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PHOTOCHEMICAL OXIDATION MODEL OF ORGANIC POLLUTANTS IN GREYWATER FROM A SMALL HOUSEHOLD

The treatment of coagulated greywater from a small household was investigated. The processes of oxidation of organic compounds with hydrogen peroxide combined with ultraviolet radiation ($\text{H}_2\text{O}_2/\text{UV}$) was described. Greywater with various initial COD and TOC concentrations was used in the $\text{H}_2\text{O}_2/\text{UV}$ process. The process parameters were hydrogen peroxide doses 0.5–4.0 kg $\text{H}_2\text{O}_2/\text{m}^3$, UV (254 nm) light intensity 75.5 W/m^2 and irradiation time – 1 h. The oxidation efficiency varied broadly from 15 to 98% and higher COD values corresponded to lower oxidation efficiencies. The average hydrogen peroxide consumption per kg of COD $w = 12.2 \text{ g H}_2\text{O}_2/\text{g O}_2 \text{ COD}$, while per TOC it was $w' = 69.0 \text{ g H}_2\text{O}_2/\text{g C}$. The experiments enabled one to developed mathematical models for coagulation and oxidation kinetics. The models showed that at the initial COD = 859 $\text{g O}^2/\text{m}^3$, the coagulant dose of 100 $\text{g Al}^{3+}/\text{m}^3$, the hydrogen peroxide dose of 4 kg $\text{H}_2\text{O}_2/\text{m}^3$ and the UV irradiation time of 3 h it is possible to decrease the COD by 98.4%.

1. INTRODUCTION

Production of water for communal purposes is becoming increasingly costly so some decisions about its economic management have to be made. As has been shown, reuse of greywater may be profitable, especially in areas where a water deficit is observed [1, 2]. Treatment of greywater can involve various unit processes, physical, chemical and biological ones [3–8]. The main physical methods include filtration with sand, gravel, charcoal, lime pebbles and natural zeolite as well as microfiltration, ultrafiltration, nanofiltration, reverse osmosis and adsorption [1, 5–8].

The main chemical methods comprise coagulation, electrocoagulation, chlorination, oxidation with hydrogen peroxide combined with UV irradiation ($\text{H}_2\text{O}_2/\text{UV}$), photocatalytic oxidation (TiO_2/UV), (O_3/UV), oxidation with the Fenton process and its mod-

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ifications. The main biological methods include membrane bioreactors, biological aerated filters, sequencing batch bioreactors, rotating biological contactors and anaerobic filters.

The above unit processes differ in the removal of predominantly organic pollutants from greywater and their process efficiency remains rather too low and insufficient to good treatment [1, 5, 6, 8]. In order to improve the overall process performance, a sequence of several unit processes has to be employed [5, 7]. The composition of greywater varies greatly with regard to both type and concentration of pollutants [2, 4–6], e.g., chemical oxygen demand (COD) can range from 100 to 2000 g O₂/m³, turbidity from 20 to 2000 NTU, total organic carbon (TOC) from 30 to 600 g C/m³ and pH from 6.3 to 8.5. Such instability of the greywater characteristic makes it difficult to develop one universal treatment technology.

Organic pollutants that remain in greywater after its pre-treatment can be removed by the advanced oxidation process (AOP) [5, 9, 10]. AOP is a complex process where the main oxidizing agents are radicals such as for example hydroxyl, hydroperoxide and others, formed during the oxidation process [3, 11, 12].

The hydroxyl radical, as an oxidizing agent, can detach hydrogen from the organic substance RH [3, 11]. Subsequently, organic carboradicals R[•] are formed with an unpaired electron at the carbon atom [3, 11]. Carboradicals react quickly with dissolved oxygen forming peroxide radicals [3, 11]. Further conversions of the ROO[•] radicals may lead to complete oxidation of organic matter to carbon dioxide and water. It should be noted that molecular oxygen comes from two sources: from oxygen originally dissolved in greywater and as a result of decomposition of hydrogen peroxide. Since hydrogen peroxide disintegrates slowly, these two sources do not provide a sufficient amount of oxygen to oxidize a large part of carbonaceous organic matters present in wastewater. Factors that stimulate decomposition include metals present in wastewater (iron, manganese and copper compounds, including their oxides that act as catalysts) or other elements with valence electrons on the d-shell (Ag, Cu, Fe, Mn, Ni, Pt, Pd, Ru) [13]. Synthesis of the oxygen molecule may result from reactions between many different intermediates of hydrogen peroxide decomposition as well as reaction products and solution components [14]. Also, a hydroperoxyl anion HO₂⁻ formed during dissociation of a weak acid H₂O₂ ($K_a = 10^{-11.6}$, [3, 11]) and reacting with hydrogen peroxide may form an oxygen molecule [11] (dissociation reaction and dismutation process reactions).

A photochemical version of AOP uses various oxidizing schemes, e.g., H₂O₂/UV, Fenton reaction/UV (H₂O₂/Fe²⁺/UV), heterogenic photo-catalysis (TiO₂/UV) or (TiO₂/H₂O₂/UV), O₃/UV and many others [12, 15].

The hydroxyl radical HO[•] is the main oxidizing agent for hydrocarbon pollutants. As a result of the dehydrogenation of organic substances, water and organic radicals are formed, which then can take part in further reactions [3]. Carbon dioxide and water become the end products of oxidation of hydrocarbon pollutants.

The hydroxyl radical is very reactive; the rate constant for the second order reaction with regard to hydroxyl and for example aromatic compounds, chlorinated hydrocarbons, alcohols and ketones is 10^8 – 10^9 dm³/(mol·s) [15] or 10^8 – 10^{11} dm³/(mol·s) [16], while for tert-butanol it is $6.6 \cdot 10^8$ dm³/(mol·s) [17]. From the wastewater treatment perspective, the amount of the hydroxyl radical in the reaction solution is very small. Accordingly, a reaction between hydroxyl and organic compounds will not limit the overall oxidation rate, which is relatively small. For example, during surfactant oxidation in H₂O₂/UV and H₂O₂/Fe²⁺/UV processes the rate constant of a pseudo-first order model was 0.1 min⁻¹, at the hydrogen peroxide concentration of 1–2 g H₂O₂/m³ (0.03–0.06 mol/dm³) and the initial COD of 450 g O₂/m³ [4]. A bimolecular reaction (H₂O₂, substrate), described by the second order rate model, had the rate constant of about 0.04 dm³/(mol·s).

The overall oxidation rate in the H₂O₂/UV process will be determined by a HO[•] production rate (mainly from H₂O₂) and the overall rate of all reactions where a substrate is oxidized to CO₂ and H₂O (mainly reactions of a substrate with HO[•] and O₂) [3, 14, 16].

Numerous radical reactions that may take place in the solution during the H₂O₂/UV process have very high second order bimolecular rates of 10^5 – 10^9 dm³/(mol·s) [19, 18] it means that they quickly disappear just after their formation, due to subsequent reactions. However, there are also some relatively slow reactions, e.g.: H₂O₂ + HO₂[•] → HO[•] + H₂O + O₂ with a rate constant of 3.0 dm³/(mol·s) or H₂O₂ + O₂[•] → HO[•] + O₂ + OH⁻ with a rate constant of 0.13 dm³/(mol·s) [16].

From a technological perspective, there is no point in considering fast and slow reactions in kinetic models of oxidation in wastewater. The slowest reactions determine the overall pollution depletion rate and an H₂O₂ consumption rate. Therefore, the overall H₂O₂/UV process rate may be approximated by simpler models that include substitute bimolecular reactions for the substrate and hydrogen peroxide. In the works [18] and [19] the authors analyzed very complex kinetic models and the constant rates were determined for pure solutions. Since in wastewater, these values might be completely different so the application of such models for technological systems would be limited; looking for several dozen kinetic constants for a complex model of wastewater treatment [18, 19] is rather tiresome. Therefore, simpler kinetic models for specific technological systems should be proposed. Once parameters of such a model are determined in laboratory conditions, it will be possible to use them to design full-scale technological systems. Degradation of 1,2-dibromo-3-chloropropane can be described by a pseudo-first order model at the given process conditions. The results indicate that the constants range from $4 \cdot 10^{-5}$ to $274 \cdot 10^{-5}$ s⁻¹ and depend on the process conditions (concentrations of hydrogen peroxide and inorganic carbon, radiation intensity and pH; always above 7.2).

It was shown that the k_0 constant increases proportionally to UV radiation intensity and decreases with an increase of carbonate and bicarbonate concentrations (inorganic carbon); also k_0 initially increases and then decreases with an increase of the initial H₂O₂

concentration. It seems that any discussions on the impact of initial concentrations of H_2O_2 and inorganic carbon, while there are actual changes of these parameters, can lead to false conclusions. In the case of acidic wastewater ($\text{pH} < 5.0$), carbonates and bicarbonates are not a problem since all organic carbon is in a form of $\text{CO}_{2,\text{aq}}$ or H_2CO_3 and as such does not serve as a HO^\bullet radical scavenger. During initial coagulation with acidic coagulants (aluminum sulfate, pre-hydrolysed (poly) aluminum sulphates(VI)) wastewater becomes acidic and such pre-coagulated wastewater has been discussed in the paper. It should be noted that CO_2 produced during oxidation can be an additional pH-reducing agent.

Kinetics of pollution removal in the $\text{H}_2\text{O}_2/\text{UV}$ process can be often described by the first order unimolecular model [4, 8, 9, 12] as well as second and third order unimolecular models [12], Elovich model [12] or unimolecular model of Langmuir–Hinshelwood [8]. The pollution removal rate increased proportionally upon increasing hydrogen peroxide concentrations up to about $0.010 \text{ mol H}_2\text{O}_2/\text{dm}^3$ and therefore a second order bimolecular model for COD and H_2O_2 was proposed [9]. The rate constant was $0.0177 \text{ dm}^3/(\text{mol}\cdot\text{s})$ for greywater at the initial COD of $225 \text{ g O}_2/\text{m}^3$.

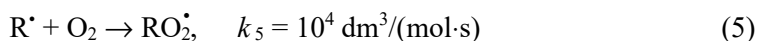
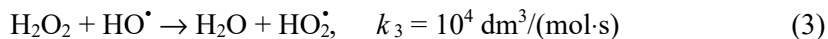
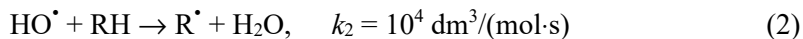
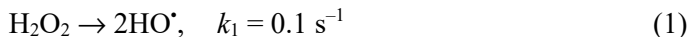
Currently, there are no good models describing the oxidation process of organic substances contained in greywater using hydrogen peroxide in the presence of UV radiation. The first order bimolecular model for each reagent was proposed by Chin et al. [9]. The model assumes that for a given dose of oxidant (H_2O_2), the concentration of the reducer decreases according to the first order monomolecular mechanism. This is a poor quality model because it cannot predict changes in oxidant concentration over time. Furthermore, the assumption of monomolecular kinetic for the reducer and oxidant is not valid due to the complexity of the oxidation mechanism. A more universal model that allows for determining the concentration of the reducer and oxidant over time is proposed in the present paper. The development of such a model was the main purpose of the research. In the work, the kinetics of the oxidation process has been described using a bimolecular model of fractional order.

2. APPROXIMATE KINETIC MODEL OF THE PHOTOCHEMICAL OXIDATION PROCESS

The rate of photochemical oxidation can be described by various kinetic equations [18]. In acidic wastewater, small amounts of carbonates and bicarbonates are present; at $\text{pH} 5.0$, a molar share of bicarbonates in the total amount of inorganic carbon is about 0.040 , carbonates about 1.67×10^{-7} while the rest is $\text{CO}_{2,\text{aq}}$ or H_2CO_3 ; at $\text{pH} 4.0$ these values are: 0.0042 and $1.77 \cdot 10^{-9}$, respectively. Therefore, they will not have a significant impact on photochemical oxidation at high doses of hydrogen peroxide. In general, radical processes have large rate constants (10^5 – $10^9 \text{ dm}^3/(\text{mol}\cdot\text{s})$) [18, 19]) and it is

the slow process that determines the overall rate of photochemical oxidation. The mechanism of photochemical oxidation is complex. There are many particles associated either with the transformation of H₂O₂ or of the oxidized substrate. The number and form of intermediate oxidation products in the case of wastewater is practically unknown.

Let us assume that the mechanism of photochemical oxidation is as follows:



where k_1 – k_5 are process rate constants.

A detailed kinetic model for reactions (1)–(5) would be as follows:

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_1[\text{H}_2\text{O}_2] - k_3[\text{H}_2\text{O}_2][\text{HO}^\bullet] - k_4[\text{H}_2\text{O}_2][\text{HO}_2^\bullet] \quad (6)$$

$$\frac{d[\text{HO}^\bullet]}{dt} = 2k_1[\text{H}_2\text{O}_2] - k_2[\text{HO}^\bullet][\text{RH}] - k_3[\text{H}_2\text{O}_2][\text{HO}^\bullet] \quad (7)$$

$$\frac{d[\text{RH}]}{dt} = -k_2[\text{HO}^\bullet][\text{RH}] \quad (8)$$

$$\frac{d[\text{R}^\bullet]}{dt} = k_2[\text{HO}^\bullet][\text{RH}] - k_5[\text{R}^\bullet][\text{O}_2] \quad (9)$$

$$\frac{d[\text{HO}_2^\bullet]}{dt} = k_3[\text{H}_2\text{O}_2][\text{HO}^\bullet] - k_4[\text{H}_2\text{O}_2][\text{HO}_2^\bullet] \quad (10)$$

$$\frac{d[\text{O}_2]}{dt} = k_4[\text{H}_2\text{O}_2][\text{HO}_2^\bullet] - k_5[\text{R}^\bullet][\text{O}_2] \quad (11)$$

$$\frac{d[\text{RO}_2^\bullet]}{dt} = k_5[\text{R}^\bullet][\text{O}_2] \quad (12)$$

The set of equations (6)–(12) was integrated up to 16 s. The initial concentrations of H_2O_2 and the reducer have been changed (Table 1). It was found that an increase of k_2 , k_3 , k_5 by several orders of magnitude does not affect oxidizer consumption per unit mass of the reducer $[\text{mol H}_2\text{O}_2/\text{mol RH}]$ (Table 1). The complex process mechanism and its complicated kinetics result in changes of the oxidizer consumption per unit mass of the reducer proportionally to the $[\text{H}_2\text{O}_2]/[\text{RH}]$ ratio. It also results from the ratios of the initial concentrations (Table 1). The higher the ratio value, the higher the oxidizer consumption per unit mass of the reducer is. The calculations have shown that effective oxidation takes place if there is an enough excess of oxidant over the reducer. In the case of oxidation of wastewater pollutants, it may be difficult or even impossible to determine all kinetic constants k_1 – k_5 . The constant rates determined for pure systems do not necessarily apply to systems with many different organic substances, e.g., wastewater. In addition, transitory substances formed during oxidation of a mixture of RH reducers remain unknown as well as the kinetics of their transformation in wastewater. Therefore, a simplified description of oxidation kinetics is worth attempting.

Table 1

H_2O_2 consumption coefficients per unit mass of the reducer (RH)

Initial concentration of H_2O_2 [mol $\text{H}_2\text{O}_2/\text{dm}^3$]	Initial concentration of reducer [mol RH/ dm^3]	Oxidizer consumption coefficient [mol $\text{H}_2\text{O}_2/\text{mol RH}]$	
		after 16 s	after 8 s
0.01	0.04	0.75	0.79
	0.02	0.99	1.07
	0.01	1.49	1.64
0.02	0.04	1.01	1.09
	0.02	1.52	1.68
	0.01	2.54	2.84
0.04	0.04	1.58	1.73
	0.02	2.62	2.91
	0.01	4.70	5.27
0.08	0.04	2.74	3.03
	0.02	4.86	5.44
	0.01	9.05	10.2
0.16	0.04	5.07	5.66
	0.02	9.34	10.5
	0.01	17.8	20.2

The sum of equations (1)–(5) leads to the equation:



Equation (13) shows that the average oxidizer consumption per unit mass of the reducer (formally it is a stoichiometric coefficient) is 2.5. In fact, the coefficient can vary within a wide range from 0.75 to 17.8 (Table 1). Such effect is caused by a higher yield of reaction (3) at higher initial H_2O_2 concentrations, which results in an apparent increase in oxidizer consumption per unit mass of the reducer; reaction (4) is less important as $k_4 \ll k_3$.

For equation (13), the overall kinetic model would be as follows:

$$\frac{d[\text{RH}]}{dt} = -k_r[\text{RH}]^\alpha[\text{H}_2\text{O}_2]^\beta \quad (14)$$

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -wk_r[\text{RH}]^\alpha[\text{H}_2\text{O}_2]^\beta \quad (15)$$

where k_r – process rate constant $[(\text{mol H}_2\text{O}_2)^{-\beta}(\text{mol RH})^{1-\alpha}\cdot\text{m}^{3(\alpha+\beta-1)}\cdot\text{s}^{-1}]$, α , β – constants, w – the coefficient of hydrogen peroxide consumption per unit mass of reducer, $[\text{mol H}_2\text{O}_2/\text{mol RH}]$.

Model (14), (15) does not include changes in oxidizer consumption per unit mass of the reducer. It will be less reliable than the model (6)–(12) when there are major changes in initial concentrations of H_2O_2 and RH. Therefore, the corrections x_1 and x_2 were introduced to the model (14), (15) considering the $[\text{H}_2\text{O}_2]/[\text{RH}]$ ratio. The improved model takes the form of:

$$\frac{d[\text{RH}]}{dt} = -k_r[\text{RH}]^\alpha[\text{H}_2\text{O}_2]^\beta \quad (16)$$

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -wk_r[\text{RH}]^{\alpha-x_1}[\text{H}_2\text{O}_2]^{\beta+x_2} \quad (17)$$

The model (6)–(12) has shown that a higher oxidizer consumption rate (17) obtained once the $[\text{H}_2\text{O}_2]/[\text{RH}]$ ratio was considered has to be compensated by an inhibition fraction ($I/(I + [\text{RH}]/[\text{H}_2\text{O}_2])$) for the reducer consumption rate (16), where I is the inhibition factor $[\text{mol H}_2\text{O}_2/\text{mol RH}]$. This way the model (16), (17) fits better to the model (6)–(12). Ultimately, the approximate kinetic model is:

$$\frac{d[\text{RH}]}{dt} = -k_r \frac{I}{I + \frac{[\text{RH}]}{[\text{H}_2\text{O}_2]}} [\text{RH}]^\alpha [\text{H}_2\text{O}_2]^\beta \quad (18)$$

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -wk_r[\text{RH}]^{\alpha-x_1}[\text{H}_2\text{O}_2]^{\beta+x_2} \quad (19)$$

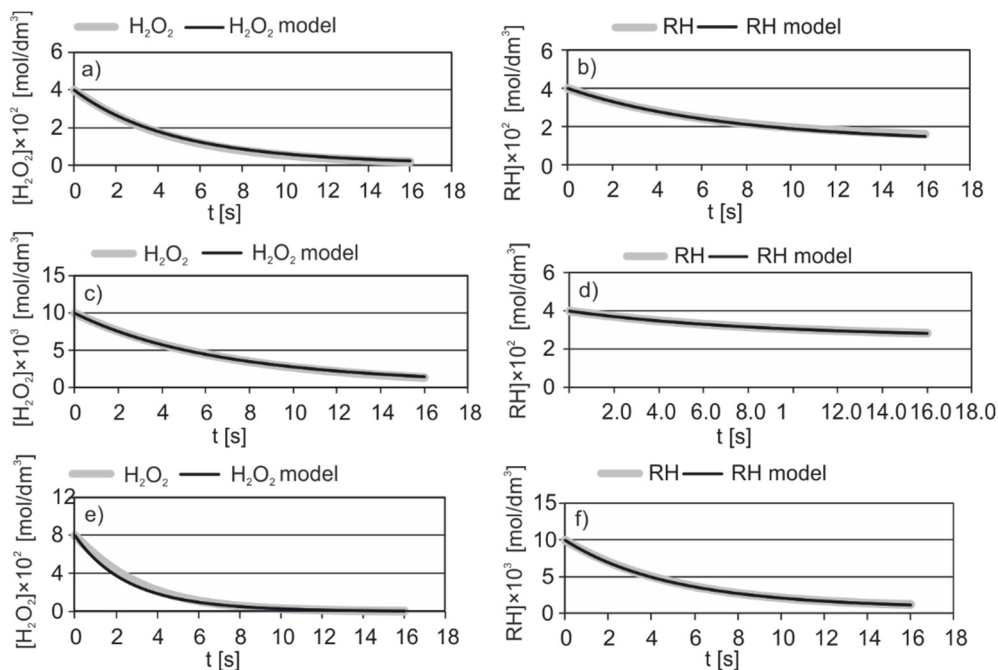


Fig. 1. Examples of fits of the approximated model, equations (18), (19) (H_2O_2 model, RH model) to the detailed model, equations (6)–(12) (H_2O_2 , RH)

The relative error of fit of model (18), (19) to model (6)–(12) is small at highly fluctuating initial H_2O_2 and RH concentrations; at the initial concentrations as in Table 1, the relative error of fit was 0.071. The model fit for the initial H_2O_2 and RH concentrations is shown in Fig. 1a–f. In model (18), (19) the unknown parameters: k_r , w , α , β , x_1 and x_2 can be determined from H_2O_2 and RH concentrations.

Parameters of the approximated model for the above values of k_1 – k_5 are:

$$k_r = 0.1527 (\text{mol H}_2\text{O}_2)^{-\beta} \cdot (\text{mol RH})^{1-\alpha} \cdot \text{m}^{3(\alpha+\beta-1)} \cdot \text{s}^{-1}, \text{ equation (18),}$$

$$k_r = 0.1527 (\text{mol H}_2\text{O}_2)^{-(\beta+x_2)} \cdot (\text{mol RH})^{1-(\alpha-x_1)} \cdot \text{m}^{3(\alpha-x_1+\beta+x_2-1)} \cdot \text{s}^{-1}, \text{ equation (19),}$$

$$\alpha = 0.8779, \beta = 0.1126, w = 1.106 \text{ mol H}_2\text{O}_2/\text{mol RH},$$

$$I = 1.731 \text{ mol RH/mol H}_2\text{O}_2, x_1 = 1.200, x_2 = 1.146.$$

It should be noted that an increase in the RH concentration is followed by a decrease of H_2O_2 consumption rate ($\alpha - x_1 < 0$). It is caused by suppression of the reactions (3), (4) due to the intensification of the reaction (2), which contributes to a lower H_2O_2 depletion rate.

If it was necessary to determine time dependences of the sum of concentrations of RH and R' in equations (18), (19), $[\text{RH}]$ should be substituted with $[\text{RH}] + [\text{R}']$, e.g., for COD and TOC. The presence of the inhibitory fraction ($I/(I + [\text{RH}]/[\text{H}_2\text{O}_2])$) in eq. (18) slows down the overall consumption rate of the reducer in the sum of $[\text{RH}] + [\text{R}']$. Such

a decrease of the overall rate is welcomed since at a higher RH concentration consumption of the HO[•] radical increases (reaction (2)) and inhibits O₂ production (reaction (4)) required for oxidation of R[•] in the reaction (5). In this case, the relative error of fit increases to around 0.148. The model fit for the initial [H₂O₂] and [RH] + [R[•]] concentrations is shown in Figs. 2 and 3. In model (18), (19), the unknown parameters: k_r , w , α , β , x_1 and x_2 can be determined from [H₂O₂] and [RH] + [R[•]] concentrations.

Parameters of the approximated model for the above values of k_1 – k_5 are:

$$k_r = 0.0226 (\text{mol H}_2\text{O}_2)^{-\beta} \cdot (\text{mol RH} + \text{R}^\bullet)^{1-\alpha} \cdot \text{m}^{3(\alpha+\beta-1)} \cdot \text{s}^{-1}, \text{ equation (18),}$$

$$k_r = 0.0226 (\text{mol H}_2\text{O}_2)^{-(\beta+x_2)} \cdot (\text{mol RH} + \text{R}^\bullet)^{1-(\alpha-x_1)} \cdot \text{m}^{3(\alpha-x_2+\beta+x_2-1)} \cdot \text{s}^{-1}, \text{ equation (19),}$$

$$\alpha = 0.4729, \beta = 0.1225, w = 8.0233 \text{ mol H}_2\text{O}_2/(\text{mol RH} + \text{R}^\bullet),$$

$$I = 0.4977 (\text{mol RH} + \text{R}^\bullet)/\text{mol H}_2\text{O}_2, x_1 = 0.7584, x_2 = 1.1012.$$

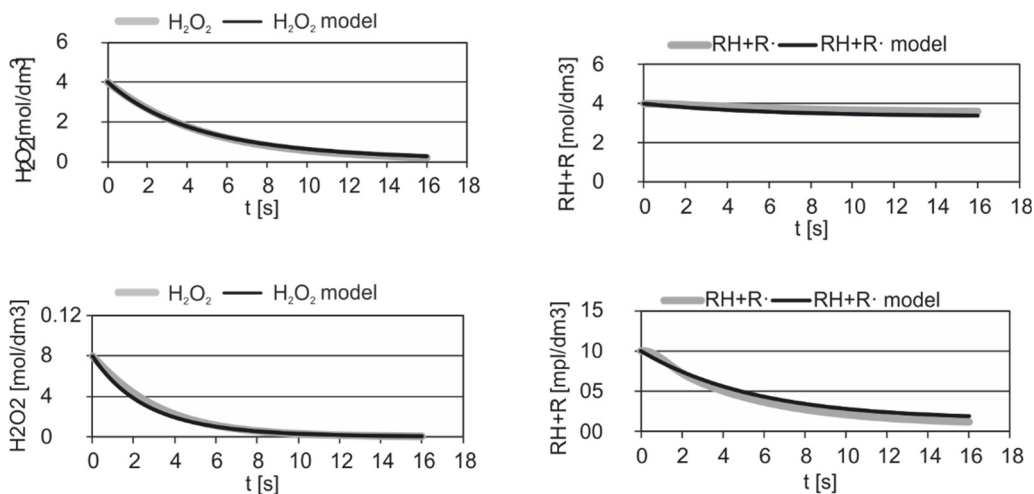


Fig. 2. Examples of fits of the approximated model, equations (18), (19) (H₂O₂ model, RH + R[•] model) to the detailed model equations (6)–(12) (H₂O₂, RH + R[•]).

It should be noted that at the initial concentration of [H₂O₂] equal to the initial concentration [RH] + [R[•]], the rate of change of concentration [RH] + [R[•]] over time is low (Fig. 2a, b). Only with a large excess of the initial concentration [H₂O₂] relative to the initial concentration [RH] + [R[•]] does the rate of change of concentration [RH] + [R[•]] increase significantly over time (Fig. 2c, d). This means that an effective oxidation process will occur with an excess of oxidant relative to the reducer.

For the intensive oxidation process represented by Fig. 2c, d, changes in the concentrations of other substances are shown in Fig. 3. These are the results of calculations obtained from the detailed model equations (6)–(12). The HO[•] and R[•] radicals (Fig. 3b, d) quickly reach their maximum concentrations. However, the R[•] radical concentration (Fig. 3d) quickly decreases to zero. In addition, the concentration of synthesized O₂

(Fig. 3e) reaches its maximum value. Numerical experiments show that in some situations, the maximum O_2 concentration can also occur shortly after the start of the process, after which it quickly decreases to zero. The decreasing values of the reducer concentration RH (Fig. 3c) correspond to the increase in the concentration of the oxidized form of the reducer RO_2^* over time (Fig. 3f).

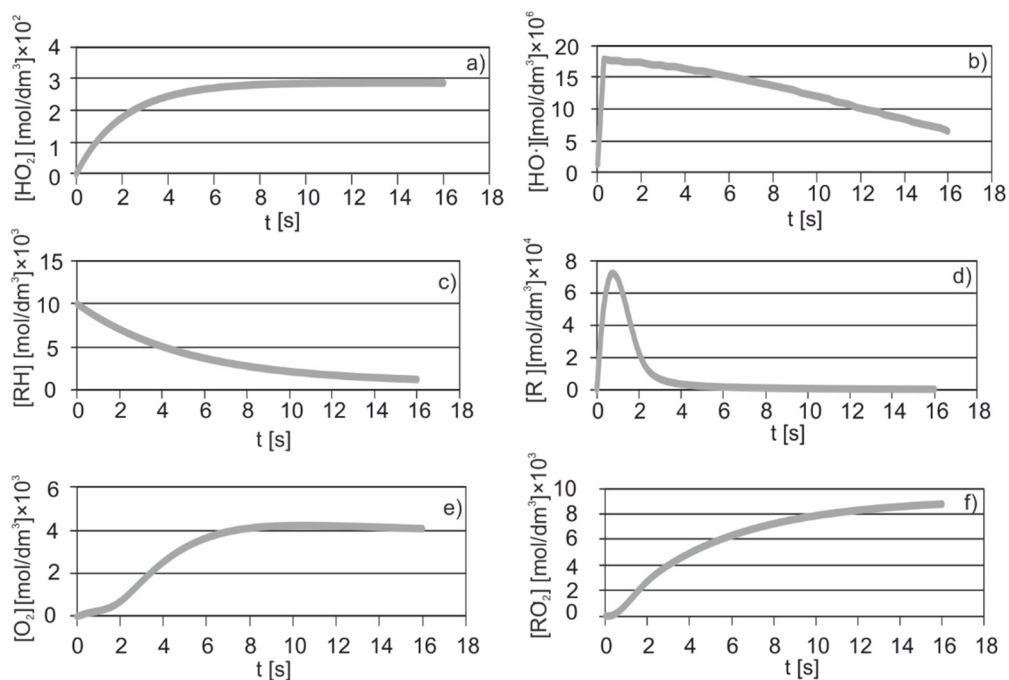


Fig. 3. Changes in reagent concentration over time obtained using the detailed model (6)–(12):

a) HO_2^* , b) HO^* , c) RH, d) R^* , e) O_2 , f) RO_2^*

3. MATERIALS AND METHODS

Greywater characteristics. The research on greywater treatment was based on laboratory-scale experiments. Greywater from a small household included water from the bathroom (57%), the kitchen sink (29%) and the washing machine (14%). The weekly greywater volume produced was about 0.28 m³ and its quality parameters varied widely (Table 2) (results of investigation of four greywater samples). Greywater was collected through about one week and stored in a vessel at 20 °C. By analyzing the TOC values, the COD values appear too high; this could be due to the presence of raw non-carbon reducers in the wastewater and biological conversion of organic carbon into inorganic carbon occurring in grey sewage when collected for several days. There are high values of the COD/TOC ratio (e.g., 7–8) [20]. The greywater was slightly alkaline, mostly due

to alkaline soaps, and its temperature was 20 °C; all the experiments were carried out at this temperature.

Table 2

Greywater characteristics

Parameter	Value
Permanganate value (PV), g O ₂ /m ³	96.9–155.0
Chemical oxygen demand (COD), g O ₂ /m ³	401.3–737.8 (1151.7)
Total organic carbon (TOC), g C/m ³	61.52–76.00
Turbidity, NTU	81.54–143.43
pH	–9.18

Analytical methods. A permanganate value (PV) and chemical oxygen demand (COD) were determined in accordance with the standard methods [21]. Turbidity measurements were made with the WTW 555IR turbidity meter. Total organic carbon (TOC) was measured with the Formacs HT analyzer from Skalar, while zeta potential was measured with the Zetasizer Nano Particle analyzer, model ZEN3600.

The COD analysis, if performed in the presence of hydrogen peroxide, require correction since H₂O₂ is oxidized by potassium dichromate (K₂Cr₂O₇). In the COD test, the sample is titrated with iron(II) sulfate and ammonium solution in an acidic environment. To oxidize 4 moles of Fe²⁺ only 1 mole of O₂, i.e., 32 g of oxygen as COD is required (4Fe²⁺ + O₂ + 4H⁺ → 4Fe³⁺ + 2H₂O). To oxidize 4 moles of Fe²⁺ 2 moles of H₂O₂, i.e., 34 g of H₂O₂ are required (4Fe²⁺ + 2H₂O₂ + 4H⁺ → 4Fe³⁺ + 4H₂O). Therefore, the coefficient used to convert hydrogen peroxide to COD is 32 g O₂ COD/(2×34 g H₂O₂) = 0.4706 g O₂ COD/g H₂O₂. The value may slightly differ [22] because it is influenced by both the hydrogen peroxide concentration and the nature of greywater.

The concentration of hydrogen peroxide was determined iodometrically in an acidic medium. A 100 cm³ test sample was acidified with 10 cm³ of sulfuric acid (1:3) and then 5 cm³ of potassium iodide solution (150 g KI/dm³) were added to the sample. After 20 min, the isolated iodine was titrated with 0.025 mol/dm³ sodium thiosulfate (Na₂S₂O₃) in the presence of starch. Simultaneously, a blank sample was prepared by the same method at 20 °C. The H₂O₂ concentration was calculated as the difference between the amount of iodine released in both samples. A number of moles and gram equivalents of Na₂S₂O₃ used in titration represent a number of H₂O₂ equivalents; a mass of 1 gram equivalent of H₂O₂ is approximately 17 g H₂O₂.

3.3. GREYWATER TREATMENT METHODS

The greywater treatment process comprised several steps. Greywater from the bathroom and the kitchen was pre-filtered with a nylon bag filter (mesh of 200 μm). Then, after settling for 0.3 h in a 0.3 m high tank, the greywater was coagulated [23] with pre-

hydrolyzed poly(aluminum) chloride PAX 16 [24]. The concentrated PAX 16 solution had the following characteristic: pH = 1.0, density = 1.343 g/cm³, alkalinity = 36.23%, aluminium concentration = 0.1099 g Al³⁺/cm³.

1 dm³ of greywater was rapidly mixed with a coagulant for 1 min at a mixing gradient of 103 s⁻¹ and then slowly mixed for 5 min at a mixing gradient of 15 s⁻¹. The precipitated sludge was let to settle for 0.25 h. Then the remaining organic matter was oxidized with hydrogen peroxide; the process was activated with ultraviolet radiation (H₂O₂/UV). A reactor with a UV lamp of 6 W was used. The lamp emitted radiation at 254 nm, its photon energy was 7.826×10⁻¹⁹ J and UV light intensity was 75.5 W/m². The thickness of the irradiated greywater layer was 0.013 m.

4. EXPERIMENTS

4.1. EFFECTS OF COAGULATION ON THE H₂O₂/UV PROCESS

Coagulation of greywater was carried out with the following doses of PAX 16 coagulant: 12.5, 25, 50, 75, 100, 125, 150, 175 and 200 g Al³⁺/m³ [23]. Since the coagulant is strongly acidic, pH of the greywater was changing from about 9.0 to almost 4.3 for the coagulant doses of 200 g Al³⁺/m³ (Fig. 4).

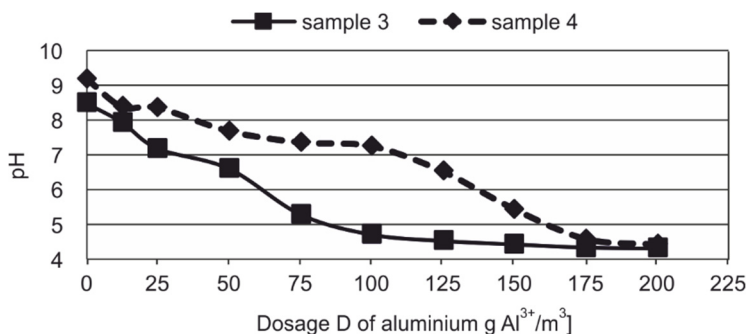


Fig. 4. Changes of pH after dosing the PAX 16 coagulant to two different samples during coagulation (sample 3, initial: COD = 1151.7 mg O₂/dm³, TOC = 76.00 mg C/dm³, sample 4, initial: COD = 401.3 mg O₂/dm³, TOC = 61.52 mg C/dm³)

The slightly acidic environment, as well as a presence of chloride ions from the coagulant, lowers the concentration of carbonate and bicarbonate anions. Such a reduction is quite useful because the anions are effective scavengers of HO[•] radicals [9] that are formed during H₂O₂ exposure to UV radiation. At a very low pH, also hydrogen ions can also lower the concentration of HO[•] radicals. At a very high pH (above 7.5), hydrogen peroxide decomposition may be observed since H₂O₂, as a weak acid ($K_a = 2.51 \times 10^{-12}$ at 20 °C [3, 11]), easily dissociates in an alkaline medium ($\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HOO}^-$ and

$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HOO}^-$). Similarly, hydrogen peroxide may react with HO^\bullet radicals at excessive H_2O_2 concentrations. Afterwards, peroxide radicals HOO^\bullet are formed and their presence weakens the overall oxidation effects. Therefore, a slightly acidic environment seems to be optimal for oxidation with hydrogen peroxide.

Changing the composition of the greywater affects PV, COD, TOC and turbidity removals in the coagulation process. The highest removal was observed for turbidity (ca. 99%) while the removals of other parameters were: PV ca. 59%, COD ca. 66% and TOC ca. 32% (Table 3).

Table 3

Removals of PV, COD, TOC and turbidity at the coagulant dose of $100 \text{ g Al}^{3+}/\text{m}^3$

Parameter	Initial value				Removal [%]			
	Sample				Sample			
	1	2	3	4	1	2	3	4
PV, $\text{g O}_2/\text{m}^3$	104.4	96.9	155.0	–	65.0	61.0	50.0	–
COD, $\text{g O}_2/\text{m}^3$	737.8	694.8	1151.7	401.3	74.7	71.3	63.5	55.7
TOC, $\text{g C}/\text{m}^3$	72.3	70.2	76.00	61.52	29.0	30.5	22.0	47.5
Turbidity, NTU	120.85	131.10	143.48	81.54	99.2	99.2	99.3	99.2

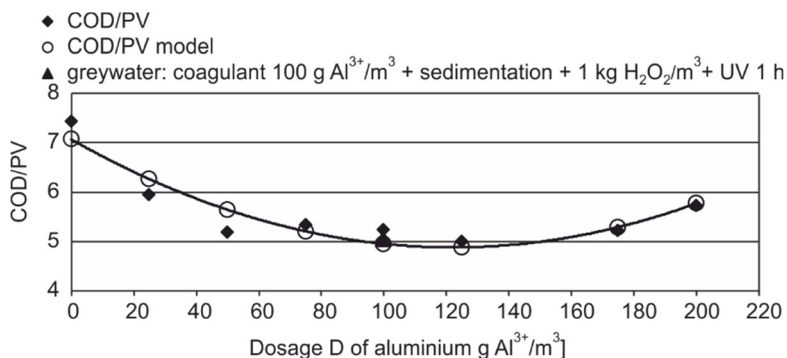


Fig. 5. The COD/PV ratio vs. aluminium doses D during coagulation

In the greywater, the amount of organic compounds poorly oxidized by KMnO_4 but easily oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ increases with a decrease of Al^{3+} doses (below $120 \text{ g Al}^{3+}/\text{m}^3$) resulting in an increase of the COD/PV ratio. Above $120 \text{ g Al}^{3+}/\text{m}^3$, the COD/PV ratio increased again because a part of the organic compounds were poorly oxidized by KMnO_4 but easily oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ and also poorly removed by coagulation (Fig. 5). The ratio is almost equal to the COD/PV ratio for greywater after coagulation only. It means that the amount of organic compounds poorly oxidized by KMnO_4 but easily oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ is similar as in the samples that were not treated with H_2O_2 and UV radiation. Changes in the proportion

of different types of organic matter in greywater after coagulation change similarly as in greywater after the oxidation process.

4.2. OXIDATION OF ORGANIC SUBSTANCES IN THE H₂O₂/UV PROCESS AFTER GREY WATER COAGULATION

The efficiency of the H₂O₂/UV process strongly depends on the concentrations of organic substances in the greywater. Two experiments were carried out using greywater coagulated with 100 g Al³⁺/m³ and a sedimentation time of 0.25 h. In the first experiment, the initial COD was 1151.7 g O₂/m³ and the TOC was 76.0 g C/m³, and after coagulation and sedimentation, the COD decreased to 420.1 g O₂/m³, and the TOC to 59.29 g C/m³. In the second experiment, the initial COD was 401.3 g O₂/m³, and the TOC was 61.52 g C/m³, and after coagulation and sedimentation, the COD decreased to 177.8 g O₂/m³, and the TOC to 32.32 g C/m³.

The H₂O₂/UV oxidation efficiency for the greywater with a high initial COD (420.1 g O₂/m³) and TOC (59.29 g C/m³) was relatively poor. The efficiency of COD and TOC removal varied from 15 to 36%, for the perhydrol concentration range of 0.5–4.0 kg H₂O₂/m³ (Fig. 6); for lower COD (177.8 g O₂/m³) and TOC (32.32 g C/m³), the H₂O₂/UV oxidation was more successful, despite the fact that its effects varied significantly. For the perhydrol dose of 0.5–4.0 kg H₂O₂/m³, the COD and TOC removal changed from 33 up to 98% (Fig. 7).

Table 4

Coagulation and H₂O₂/UV oxidation – process parameters

Sample	Parametr	Experiment 1	Experiment 2
Greywater	COD, g O ₂ /m ³	1151.7	401.3
	TOC, g C/m ³	76.0	61.52
	COD/TOC, g O ₂ /g C (coagulant dose: 12.5–200 g Al ³⁺ /m ³)	7.07±0.62	5.88±0.68
Greywater after coagulation with 100 g Al ³⁺ /m ³	COD, g O ₂ /m ³	420.1	177.8
	TOC, g C/m ³	59.29	32.32
	COD/TOC, g O ₂ /g C (H ₂ O ₂ /UV oxidation at a dose of 0.5–4.0 kg H ₂ O ₂ /m ³)	6.91±0.98	5.75±0.80
	Δ[H ₂ O ₂]/ΔCOD, g H ₂ O ₂ /g O ₂ COD	11.75±5.44	9.56±1.36
	Δ[H ₂ O ₂]/Δ[TOC], g H ₂ O ₂ /g C	74.32±25.37	49.83±10.10
	(Δ[H ₂ O ₂]/Δ[TOC])/(Δ[H ₂ O ₂]/Δ[COD]) = COD/TOC, g O ₂ /g C	6.33	5.21

In the first experiment, the greywater with a high initial COD (1151.7 g O₂/m³) and TOC (76 g C/m³) was analyzed. The average COD/TOC ratio was 7.07±0.62 g O₂ COD/g C during coagulation with the aluminum dose of 12.5–200 g Al³⁺/m³. The average COD/TOC ratio for the H₂O₂/UV oxidation process was 6.91±0.98 g O₂ COD/g C for

the hydrogen peroxide doses of 0.5–4.0 kg H₂O₂/m³; the initial COD and TOC concentrations in the greywater after coagulation with 100 g Al³⁺/m³ were 420.1 g O₂/m³ and 59.29 g/m³, respectively (Fig. 6, Table 4). Just a slight difference between the COD/TOC ratios means that various types of organics are removed with a similar efficiency during coagulation followed by oxidation with hydrogen peroxide.

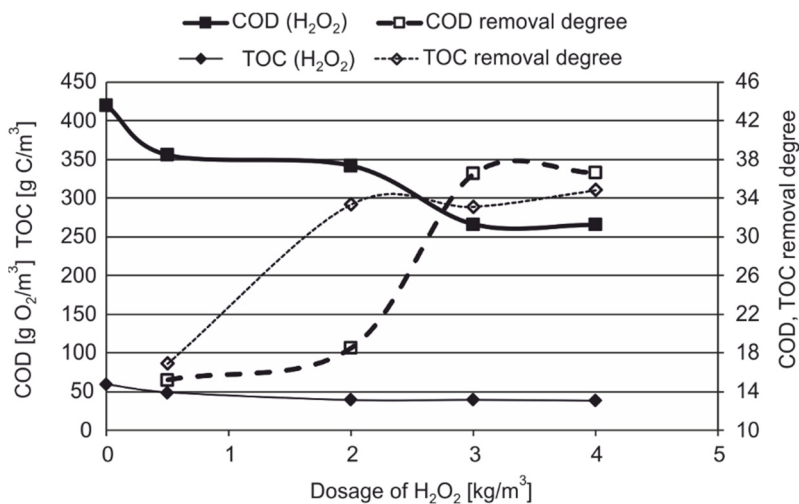


Fig. 6. COD and TOC values as well as COD and TOC removal vs. H₂O₂ doses (experiment 1)

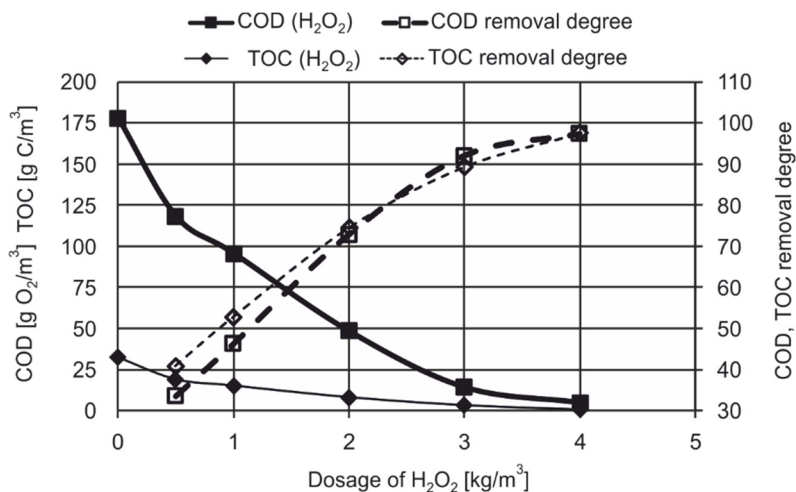


Fig. 7. COD and TOC values as well as COD and TOC removal vs. H₂O₂ doses (experiment 2)

The average consumption of hydrogen peroxide per kg of COD removed was 11.75 ± 5.44 g H₂O₂/g O₂ COD. The average consumption of hydrogen peroxide per kg of TOC removed was 74.32 ± 25.37 g H₂O₂/g C. The average ratio of the above values

(74.32/11.75) results in the COD/TOC ratio of 6.33 g O₂ COD/g C; the value is slightly lower than the one presented in previous calculations (6.91 g O₂ COD/g C) (Table 4) since the arithmetic operations are carried on the average values.

In the second experiment, the greywater with a relatively low COD (401.3 g O₂/m³) and TOC (61.52 g C/m³) was analyzed (Table 4). The average COD/TOC ratio was 5.88±0.68 g O₂ COD/g C for coagulation with the aluminum dose range of 12.5–200 g Al³⁺/m³. The average COD/TOC ratio for the H₂O₂/UV oxidation process was 5.75±0.80 g O₂ COD/g C for the hydrogen peroxide doses of 0.5–4.0 kg H₂O₂/m³; the initial COD and TOC concentrations in the greywater after coagulation with 100 g Al³⁺/m³ were 177.8 g O₂/m³ and 32.32 g C/m³, respectively (Fig. 7, Table 4). Also, in this experiment, the COD/TOC ratios did not vary much, which means that various types of organics are removed with a similar efficiency during coagulation followed by oxidation with hydrogen peroxide.

The average consumption of hydrogen peroxide per kg of COD removed was 9.56 ±1.36 g H₂O₂/g O₂ COD. The average consumption of hydrogen peroxide per kg of removed TOC was 49.83±10.10 g H₂O₂/g C. The average ratio of the above values (49.83/9.56) results in the COD/TOC ratio of 5.21 g O₂ COD/g C; the value is slightly lower than the one presented in previous calculations (5.75 g O₂ COD/g C) (Table 4) since arithmetic operations are carried on the average values.

5. RESULTS AND DISCUSSION

5.1. THE KINETIC MODEL OF OXIDATION WITH HYDROGEN PEROXIDE ADOPTED FOR VERIFICATION

A set of kinetic equations describes a COD decrease resulting from oxidation of organic substances and consumption of hydrogen peroxide H₂O₂ (equivalent to the set (14), (15)):

$$\frac{d[\text{COD}]}{dt} = -k_r[\text{COD}]^\alpha[\text{H}_2\text{O}_2]^\beta \quad (20)$$

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -wk_r[\text{COD}]^\alpha[\text{H}_2\text{O}_2]^\beta \quad (21)$$

where k_r – process rate constant, (kg H₂O₂)^{-β}·(g O₂ COD)^{1-α}·m^{3(α+β-1)}·h⁻¹, α , β – constants, w – coefficient of H₂O₂ consumption per kg of COD removed, kg H₂O₂/g O₂ COD.

The TOC model has a similar formula:

$$\frac{d[\text{TOC}]}{dt} = -k'_r[\text{TOC}]^{\alpha'}[\text{H}_2\text{O}_2]^\beta \quad (22)$$

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -w'k'_r[\text{TOC}]^{\alpha'}[\text{H}_2\text{O}_2]^\beta \quad (23)$$

where k'_r – process rate constant, $(\text{kg H}_2\text{O}_2)^{-\beta} \cdot (\text{g C})^{1-\alpha} \cdot \text{m}^{3(\alpha+\beta-1)} \cdot \text{h}^{-1}$, α' , β' – constants, w' – coefficient of H_2O_2 consumption per kg of TOC removed, $\text{kg H}_2\text{O}_2/\text{g C}$.

Models (20), (21) and (22), (23) do not reflect the pH dependence of the process kinetics. Chin et al. [9] showed that the process kinetics was only slightly pH dependent at a pH range of 3–7 due to a poor dissociation of the H_2O_2 acid and a lower content of HCO_3^- and CO_3^{2-} comparing to that in samples with $\text{pH} > 7.0$. Carbonates and bicarbonates are scavengers of HO^\bullet radicals. The acidic coagulant enhances reduction of carbonates and bicarbonates concentrations by the introduction of chloride ions into the greywater.

Models (20), (21) and (22), (23) were numerically integrated using the Euler method with a step size $\Delta t = 0.002$ h.

5.2. OXIDATION OF ORGANIC SUBSTANCES (COD)

The studies on the oxidation kinetics of organic substances (COD) enabled us to determine the parameters of the model (20), (21) as well as an oxidation rate. The actual COD and H_2O_2 concentrations, as well as the ones calculated from the model (20), (21) are summarized in Table 5.

Parameters of the model (20), (21) were determined by the least-squares method applied for both measured and calculated COD values and measured and calculated H_2O_2 concentrations. The following parameters were calculated:

$$k_r = 24.669 (\text{kg H}_2\text{O}_2)^{-\beta} \cdot (\text{g O}_2 \text{ COD})^{1-\alpha} \cdot \text{m}^{3(\alpha+\beta-1)} \cdot \text{h}^{-1}, \alpha = 0.270, \beta = 0.587,$$

$w = 0.0122 \text{ kg H}_2\text{O}_2/\text{g O}_2$, $\text{COD} = 12.2 \text{ g H}_2\text{O}_2/\text{g O}_2 \text{ COD}$. The coefficient $w = 12.2 \text{ g H}_2\text{O}_2/\text{g O}_2 \text{ COD}$ was close to the experimental one (Table 4).

The average relative errors of the model fit for COD and $[\text{H}_2\text{O}_2]$ were 0.138 and 0.113, respectively (Table 5). The model fit to the experimental data is presented in Figs. 8 and 9; the squared correlation coefficients were high ($R^2 = 0.975$ (COD), $R^2 = 0.9446$ (H_2O_2)) proving a good model fit.

Equation (20) describes the COD removal rates for different COD and H_2O_2 doses making it possible to draw up a contour plan for the rate of COD removal as a function of COD and the doses of H_2O_2 (Fig. 10). The charts allow for quickly estimating the rate of the greywater treatment process depending on the COD values and the H_2O_2 doses. Some significant changes in a COD removal rate and rather small COD changes were observed at $\text{COD} < 50 \text{ g O}_2 \text{ COD}/\text{m}^3$ and $[\text{H}_2\text{O}_2] > 2 \text{ kg H}_2\text{O}_2/\text{m}^3$ (Fig. 10).

Table 5

Data on oxidation kinetics of organic substances (COD)

Time [h]	[COD] [g O ₂ /m ³]		[H ₂ O ₂] [kg H ₂ O ₂ /m ³]		[COD] model [g O ₂ /m ³]	[H ₂ O ₂] model [kg H ₂ O ₂ /m ³]	Relative error		
	initial	final	initial	final			[COD]	[H ₂ O ₂]	
Sample 1, pH = 4.71									
	420.10				441.15		0.0501		
1.00	441.15	356.20	0.50	0.00531	400.65	0.005358	0.125	0.00905	
1.00	441.15	342.32	2.00	0.436	314.06	0.4482	0.0826	0.0280	
1.00	441.15	266.74	3.00	1.222	271.86	0.9330	0.0192	0.236	
1.00	441.15	266.22	4.00	1.721	235.94	1.4946	0.114	0.132	
Sample 2, pH = 7.25									
	177.80				141.73		0.203		
1.00	141.73	118.30	0.5	0.0664	105.14	0.0532	0.111	0.199	
1.00	141.73	95.67	1.00	0.221	80.13	0.248	0.162	0.125	
1.00	141.73	48.44	2.00	0.619	44.88	0.818	0.0734	0.322	
1.00	141.73	14.35	3.00	1.464	20.48	1.521	0.427	0.0390	
1.00	141.73	4.95	4.00	2.016	4.20	2.323	0.151	0.152	
Average relative error							0.138	0.113	

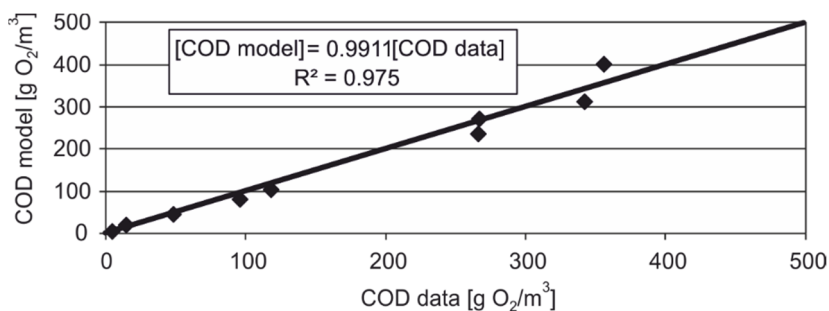


Fig. 8. A model fit for the calculated (COD model) and experimental (COD data) results; model (20), (21)

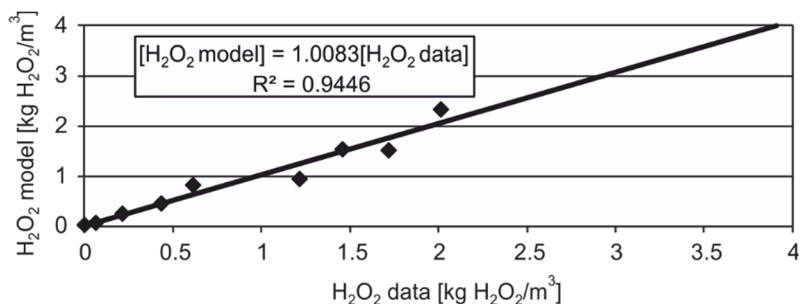


Fig. 9. A model fit for calculated ([H₂O₂] model) and measured ([H₂O₂] data) hydrogen peroxide concentrations; model (20), (21)

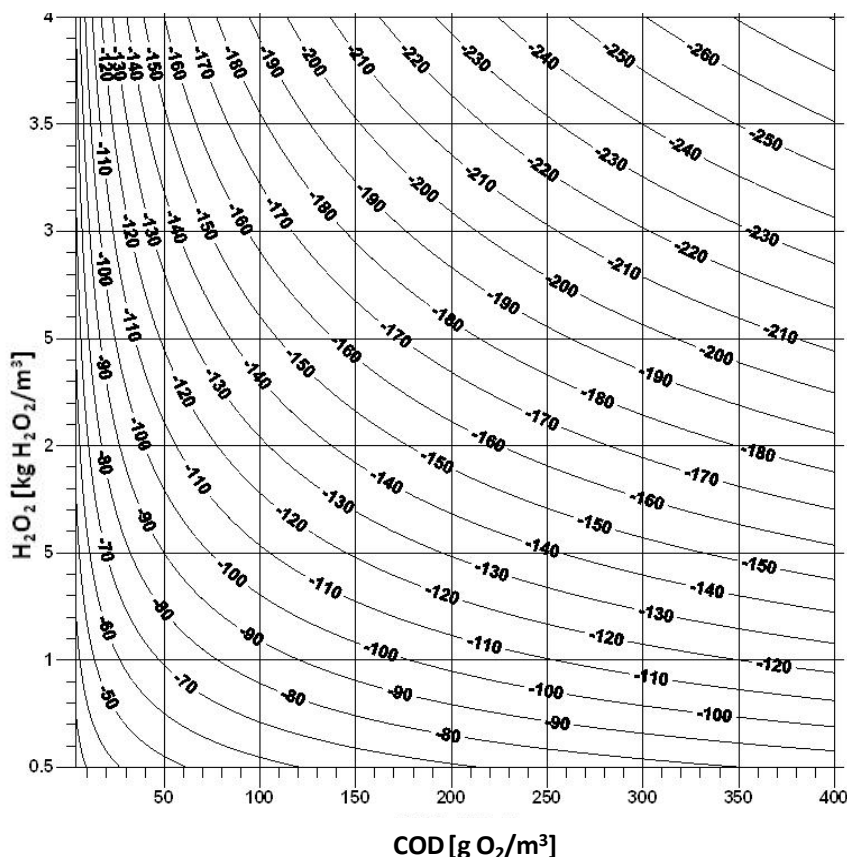


Fig. 10. A contour plan of a COD removal rate [$\text{g O}_2 \text{ COD}/(\text{m}^3 \cdot \text{h})$]

A decrease of COD (due to oxidation of organic substances) and consumption of hydrogen peroxide H_2O_2 was also analyzed with the model (18), (19). The following parameters were calculated:

$$k_r = 31.415 (\text{kg H}_2\text{O}_2)^{-\beta} \cdot (\text{g O}_2 \text{ COD})^{1-\alpha} \cdot \text{m}^{3(\alpha+\beta-1)} \cdot \text{h}^{-1}, \text{ equation (18),}$$

$$k_r = 31.415 (\text{kg H}_2\text{O}_2)^{-(\beta+x_2)} \cdot (\text{g O}_2 \text{ COD})^{1-(\alpha-x_1)} \cdot \text{m}^{3(\alpha-x_1+\beta+x_2-1)} \cdot \text{h}^{-1}, \text{ equation (19),}$$

$$\alpha = 0.328, \beta = 0.324, w = 9.23 \text{ g H}_2\text{O}_2/\text{g O}_2 \text{ COD},$$

$$I = 0.405 \text{ mol O}_2 \text{ COD/mol H}_2\text{O}_2, x_1 = 0.0518, x_2 = 0.270.$$

The average relative errors of model fit for COD and $[\text{H}_2\text{O}_2]$ were 0.0993 and 0.139, respectively, so the model (18), (19) did not prove significantly better than the model (20), (21), hence the model (14), (15) in a general way.

5.3. OXIDATION OF ORGANIC SUBSTANCES (TOC)

The studies on the oxidation kinetics of organic substances (TOC) enabled developing parameters of the model (22), (23) and an oxidation rate. The actual TOC and

H_2O_2 concentrations, as well as the ones calculated with the model (22), (23) are summarized in Table 6.

Table 6

Data on the oxidation kinetics of organic substances (TOC)

Time [h]	[TOC] [g C/m ³]		[H ₂ O ₂] [kg H ₂ O ₂ /m ³]		[TOC] model [g C/m ³]	[H ₂ O ₂] model [kg H ₂ O ₂ /m ³]	Relative error		
	initial	final	initial	final			[TOC]	[H ₂ O ₂]	
Sample 1, pH = 4.71									
	59.29				66.41		0.120		
1.00	66.41	49.25	0.50	0.00531	59.23	0.005521	0.203	0.0398	
1.00	66.41	39.64	2.00	0.436	43.98	0.454	0.110	0.0417	
1.00	66.41	38.63	3.00	1.222	36.64	0.948	0.0515	0.224	
1.00	66.41	38.63	4.00	1.721	30.47	1.523	0.211	0.115	
Sample 2, pH = 7.25									
	32.32				25.68		0.205		
1.00	25.68	19.11	0.50	0.06641	19.10	0.04643	0.000680	0.301	
1.00	25.68	15.27	1.00	0.2205	14.53	0.2317	0.0479	0.0506	
1.00	25.68	8.24	2.00	0.6189	8.11	0.7891	0.0155	0.275	
1.00	25.68	3.44	3.00	1.4636	3.69	1.4855	0.0742	0.0150	
1.00	25.68	0.791	4.00	2.0161	0.7872	2.2862	0.00489	0.134	
Average relative error							0.0949	0.133	

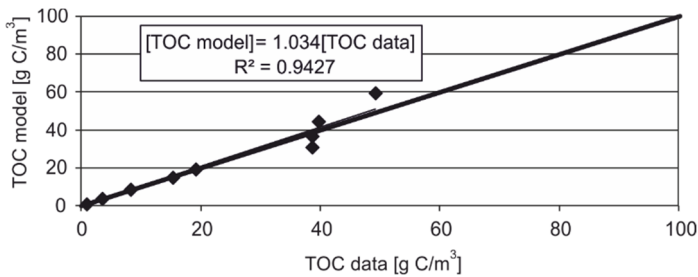


Fig. 11. A model fit for the calculated (TOC model) and experimental (TOC data) results; model (22), (23)

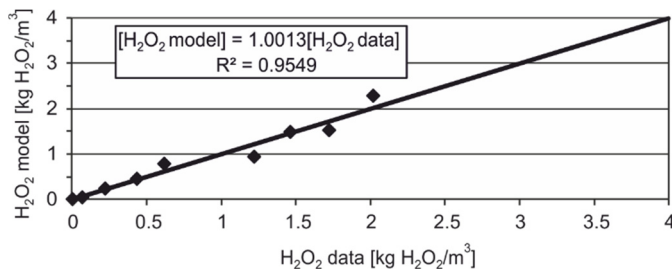


Fig. 12. A model fit for the calculated ([H₂O₂] model) and measured ([H₂O₂] data) hydrogen peroxide concentrations; model (22), (23)

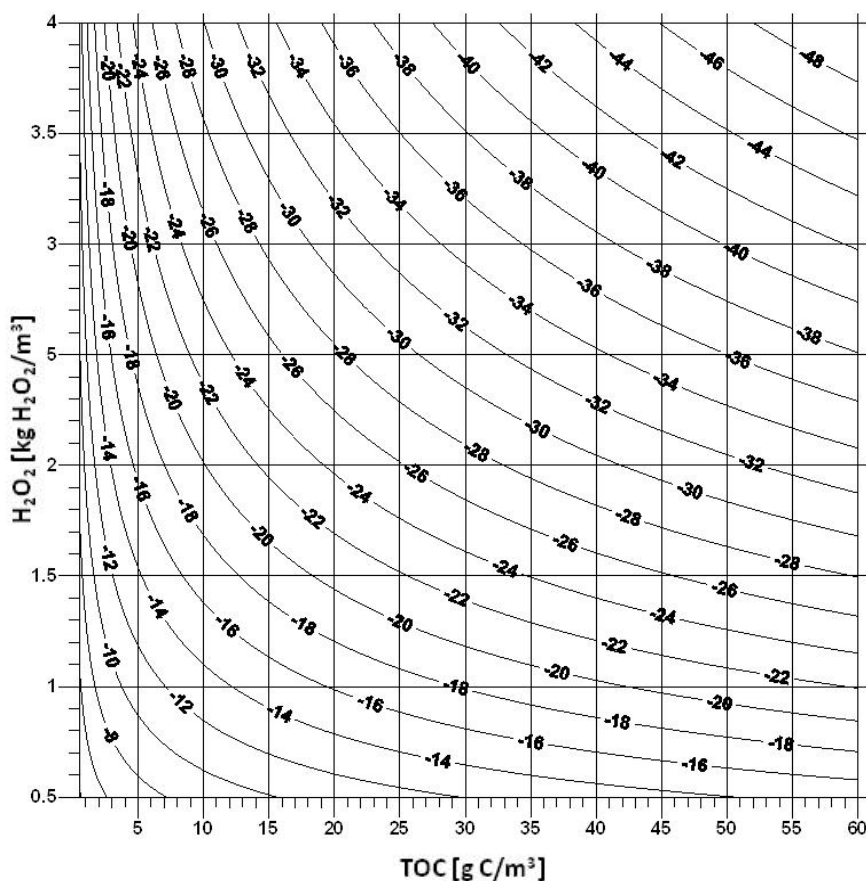


Fig. 13. A contour plan for a TOC removal rate [$\text{g C}/(\text{m}^3 \cdot \text{h})$].

Parameters of the model (22), (23) were determined by the least square method applied for both measured and calculated TOC values and H_2O_2 concentrations. The following parameters were calculated:

$$k'_r = 6.853 (\text{kg H}_2\text{O}_2)^{-\beta'} \cdot (\text{g C})^{1-\alpha'} \cdot \text{m}^{3(\alpha'+\beta'-1)} \cdot \text{h}^{-1}, \alpha' = 0.286, \beta' = 0.589,$$

$w' = 69.0 \text{ g H}_2\text{O}_2/\text{g C}$, the coefficient $w' = 69.0 \text{ g H}_2\text{O}_2/\text{g C}$ was similar to the experimental one (Table 4).

It should be noted that the coefficients α , α' and β , β' are approximately equal in pairs; it suggests that the mechanisms of COD or TOC removal are the same. Exponents α , α' and β , β' are less than one and differ from the value one found in the literature [9, 18]. An overall mechanism of oxidation of organic substances may not follow the first-order mechanism due to a complex and changing composition of greywater.

The average relative error of the model fit for TOC was 0.0949 while for H_2O_2 it was 0.133 (Table 6). The model fit to the experimental data was presented in Figs. 11 and 12; the squared correlation coefficients were high ($R^2 = 0.9427$ (TOC), $R^2 = 0.9549$ (H_2O_2)) proving a good model fit.

Equation (22) describes TOC removal rates for different TOC and H_2O_2 doses. This makes it possible to draw up a contour plan for the rate of TOC removal as a function of TOC and the doses of H_2O_2 (Fig. 13). The charts allow one for simple estimating the rate of the greywater treatment process depending on the TOC values and the H_2O_2 doses. Some significant changes in a TOC removal rate accompanied with small TOC changes were observed at $\text{TOC} < 5 \text{ g C/m}^3$ and $[\text{H}_2\text{O}_2] > 2 \text{ kg H}_2\text{O}_2/\text{m}^3$ (Fig. 13).

5.4. OVERALL EFFICIENCY OF GREYWATER TREATMENT

For raw greywater with $\text{COD } 859 \text{ g O}_2/\text{m}^3$, the coagulation efficiency, based on the model [23], at a dose of about $100 \text{ g Al}^{3+}/\text{m}^3$, was about 62% (the effluent $\text{COD} = 324 \text{ g O}_2/\text{m}^3$). Further treatment, involving oxidation of organic compounds in the $\text{H}_2\text{O}_2/\text{UV}$ process for 1 h, with a dose of hydrogen peroxide $4 \text{ kg H}_2\text{O}_2/\text{m}^3$, enables a decrease of COD by only 58.3% (Table 7). Therefore, the overall efficiency of the greywater treatment process could reach only 84.3%.

Table 7

COD and H_2O_2 concentrations and process efficiencies η calculated from the model (20), (21) for two $[\text{H}_2\text{O}_2]_0$ doses

Time [h]	COD ($[\text{H}_2\text{O}_2]_0$ 3 kg $\text{H}_2\text{O}_2/\text{m}^3$) [g O_2/m^3]	η COD [%]	$[\text{H}_2\text{O}_2]$ [kg $\text{H}_2\text{O}_2/\text{m}^3$]	COD ($[\text{H}_2\text{O}_2]_0$ 4 kg $\text{H}_2\text{O}_2/\text{m}^3$) [g O_2/m^3]	η COD [%]	$[\text{H}_2\text{O}_2]$ [kg $\text{H}_2\text{O}_2/\text{m}^3$]
0	324.0		3.000	324.0		4.000
0.5	230.3	28.9	1.856	212.3	34.5	2.637
1	166.7	48.5	1.080	135.1	58.3	1.694
1.5	125.1	61.4	0.572	83.1	74.4	1.058
2	99.5	69.3	0.258	48.9	84.9	0.641
2.5	85.2	73.7	0.085	27.1	91.6	0.376
3	79.2	75.5	0.011	13.8	95.7	0.213

If further treatment, involving oxidation of organic compounds in the $\text{H}_2\text{O}_2/\text{UV}$ process for 3 h, then based on the model, with a hydrogen peroxide dose of $4 \text{ kg H}_2\text{O}_2/\text{m}^3$, it would be possible to decrease the COD by 95.7% (Table 7). Consequently, global greywater treatment efficiency would be even as much as 98.4%.

Lowering the hydrogen peroxide dose to $3 \text{ kg H}_2\text{O}_2/\text{m}^3$ prevents high purification efficiency from being achieved since after 3 h of the process the oxidant concentration,

calculated on the basis of the model, decreases to a low value of $0.011 \text{ kg H}_2\text{O}_2/\text{m}^3$ – substrate deficit (Table 7).

Oxidation of organic substances in the greywater does not proceed fast. Such observations have been confirmed by other studies [9], which showed that after 3 h of irradiation and the process parameters: initial COD $\approx 200 \text{ g O}_2/\text{m}^3$, initial $[\text{H}_2\text{O}_2] = 0.34 \text{ kg}/\text{m}^3$ and pH 3–7, the COD removal was 80% (the effluent COD was ca. $40 \text{ g O}_2/\text{m}^3$).

The studies described by Arslan-Alaton et al. [4] showed that oxidation of surfactants (dodecyl sulfo succinate, aniline-4-beta-ethyl sulfonyl-2-sulphonic acid) at the initial COD of $450 \text{ g O}_2/\text{m}^3$ required rather high initial concentrations of hydrogen peroxide reaching $1.02\text{--}2.04 \text{ kg H}_2\text{O}_2/\text{m}^3$. Only at such conditions was a high oxidation efficiency possible.

The experiments confirmed that organic substances present in greywater were poorly oxidized in the $\text{H}_2\text{O}_2/\text{UV}$ process due to a high content of natural organic compounds and surfactants and high doses of hydrogen peroxide had to be used.

6. CONCLUSIONS

- In the oxidation process in the $\text{H}_2\text{O}_2/\text{UV}$ system, a variable amount of oxidant consumption per unit mass of the used reducer is observed, depending on the concentration of reagents.
- Higher oxidizer consumption is mainly caused by the decomposition of H_2O_2 by the radicals HO^\bullet and HO_2^\bullet and the O_2^- anion.
- Excess of the reducer in relation to the oxidant increases the consumption of hydroxyl radical and reduces the synthesis of oxygen necessary for the oxidation of the reducer.
- Lower pH values observed after coagulation of the greywater with polyaluminium chloride had a positive effect on oxidation with hydrogen peroxide.
- The overall mechanism of oxidation of organic substances had an order of less than one.
- Consumption of hydrogen peroxide during oxidation of organic compounds in greywater was for COD: $w = 12.2 \text{ g H}_2\text{O}_2/\text{g O}_2 \text{ COD}$ and for TOC $w' = 69.0 \text{ g H}_2\text{O}_2/\text{g C}$.
- Only long UV radiation times, even up to 3 h and a large excess of oxidant compared to the COD, assure oxidation of organic substances with hydrogen peroxide at high efficiency.
- For the average greywater COD of $112 \text{ g O}_2/\text{m}^3$ (initial COD = $324 \text{ g O}_2/\text{m}^3$), the average hydrogen peroxide concentration of $1.4 \text{ kg H}_2\text{O}_2/\text{m}^3$ (initial concentration of $4.0 \text{ kg H}_2\text{O}_2/\text{m}^3$) and the oxidation time of 3 h, the average COD removal rate was ca. $107 \text{ g O}_2 \text{ COD}/(\text{m}^3 \cdot \text{h})$ while the average hydrogen peroxide disappearance rate was $1.3 \text{ kg H}_2\text{O}_2/(\text{m}^3 \cdot \text{h})$.
- Combining coagulation with H_2O_2 oxidation and UV radiation it is possible to reduce the greywater COD even by up to 98.4%.

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