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Comparative study on classical and modified UV/H_2O_2 and Fenton reaction based methods for the removal of chemical pollutants in water treatment

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ABSTRACT

Conventional methods are unable to remove many organic compounds. It becomes critical that the treatment technologies used are effective and do not create harmful by-products by reacting with the pollutants being removed. Such methods include advanced oxidation processes (AOPs), deep oxidation methods, which form highly reactive HO$^{\bullet}$ radicals that are capable of reacting with all organic compounds. The aim of this study was to evaluate the effectiveness of the processes of AOPs in the degradation of micropollutants from model wastewater and effluent collected in one of the wastewater treatment plants of the Kraków agglomeration. The amount of micropollutants degradation was determined on the basis of changes in the chemical oxygen demand index. The UV/H_2O_2 method and the photocatalytic Fenton reaction were applied. The conducted experiments enabled the selection of the most optimal conditions for conducting AOPs processes (doses of H_2O_2, UV and the matrix effect). For the UV/H_2O_2 method, after 2 h, a 90% removal of micropollutants in the model sewage was obtained, and in real wastewater it was 75%. The UV-Fenton reaction was modified by direct irradiation of H_2O_2. This innovative approach enabled a 30% removal of pollutants within 30 min, while for the UV/H_2O_2 method it was only 10%.

Keywords: Wastewater; Photolysis; Photocatalysis; Hydroxyl radicals

1. Introduction

Wastewater treatment technology, despite the enormous development in the last dozenor so years in the field of reducing or removing large quantities of pollutants, still struggles with the problem of the presence of compounds in very small concentrations. Micropollutants constitute a huge group of compounds of anthropogenic and natural origin, which show resistance to biodegradation and often also toxicity towards living organisms. These include pharmaceuticals, industrial chemicals, steroid hormones and pesticides [1–7]. Their harmful effects on the natural environment have been recognised by the European Parliament. In 2013, a directive (2013/39/EU) was created, which includes 45 priority substances, the concentrations of which must be constantly monitored [8]. But these substances do not include groups of compounds such as pharmaceuticals, steroid hormones or personal care products. For this reason, further studies showing the harmful effect of these substances on the environment, but also on humans, are of great importance [9,10]. The contaminants

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present in municipal wastewater and in livestock wastewater are constant [11]. Unfortunately, industrial wastewater is characterised by a large variety of these pollutants, in particular those from industries such as the chemical, petrochemical, coke, gas and carbochemical industries and from plants producing batteries, fertilisers, pesticides, pigments, detergents, processing of coal degassing products and mining and processing of ores [12–14]. In terms of domestic wastewater, a large group of contaminants are pharmaceuticals, personal care products, surfactants and steroid hormones [15–17].

Advanced oxidation processes (AOPs) are techniques that can remove most organic pollutants with high persistence [18]. The key element of these methods is the generation of highly reactive hydroxyl radicals $HO^{\bullet}$, which through their non-selective oxidation, degrade organic pollutants with high efficiency. This is because these radicals have a very high oxidoreduction potential of 2.8 V. The undoubted advantage is that there is very little chance of the formation of organochlorine compounds and other by-products that may be harmful to humans and the environment. In addition to the high degradability of many organic pollutants contained in wastewater, these methods make it possible to increase the biodegradability of wastewater, remove odours and colour, remove pathogens, reduce the biochemical oxygen demand (BOD) and the chemical oxygen demand (COD) and also reduce or completely eliminate the toxicity of wastewater [19]. Despite their considerable benefits, AOPs processes are mainly used on a laboratory scale, but solutions based on these processes are increasingly appearing on a technical scale, most often in industrial wastewater treatment plants [10]. Generally, AOPs can be divided into three groups. The first group includes chemical processes that take place in a single-phase system without the use of radiation. $HO^{\bullet}$ radicals are produced by the joint action of ozone and hydrogen peroxide (O_3/H_2O_2 – peroxone method), ozone in an alkaline environment (O_3/OH^-) and a mixture of H_2O_2 and Fe^{2+} ions (Fenton's reagent). The second group consists of single-phase processes combined with electromagnetic radiation. The third group consists of photocatalytic processes taking place under the influence of UV radiation in the presence of a semiconductor photocatalyst (usually TiO_2) [20,21].

The aim of the conducted research was to show that the selected methods of advanced oxidation processes can be applied to the degradation of micropollutants in wastewater, difficult to neutralise by means of traditional methods. The non-selective oxidising effect of $HO^{\bullet}$ radicals gives rise to the assumption that these methods will simultaneously act on a large number of various pollutants [21]. The scope of the work included the application of AOPs techniques, that is, the generation of hydroxyl radicals $HO^{\bullet}$, in the removal of organic micropollutants. The experimental parameters and technical conditions have a significant influence on the removal efficiency of pollutants in water treatment. The methods used were the photocatalytic Fenton reaction ($H_2O_2/Fe^{2+}/UV$) and hydrogen peroxide and UV radiation (H_2O_2/UV). The implementation of modification of Fenton reaction in the hydroxyl radical release by directly UV irradiation of H_2O_2 and its dosing to reactor was performed. The efficiency of the used methods of degradation was determined on the basis of COD index measurements.

2. Materials and methods

2.1. Chemicals and materials

The following reagents used to prepare model wastewater and conduct the experiments – ethyl alcohol 96% solution and an aqueous 30% hydrogen peroxide solution – were purchased from POCH, Poland. All reagents of analytical grade $FeSO_4 \cdot 7H_2O$ (CHEMPUR, Poland), H_2SO_4, min. 95% (POCH, Poland), Ag_2SO_4 (CHEMPUR, Poland), $K_2Cr_2O_7$ (POCH, Poland), potassium hydrogen phthalate (POCH, Poland) and 20% NaOH solution (POCH, Poland) were used to perform chemical measurements. Deionised water was supplied by HLP5 pure water system (Hydrolab, Poland). Quantofix peroxides test sticks 1000 from Macherey-Nagel was used to check the presence of hydrogen peroxide in the solution.

2.2. Determination of the chemical index of oxygen demand

The COD has been marked according to the standard ISO 15705:2005 Water quality — Determination of the chemical oxygen demand index (ST-COD) — Small-scale sealed-tube method [22]. According to the aforementioned standard, a calibration curve was prepared which enabled the determination of COD in the tested samples by measuring the absorbance. In brief, 2 mL of the test solution were collected from the reaction vessel with an automatic pipette and transferred to tubes with a mineralising solution. The tubes were placed in a HACH DRB200 COD digester and heated for 2 h at 150°C. After cooling, the sample was placed in HI83224 Photometer (Hanna Instruments) and the absorbance at 600 nm was measured. The value of COD of wastewater sample was calculated according to the known calibration curve of the correlation of absorbance and COD value. All COD measurements were performed in triplicate. The initial COD values for model wastewater and wastewater from treatment plants were 842 ± 49 and 775 ± 85 mg O_2/L, respectively.

2.3. Course of the study

2.3.1. H_2O_2/UV method

The test stand consisted of a high-pressure mercury lamp (LRF 125W, POLAMP, with the highest radiation intensity for the 300–400 nm and 550–600 nm ranges), a magnetic stirrer and a glass reactor which was used to perform the photochemical reaction (Fig. 1).

The volume of 100 mL of model wastewater with an ethanol concentration of 8.8 mol/L after an addition of an appropriate dosage of H_2O_2 (15 or 30 μg/L) was stirred and UV irradiated for 2 h. 2 mL samples were taken at specified time intervals 5, 10, 15, 30, 45, 60, 75, 90, 105 and 120 min of irradiation.

The evaluation of the influence of the UV radiation dosage on the degradation efficiency was carried out by covering the upper part of the reaction vessel with a filter made of aluminum foil with an aperture of appropriate diameter, so that the irradiation field was 50% and 25%.

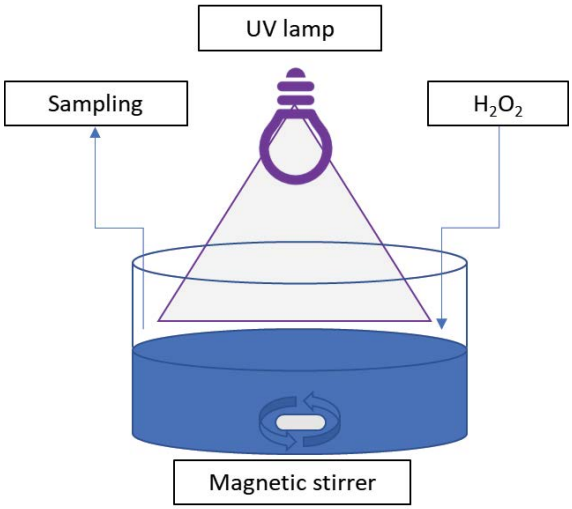

Fig. 1. Schematic diagram of UV/H_2O_2 reactor.

2.3.2. Fenton reaction

The evaluation of the matrix influence on degradation efficiency by means of treated wastewater collected in one of the wastewater treatment plants (WWTP) of the Kraków agglomeration was conducted. The wastewater was previously filtered with GF-1 glass microfiber filters purchased from Macherey-Nagel. 100 mL of purified wastewater enriched with 50 μL of ethyl alcohol was used for the experiment. The amount of H_2O_2 addition was 30 μg/L.

The test stand for the activation of H_2O_2 included a UVC lamp (TUV TL 16 W, PHILIPS, with a maximum in a wavelength between 240 nm and 260 nm) a container with a 30% hydrogen peroxide solution, a peristaltic pump, linked with silicone and quartz tubes as in Fig. 2. Activation of hydrogen peroxide was tested for two flow rates at 100 and 150 mL/min. The investigated H_2O_2 dosages were 60, 120, 150 and 300 μg/L.

The model wastewater (500 mL) of pH lowered to 3 with H_2SO_4 and an appropriate amount of $FeSO_4{\cdot}7H_2O$ hydrate (keeping the molar ratio of Fe^{2+}:H_2O_2 = 1:3 or 1:4) was spiked with activated H_2O_2 and stirred for 30 min. The resultant wastewater was neutralized to pH 7 with an NaOH solution and allowed to settle. After precipitation samples were filtered with glass microfibre filters and 2 mL was taken to a COD test.

The UV lamps were turned on 15 min before the experiments to ensure a stable lamp output in each operation. Control samples without ethanol but spiked with H_2O_2 were conducted in the same steps as the test systems to eliminate increase in COD because of unreacted hydrogen peroxide, iron(II) hydroxide remaining after the process. Absolute COD values were determined by subtracting the COD values obtained for samples and control samples.

All experiments were repeated three times.

2.4. Radiation dose

In the case of wastewater treatment, ultraviolet radiation is used for disinfection as well as to support the decomposition of organic pollutants [23]. The wastewater subjected to the irradiation process is characterized not only by a lower bacterial content [24], but also low turbidity, no total suspended solids, iron, organic matter, ammonia, nitrites, sulfur in the second oxidation stage and phenol [25]. The dose of UV radiation used depends on its intensity (the number of UV rays per unit area) and the contact time (exposure time, time during which the microorganisms are exposed to the radiation). It was calculated according to the following formula [26]:

$$\text{UV dose}\left[\frac{W\cdot s}{m^2}=\frac{J}{m^2}\right]=\text{intensity}\left[\frac{W}{m^2}\right]\cdot\text{exposure time}\left[s\right] \quad (2)$$

During the operation of UV lamps, there is a possibility of the phenomenon of fouling associated with covering the lamp's quartz cover with a layer of sediments constituting a component of the treated water matrices. This phenomenon leads to a gradual reduction in the intensity of ultraviolet radiation and consequently reduces their effectiveness. The phenomenon of the fouling of quartz lamp covers is particularly pronounced during the irradiation of waters characterised by high hardness caused by the presence of such compounds as $CaCO_3$, $CaSO_4$, $MgSO_4$, $Al_2(SO4)_3$. Activation of only the hydrogen peroxide and dosing it into the treated water enables the elimination of this phenomenon [21].

3. Results

3.1. H_2O_2/UV method

3.1.1. Effect of H_2O_2 dosage

In order to assess the efficiency of degradation of selected micropollutants using the H_2O_2/UV method, the changes in the ratio COD to COD_0 for model wastewater (ethyl alcohol solution with a concentration of 8.8 mol/L) were measured. Preliminary degradation experiments for the model wastewater by H_2O_2/UV using two initial H_2O_2 dosages were carried out first. The ratio between COD/COD_0 and the time variation is illustrated in Fig. 3. The blue markers correspond to the dosage of 15 μg/L H_2O_2, the red ones for 30 μg/L H_2O_2 that were used to model wastewater treatment. The removal efficiencies for model wastewater generally increased with increasing H_2O_2 dosage.

At a dose of 30 μg/L H_2O_2, lower COD/COD_0 indices were obtained than for a dose of 15 μg/L H_2O_2, obtained after the same time. Only for samples taken after 120 min of UV irradiation did these results differ to a lesser extent. According to Polish legislation, in order to introduce wastewater into water or soil, the minimum percentage of the total treatment effect in removing pollutants should be at least 75% [27]. In the case of a higher addition of H_2O_2, the recommended percentage of removal was achieved in the seventy-fifth minute of the experiment, and in a smaller dose of H_2O_2, as much as 105 min were needed. The greater amount of H_2O_2 enables one shorten the exposure time by 30 min, which also suggests that the addition of 30 μg/L of H_2O_2 should be used in further experiments.

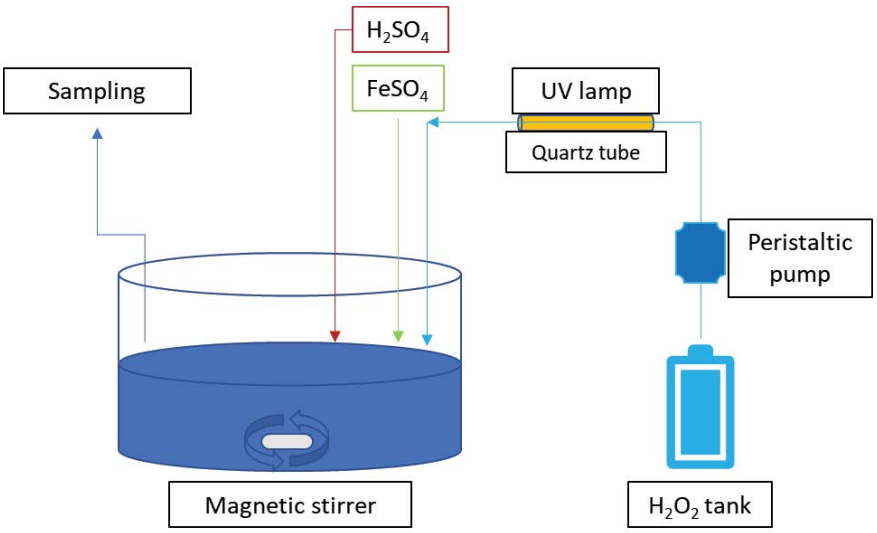

Fig. 2. Schematic diagram of a Fenton reactor with a flow-through UV lamp for dosing of activated hydrogen peroxide.

3.1.2. Effect of UV dosage

Using the UV dose Eq. (2), 100% of the UV dose was calculated for the experiment for each time the test sample was taken. The results are presented in Table 1. When the irradiation area was limited, these values changed. They decreased by a half and a quarter, respectively.

The experiment of UV dosage effectivity was carried out for both model wastewater and treated wastewater using three equal doses of radiation. When one created an aluminum foil filter, one compared the influence of the UV radiation dosage on the removal efficiency. By using a foil filter, the irradiation area of reactor was limited to 50% and 25%, which influences the dose of ultraviolet radiation [25]. The results of the experiment performed are presented in Fig. 4. The graph shows the variation of COD relative to the UV radiation dosage unit over time for the different surfaces of UV radiation. These are average values for which the coefficient of variation (CV) does not exceed 10%. The different variants of the experiment are shown with distinct colours of the markers.

In the case of model wastewater (ethyl alcohol solution with a concentration of 8.8 mol/L), the COD/radiation dose index dropped the fastest in time for the irradiation area equal to 100%. Up to the 60th min of the experiment, the loss of COD at the full irradiation area was twice as large as for 50%. This value increased successively and for the last half an hour it was equal to 4. This means that in the last 30 min the efficiency of the AOP process for 100% of the radiation dose was four times higher than for the half of its value. However, when comparing the organic surface of the irradiation by 75% and its full value, even greater differences in the efficiency of COD degradation can be noticed. The index change values for the above-mentioned irradiation surfaces presented in the graph differ by 3–4.5 times in the first 45 min, and by the last 45 min it was on average 10 times. In the case of such a large reduction in the radiation dose, there are significant differences in the efficiency of chemical pollutants degradation.

Moreover, for treated wastewater with the addition of ethanol, which was the same as for the model wastewater, similar relationships were obtained, especially considering the full radiation dose and its reduction to 25%. For the first 45 min, the difference between the COD/radiation dosage unit for 100% of the irradiation area and the four-fold reduction was constant. The obtained values differed four times from each other. The next hour of the experiment means six-seven-fold differences, and the last measurement is twelve-times lower index values for the full irradiation area. The obtained results indicate that the radiation dose levels have a significant impact on the COD decrease.

3.1.3. Effect of matrix

It was also checked whether the size of the COD changes was also influenced by the matrix in which this parameter is determined. The diagram (Fig. 5) shows how the COD/COD_0 changes relative to time for the treated wastewater with the addition of ethyl alcohol (blue markers) and for the model wastewater (red markers).

Comparing the graph for the model effluent and the treated wastewater with the addition of ethanol, one may see that it is similar for both effluents. In both cases, there is an initial increase in the COD/COD_0, which begins to decrease after 15 min of the experiment. This may indicate that in the treated wastewater, also the products of ethanol metabolism, that is, acetaldehyde and acetic acid, are formed. In addition to ethanol, the treated wastewater contained other organic and inorganic compounds that reacted with hydroxyl radicals, oxidising to other compounds, which also increased the COD.

The final COD/COD_0 value obtained after 120 min of exposure to the test solution was compared with the COD/COD_0 index value from which the test was started, one may see that greater degradation of pollutants occurred in the model effluent (Table 2). The efficiency that was obtained after 120 min for the wastewater treated for the model wastewater was obtained 45 min earlier.

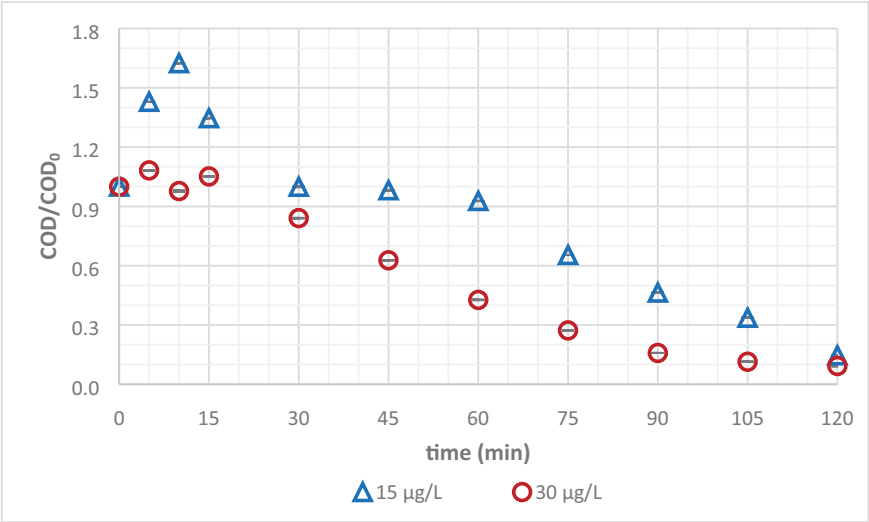

Fig. 3. Variation of COD/COD$_0$ index over time for the model wastewater at various points of H_2O_2 dosage.

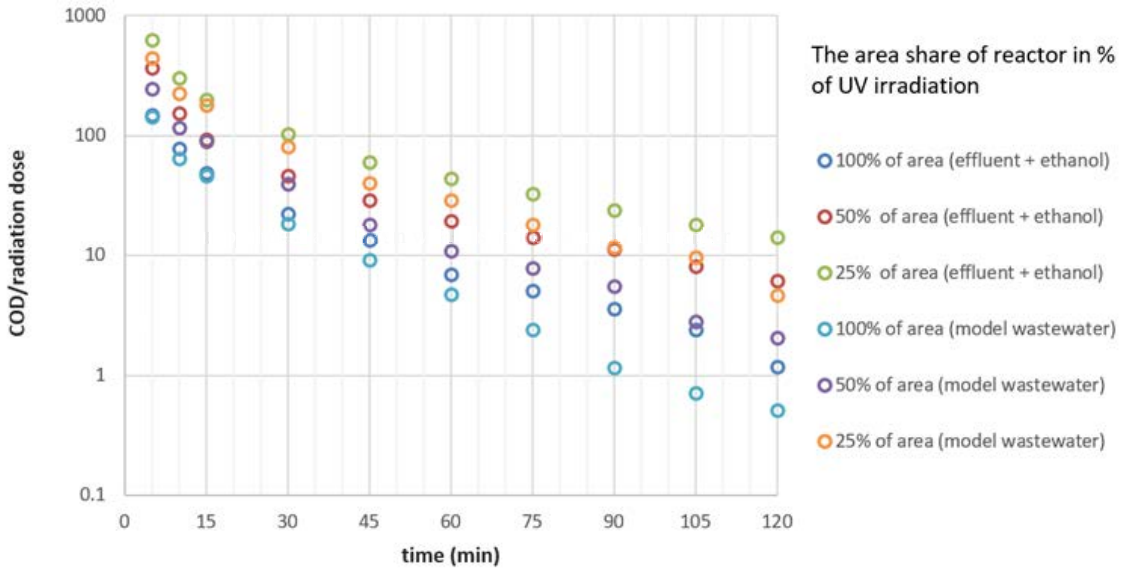

Fig. 4. Variation of COD/radiation dose index over time for the model wastewater and treated wastewater.

3.2. Photocatalytic Fenton reaction

As a result of the AOPs process in the form of the Fenton reaction, the amount of ethyl alcohol was degraded, which in the model wastewater corresponds to the micropollutant in the real wastewater. Initially, the most optimal conditions for carrying out the Fenton reaction were established for the model wastewater, followed by tests on treated wastewater.

3.2.1. Effect of Fe^{2+}:H_2O_2 molar ratio and effect of UV dosage on activation of H_2O_2

The effect of the molar ratio of Fe^{2+} to H_2O_2 on the removal of chemical pollutants was established. As the concentration of Fe^{2+} ions increases, a greater efficiency of the pollutant degradation process is obtained, until reaching the limit concentration above which increasing the amount of iron ions becomes ineffective [28,29]. It is generally believed that a Fe^{2+}/H_2O_2 molar ratio above 50% is not recommended as it will not improve the efficiency of the process, and even an excess of Fe^{2+} may lead to its reaction with the HO$^\bullet$ radicals formed [30]. The second very important factor is the influence of the dose of UV radiation on the activation of H_2O_2. Thanks to UV light, Fe^{2+} ions are regenerated and additional HO$^\bullet$ radicals are produced. Additionally, the generated radicals contribute to the increase of the pollutant degradation process [21].

With the above assumptions in mind, a study of the effect of hydrogen peroxide flow rate through the system

was carried out for two different molar ratio Fe^{2+}/H_2O_2 = 1:3 and 1:4. The flow rates that were compared in the study were 100 and 150 mL/min. H_2O_2 dosage was 150 μg/L. The results obtained are presented in a visual manner in Fig. 6.

The degree of degradation of micropollutants was assessed on the basis of changes in the COD index. When one compares the results, one may state immediately that the best efficiency of the AOP process was achieved for the molar ratio of Fe^{2+}/H_2O_2 equal to 1:3 and at the flow rate of 150 mL/min. For these parameters of the experiment, the lowest value of the COD/COD_0 index was achieved. The decomposition of micropollutants was almost one-third.

On the other hand, for a 1:4 molar ratio, greater efficiency was achieved with a flow rate of 100 mL/min. Nevertheless, in this case, the removal of micropollutants is only slightly more than 6%, and with increased H_2O_2 flow, they did not change and were followed by the initial increase in the COD/COD_0 index. For a molar ratio of 1:4, lower hydrogen peroxide flow rates should be used to improve the degradation efficiency.

Table 1
Variation of the radiation dosage depending on the exposure time for the H_2O_2/UV method

Exposure time (min)	UV dosage (MJ/m^2)
5	5.9
10	11.8
15	17.7
30	35.4
45	53.1
60	70.7
75	88.4
90	106.1
105	123.8
120	141.5

3.2.2. *Effect of dosage of activated H_2O_2*

Another factor that determines the effectiveness of the Photocatalytic Fenton Reaction is the target dosage of H_2O_2, which increases the effects of the oxidation process of pollutants [28,31]. The dose of hydrogen peroxide should also be adjusted according to the type of contamination. Due to an excessive amount of H_2O_2 in relation to the substrate to be oxidised, it can lead to the binding of hydroxyl radicals by this compound [32].

Fig. 7 shows the results obtained for model wastewater (ethanol solution 8.8 mol/L) at a molar ratio of Fe^{2+}/H_2O_2 = 1:3 for different doses of activated hydrogen peroxide. Measurements were performed for a flow rate of H_2O_2 through the lamp of 150 mL/min. H_2O_2 dosage volumes were selected in accordance with the specialist literature [33,34].

The H_2O_2 dosage for which one achieved the lowest value of the COD/COD_0 index, and thus the best degradation effect, was 150 μg/L. Using a H_2O_2 dose of 150 μg/L the greatest decrease micropollutant in the model effluent was achieved, and thus the best degradation effect.

Table 2
Comparison of process efficiency for model and treated wastewater

Wastewater type	COD/COD_0 value at 120 min	Treatment efficiency (%)
Model	0.093	91
Treated + Ethanol	0.225	75

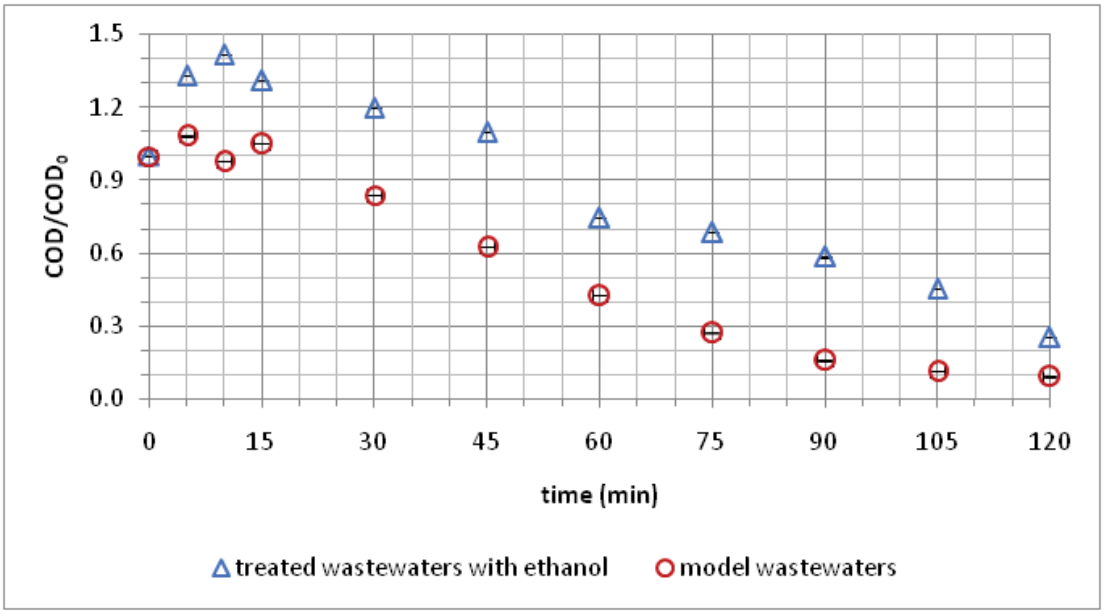

Fig. 5. Variation of COD/COD_0 index over time for various matrices.

For lower doses of H_2O_2 equal to 60 and 120 μg/L, the value of the index decreased, reaching the minimum for 150 μg/L. However, for 300 μg/L, the COD/COD_0 ratio was the highest. This means that as a result of the application of H_2O_2, an initial increase in COD occurs, and only then can the reaction slowly begin. A similar relationship may exist for H_2O_2 doses of 60 and 120 μg/L, but in this case the insufficient number of $HO^\bullet$ radicals is due to an insufficient volume of hydrogen peroxide used, relative to the size of the impurity [21].

Ultimately, the most optimal system for the photocatalytic Fenton reaction to Fe^{2+}/H_2O_2 molar ratio = 1:3, with a flow rate of hydrogen peroxide through the lamp at a rate of 150 mL/min. The concentration of H_2O_2 was 150 μg/L.

4. Discussion

4.1. H_2O_2/UV method

In our experiments, two H_2O_2 additions of 15 and 30 μg/L were analysed. It has been found that this larger supplement gives better results, so it is used for further experiments. Regardless of the amount of hydrogen peroxide that was added to the model effluent, there is always an initial increase in the COD/COD_0 index before a gradual decrease. This may be due to the fact that initially a reaction takes place in which derivatives are formed from the oxidation of ethanol such as acetaldehyde (5) and acetic acid (6) [35]

$$HO^\bullet + CH_3CH_2OH \rightarrow H_2O + CH_3C^\bullet HOH \quad (3)$$

$$CH_3C^\bullet HOH + O_2 \rightarrow CH_3\left(COO\right)^\bullet HOH \quad (4)$$

$$CH_3\left(COO\right)^\bullet HOH \rightarrow CH_3CHO + HOO^\bullet \quad (5)$$

$$CH_3\left(COO\right)^\bullet HOH + CH_3CH_2OH \rightarrow CH_3COOH + H_2O + CH_3C^\bullet HOH \quad (6)$$

These substances also have specific chemical oxygen demand values, which causes a temporary increase in the COD value. With the increasing degree of oxidation, simple compounds such as CO_2 and H_2O were finally formed, which do not affect the COD index. The reactions of the complete oxidation of ethanol are shown in the following equation [36]:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \quad (7)$$

Analysing the data presented in Fig. 3, one noticed that an increase in the addition of H_2O_2 causes an increase in the degradation rate of micropollutants. The same conclusion was reached by Bezak-Mazur and Dąbek [37] during the analysis of the rate of decomposition of dyes, that is, hardly biodegradable substances, into aqueous solutions. In their research, doses of H_2O_2 about two, three and nine times higher were used, but even the smallest addition of hydrogen peroxide resulted in a 90% effectiveness of the treatment being obtained within a few minutes [37]. Analyses of the influence of AOPs on the degradation of bisphenol A have shown that the higher the dose of H_2O_2, the higher the degree of micropollutant degradation [38]. Afonso-Olivares et al. [39] in a study of the degradation of twenty-three pharmaceuticals, determined that for the degree of removal of all of them to be 90%, 75 min of UV irradiation is needed with a dose of H_2O_2 twice as big as the one used for our research. In the case of wastewater treatment with the addition of a standard mixture of 30 pharmaceuticals, it was found that in order to achieve 90% degradation of all compounds within 30 min, the same dose of H_2O_2 that we used for our experiment is needed [40]. Subsequent research presented by Kim et al. [41] demonstrated the possibility of applying the discussed method to wastewater treatment. The conducted experiment on a laboratory scale shows that the treatment of wastewater with 12 antibiotics and 10 analgesics with a 90% removal efficiency is possible with the use of a dose of H_2O_2 similar to that used in our research [41]. Additionally, the validity of using AOPs methods in wastewater treatment was shown in an article by Del Moro et al. [42]. Thanks to the combination of biological treatment and H_2O_2/UV, a removal efficiency higher than 80% was obtained for all compounds [42].

The obtained UV radiation dosage values are very high (Table 1). Therefore, it may be assumed that apart from the degradation of micropollutants by the action of hydroxyl

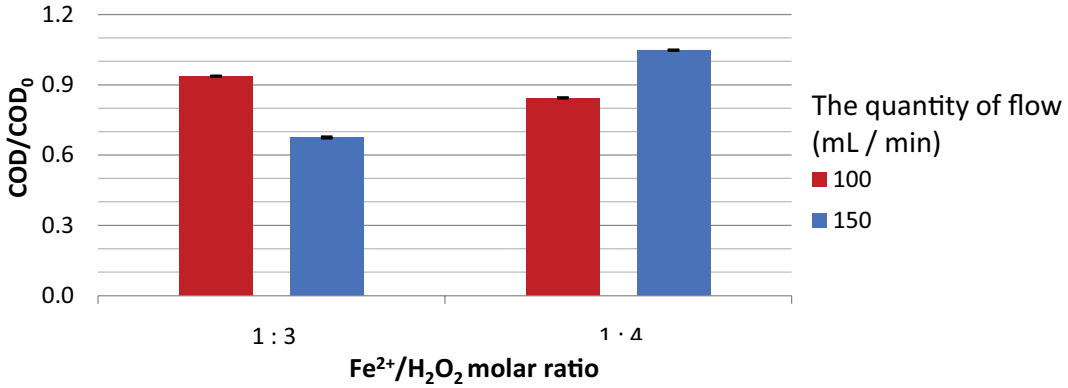

Fig. 6. Variation of COD/COD_0 index depending on the Fe^{2+}/H_2O_2 molar ratio and the activation time of H_2O_2.

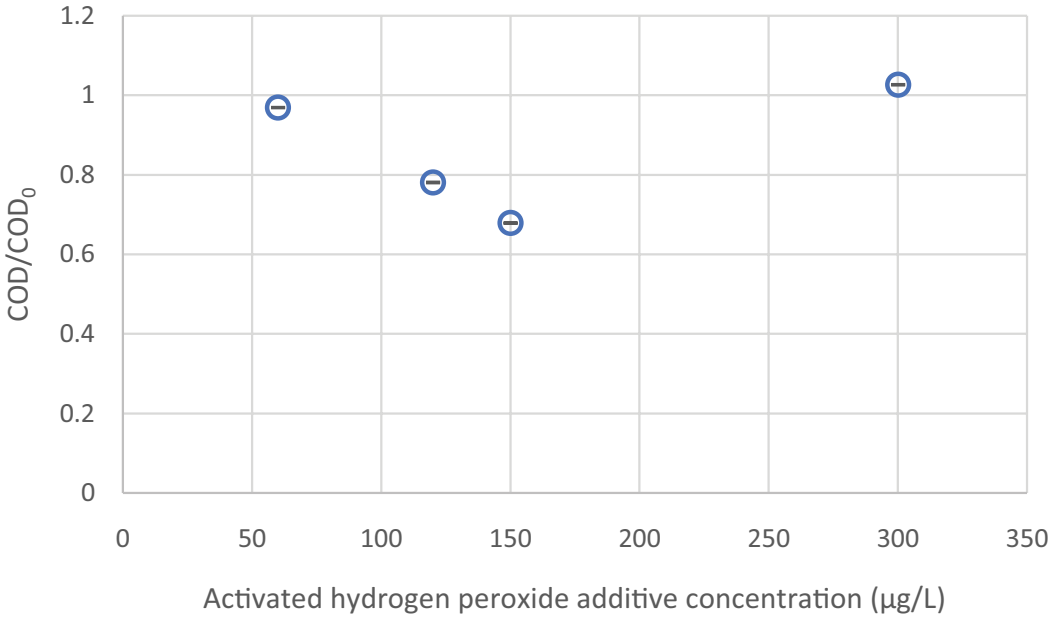

Fig. 7. Variation of COD/COD_0 index in model wastewater for different concentration of H_2O_2.

radicals (indirect photolysis), direct photolysis took place, that is, degradation of the pollutant by the action of UV photons with the organic substance [43]. This assumption is confirmed by studies conducted by Miller [44]. As it turned out in our research, both the UV irradiation area and the type of metric used are also important when it comes to the degree of degradation of micropollutants (Fig. 4). In general, the longer the experiment time, the greater the difference between the COD/radiation dose index for different irradiation surfaces. The smaller the surface area to which the UV radiation is emitted, the higher the COD index that one achieves and, consequently, the lower the micropollutant removal efficiency. This is directly linked to the intensity of hydroxyl radicals generated, as the lower the number of radicals produced is in the effluent solution, the lower the effect of decreasing micropollutant content during the process. With an irradiation duration of less than 60 min, the results obtained do not show large changes in micropollutant concentration, which can be attributed to the reaction time which is too short. Significant differences in results are observed after a reaction time of 60 min. This is in line with many ongoing studies [45–47]. Thus, by reducing the amount of UV radiation, the efficiency of the AOP process decreases. The size of the UV radiation dose is not insignificant. The greater its quantity, the faster the COD is decreasing. This is also confirmed by the research of Shu et al. [48], where the increase in UV power resulted in the decrease of COD under the influence of various doses of H_2O_2. In all cases, the height occupied by the solution in the reaction vessel was the same, so in order to achieve a satisfactory degree of micropollutant removal, it is necessary to provide as much surface area as possible for a given volume of liquid. The fouling process of the lamp's quartz cover with a layer of sediments limits the UV radiation dosage and removal efficiency of pollutants [21].

The effect of the matrix effect is included in Table 2. A different degree of degradation for the two matrices is due to the fact that distilled water was used to prepare the model effluent, while the treated wastewater contained other organic and inorganic compounds in addition to some ethanol. It would have been necessary to use a higher dose of hydrogen peroxide to degrade, in addition to ethanol, the other substances present in the treated wastewater and to achieve results as satisfactory as in the case of the model wastewater. This experiment shows that the greater the amount of micropollutants in the wastewater, the more difficult it is to degrade them. In the case of our matrix in the form of wastewater enriched with ethanol, achieving a change of over 95% of the COD/COD_0 index required at least 120 min of the AOPs process. Literature data show that such an effect can be achieved for the experiment duration that is less than 60 min and with a dose of H_2O_2 half the dose used by us [49]. However, it should be noted that the value of COD_0 was twice as high in our research than in the cited publication, which causes a difference in the final results. In our case, the initial mass load was much higher, which confirms the theory that with the increase in the amount of micropollutants, the degree of difficulty in their degradation increases.

4.2. Photocatalytic Fenton reaction

In general, according to literature reports, it is believed that an increase in the dose of H_2O_2 or an extended reaction time has a positive effect on the global degradation of micropollutants [9]. As a result of the conducted experiments, it was found that the most optimal conditions for the photocatalytic Fenton reaction were the molar ratio Fe^{2+}/H_2O_2 = 1:3 and the flow of hydrogen peroxide at a rate of 150 mL/min and the addition of H_2O_2 with a concentration of 150 µg/L.

It can be concluded that the higher the flow velocity and the smaller the molar ratio, the greater the loss of ethanol in the model wastewater. hydroxyl radicals exhibit very high reactivity as evidenced by their very high rate constants for reactions with many substances [44,50]. By this, one may consider that a higher flow rate will provide a greater amount of reactive $HO^{\bullet}$ radicals delivered to the effluent solution. This may be because fewer of these highly reactive radicals react with contaminants encountered in system components before a given volume of H_2O_2 enters to the reactor. Ultimately, for the best AOP efficiency, a molar ratio Fe^{2+}/H_2O_2 = 1:3 should be used in further testing. This value is confirmed by studies conducted by Barbusiński [21] and Miller [44]. The recommended hydrogen peroxide flow rate through the UV lamp is 150 mL/min.

In studies reported by Schrank et al. [33], a similar relationship between the decrease in COD value and the amount of H_2O_2 added was observed. Their subjects included the addition of H_2O_2 in the dose range considered by us to be the most optimal, up to 1/10 of this dose. It was observed that with the increase in the amount of hydrogen peroxide, the amount of COD decreased, and the best efficiency equal to 80% was obtained at the highest analysed dose. However, the analysis time was four times longer than in our research [33]. The photocatalytic Fenton reaction has also been proposed as a method for treating leachate from a Chinese landfill in Wuhan. The parameters of this method are the dose of H_2O_2 10 times greater and the molar ratio of Fe^{2+}/H_2O_2 = 1:9. For these parameters, a COD change of 60% was achieved [51]. Literature reports show that this method can be used for wastewater treatment from the Wooden Floor Industry. In this case, the sewage was treated to a great extent COD downgraded by 79% [52]. The study of the laundry wastewater was carried out for 3 h and as a result of the discussed AOP method, almost 100% surfactant degradation was obtained [53]. Photo-Fenton is a process of wastewater treatment of the future, as it is used in the degradation of antibiotics (meropenem and ceftriaxone) in over 90% within 60 min [54]. The research of Klamerth et al. [55] showed that this process was able to decompose 48 compounds below their detection limit out of 52 analysed micropollutants (PPCP and pesticides) in sewage treatment plant effluents.

5. Conclusion

This study focuses on evaluating the effectiveness of two AOPs techniques, that is, the photocatalytic Fenton reaction (H_2O_2/Fe^{2+}/UV) and a method using a 30% solution of hydrogen peroxide and ultraviolet radiation (H_2O_2/UV). The COD index for model wastewater and effluent was measured for assessing the process performance and comparison removal efficiency of chemical contaminants. By analysing factors such as dosages of H_2O_2, UV and matrix effect, the optimum parameters for each of the selected methods were determined. For the H_2O_2/UV, a higher dose of H_2O_2 proved to be better. One achieved over 60% and 90% degradation of chemical contaminants in 60 min and 120 min when 10 μL H_2O_2 per 100 mL of model wastewater was used. This dose should be adjusted to minimise the risk of formation of oxidation intermediates and to maximise the formation of simple end products such as CO_2 and H_2O. A decomposition of 75% of micropollutants for the effluent was achieved, after 2 h. It was concluded that the obtained COD/radiation dosage values vary significantly as a function of matrix.

In the case of the UV-Fenton reaction, removal of COD by 30% for the model wastewater was achieved after 30 min, compared with only 10% degradation achieved in H_2O_2/UV method. The implemented modification of Fenton reaction in the hydroxyl radical release by directly UV irradiation of H_2O_2 and its dosing to reactor confirmed its useful. The results showed that higher flow rate of H_2O_2 of 150 mL/min through the UV lamp was more effective for its activation. The effects of Fe^{2+}/H_2O_2 molar ratio and H_2O_2 dosage were investigated in this study. It was observed that Fe^{2+}/H_2O_2 molar ratio of 1:3 and addition of H_2O_2 at a concentration of 150 μg/L to model wastewater resulted in a higher decomposition of value COD index in the solution. Modification of the method through the use of activated hydrogen peroxide as a result of direct irradiation with H_2O_2 significantly reduces the energy consumption necessary to irradiate treated wastewater in the photolysis method. Moreover, it does not cause the formation of deposits on the lamp, which is the case with the flow photolysis method. When one develops a system to remove organic micropollutants, process parameters must be selected so as not to exceed the effective dosage. The effective removal of micropollutants is influenced by the irradiation area. The parameters of advanced oxidation processes should be adjusted according to the type and concentration of the micropollutants to be removed.

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