taking into account the economical aspect, the aeration intensity was set on the level of 550 dm³/h. The percentage changes of COD in the range of aeration varying from 500 to 600 dm³/h are insignificant, that is why the middle value was chosen. The final value of this parameter should be verified and established by means of experiments on the pilot or technical scale.

Optimal concentration of the copper ions was established based on the percentage changes in COD and the concentration of sulfamethoxazole. The process was carried

out under the above mentioned optimal conditions, i.e., $0.55 \text{ g Fe}^{2+}/\text{dm}^3$ and the aeration intensity amounting to $550 \text{ dm}^3/\text{h}$. The results of the experiments are presented in figures 4 and 5.

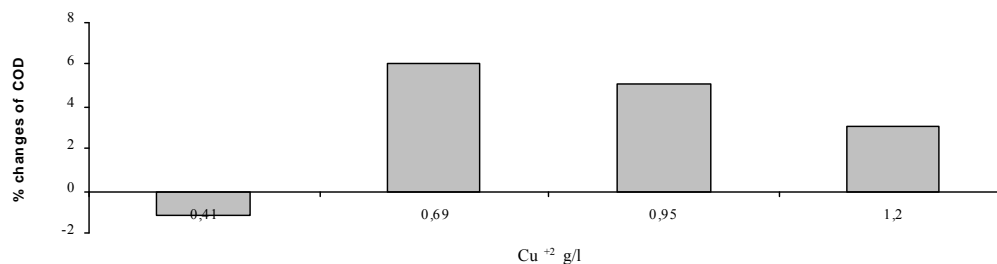


Fig. 4. The percentage changes of COD at different concentration of copper ions

A negative value of the COD percentage change in the case of the 0.41 g/dm^3 dosage was caused by the fact that after the iron and copper salts were added, the amount of COD increased quite substantially and after the reaction was completed, the final COD was higher than the initial one.

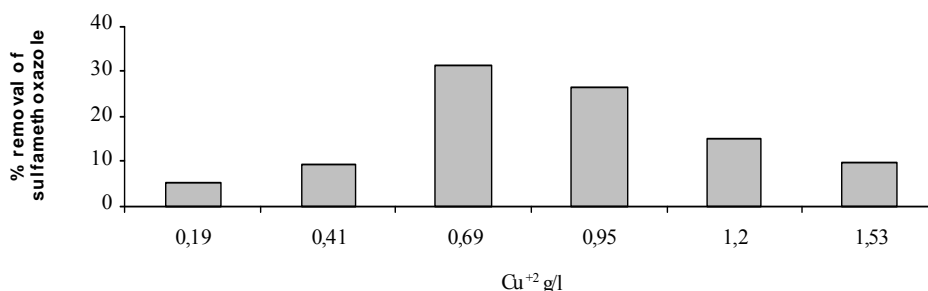


Fig. 5. The percentage changes of sulfamethoxazole concentration at different concentration of copper ions

Comparing figures 4 and 5 it is visible that the dose of copper ions of 0.69 g/dm^3 is most stimulating. It gave $0.43 \text{ g Cu}^{2+}/100 \text{ mg DOC}$ of the bisepitol solution.

The optimal insolation time was established based on the percentage changes of sulfamethoxazole concentration. The experiment was carried at optimal parameters – $0.55 \text{ Fe}^{2+} \text{ g/dm}^3$, $0.69 \text{ Cu}^{2+} \text{ g/dm}^3$ being established earlier, and aeration intensity amounting to $550 \text{ dm}^3/\text{h}$. During the insolation the reactive mixture was poured into the low reactor, with greater exposure surface, where the oxygen dissolution is limited due to restricting the time when the air bubbles are present in the liquid as the transport distance is shortened. That is why the process was always commenced with aeration which facilitates the dissolution of the greatest amount of the oxygen

necessary to form peroxide hydrogen. The change allowing aeration and insulation could lengthen the process. The results of the experiments were presented in figure 6.

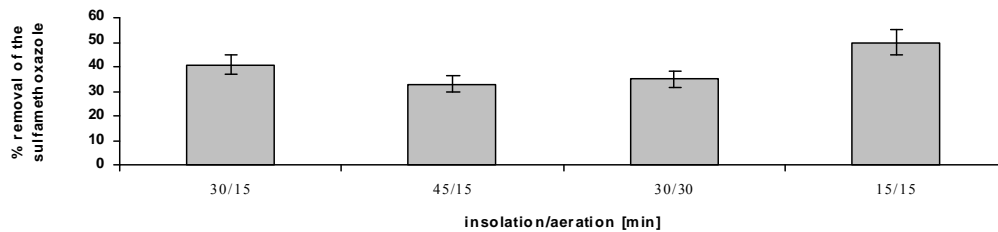


Fig. 6. Percentage changes of the sulfamethoxazole concentration at different time of insulation

The research proves that the insulation should last 15 min and should be carried out after each 15 min aeration, then the best results are obtained.

Optimal pH of the solution was also established by measuring the percentage removal of the pharmaceutical from the reactive mixture using all the predetermined optimal parameters. During the process, a double alkalization takes place. pH of the bi-septol solution has reached the value of 4. Figure 7 shows the influence of the preliminary pH adjustment on the performance of the process.

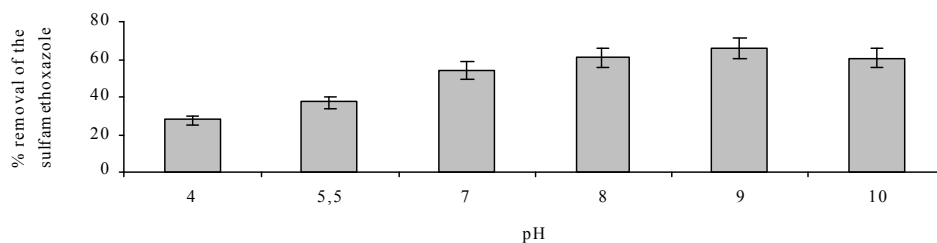


Fig. 7. Percentage changes in the removal of sulfamethoxazole, depending on preliminary pH adjustment

The research proves that the preliminary alkalization of the solution to pH 9 brings about the best results. In terms of the economical aspect and caustic features of the substance, the preliminary pH adjustment was set at lower value of 7.

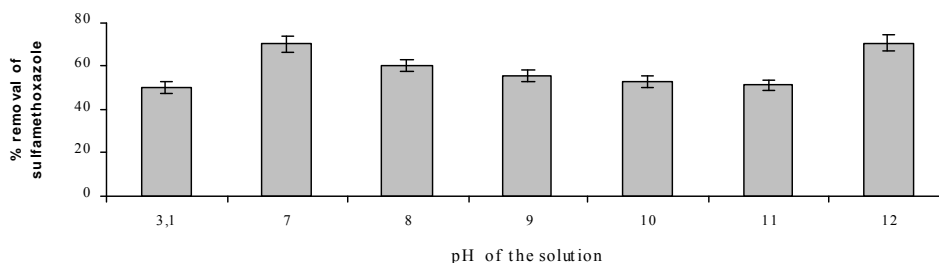


Fig. 8. Percentage changes in the removal of the sulfamethoxazole, depending on final pH adjustment

The post-reactive mixture had an acid reaction (pH 3.1). It turned out that repeated alkalization of the solution was responsible for precipitation effect, simultaneously causing the coagulation of the ferric hydroxide(III), which contributed to greater removal of sulfamethoxazole. The results of the experiment are presented in figure 8.

The best results of the sulfamethoxazole removal were accomplished after final pH adjustment to 12 and 7. Liquids whose pH is 12 are dangerous for the environment and according to standards they cannot be disposed. Therefore, the ultimate optimal value of the process parameter was determined as pH 7. Such a choice is justified by environmental and economical reasons.

3. CONCLUSIONS

The analysis carried out allows determination of the parameters for aeration with ferrous salts. Each 100 mg DOC of the bisepitol (37.5 mg of sulfamethoxazole) should be treated with 0.34 g/dm^3 ferrous ions (Fe^{+2}) and 0.43 g/dm^3 of copper ions (Cu^{+2}) with the simultaneous aeration with compressed air at the rate of to $550 \text{ dm}^3/\text{h}$. Preliminary and final adjustment of pH value was set at 7. The insolation with UV light should be carried out periodically after every 15 minutes of the aeration and should last 15 minutes.

Suggested modification of Fenton's reaction is cheaper than the traditional one as the hydrogen peroxide is replaced with compressed air. The method presented in this paper was successfully applied in removing pure sulfamethoxazole from the water solution and organic contaminants from the municipal landfill leachates [4], [9]. As a result of the modified Fenton's process an eightfold increase in the BOD_5/DOC ratio was observed, which confirmed the enhanced bioavailability of the substance for the microorganisms and therefore usefulness of the method proposed for preliminary chemical purification [5].

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PARAMETRY PROCESU WSTĘPNEGO OCZYSZCZANIA CHEMICZNEGO
ZA POMOCĄ ZMODYFIKOWANEJ REAKCJI FENTONA

Ze względu na obecność w ściekach komunalnych farmaceutyków, które, docierając do miejskich oczyszczalni ścieków, bardzo często nie są w nich całkowicie usuwane, wydaje się zasadne zastosowanie wstępnego chemicznego oczyszczania, gdy stanowią one znaczną część w strumieniu ścieków (szpitale, kliniki, zakłady produkcji farmakologicznej). Zaproponowano metodę będącą modyfikacją reakcji Fentona, polegającą na zastąpieniu nadtlenu wodoru sprężonym powietrzem, i wspomaganą promieniami UV oraz kationami miedzi (Cu^{+2}) spełniającymi rolę katalizatora. Wszystkie parametry procesu zostały określone eksperymentalnie. Wzięto również pod uwagę ewentualne wdrożenie procesu na skalę techniczną i wielkości parametrów takich jak odczyn czy intensywność napowietrzania. Mimo że ich wyższe wartości dawały lepsze efekty prowadzenia procesu, wielkości powyższych parametrów zostały ustalone na

nizszym poziomie.