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Combination of Fenton and Biological Oxidation for Treatment of Heavily Polluted Fermentation Waste Broth

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Abstract

The aim of our work was to study the biotreatability of heavily polluted pharmaceutical fermentation broth (COD value of 124,500 mg·L^{-1}) as well as application of Fenton oxidation for effective pretreatment. Because waste broth expressed biodegradability (BOD_5/COD ratio was 0.40), biological treatment was the first choice. At the same time, in preliminary ready biodegradability assessment test, diluted broth degraded 65% as well it was not toxic to mixed bacterial culture of activated sludge. Further experiments in pilot laboratory biological treatment plant confirm acceptable treatment efficiency up to 0.01 vol% of the broth added (76%). However, we had considered additional pretreatment method to be able to enhance biotreatability. Fenton procedure was optimised in batch reactor using different concentrations of Fe^{2+}, H_2O_2, temperatures (40/45 °C), as well as different retention times (up to 30 minutes). The highest treatment efficiency reached only 44% according to COD, but ready biodegradability of the sample increased (82%). Fenton oxidation was confirmed as possible method for pretreatment of broth, because it slightly enhanced biodegradability, it reduced organic pollution and formed products were non-toxic. We have focused our future work into a study on optimisation of applied procedure for improving biotreatability of the investigated broth.

Key words: biodegradability, biological treatment, pharmaceutical waste broth, Fenton oxidation, toxicity

Introduction

Up-to-date approach to management of the wastewaters is mainly based on quantity minimisation as well as "*in-situ*" pollution prevention. In spite of use of available BATs (Best Available Technologies), generation of wastewaters in industrial processes is sometimes unavoidable and in most cases a process to reduce the organic load and other contaminants must be employed before water discharge.[1] To remove majority of the organic load, biological processes are usually used, because they are more economic then chemical ones. At the same time, they are environmental friendly, using optimised natural pathways to actually destroy pollution not only transform it into another form.[2] In some cases, however, due to the high organic load, toxicity, or presence of persistent compounds, biological treatment is not feasible. In such a case, chemical pretreatment is usually investigated, because it can adequately increase biodegradability and remove toxicity of the wastewater prior to biological treatment.[3,4]

Advanced oxidation processes have been often used to reduce organic load or toxicity of different wastewaters, recently.[5,6] They are defined as oxidation processes, which generate hydroxyl free radicals with a high electrochemical oxidant potential (2.8 V vs. normal hydrogen electrode) in sufficient quantity to affect water constituents. They could be formed using classical oxidants (hydrogen peroxide, ozone, Etc.) and UV radiation or catalyst.[7,8] Hydroxyl radicals than react with organics and broke them down gradually into smaller fragments with higher biodegradation potential. Sometimes organics are even completely degraded mainly into CO_2 and water. One common feature of such systems is high demand on electrical energy for devices such as ozonizers, UV lamps, ultrasounds and this result in higher treatment costs. The only exception is Fenton process, where under acidic conditions, a Fe^{2+}/H_2O_2 mixture produces hydroxide radicals in a very cost-effective manner (Reaction 1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$
$$k = 76.5\ mol^{-1}s^{-1}$$

Formed Fe(III) can react with H_2O_2 in the so-called Fenton-like reactions (Reactions 2–4) regenerating Fe^{2+} and thus supporting the Fenton process:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \qquad (2)$$
$$k = 2 \times 10^{-3}\ mol^{-1}s^{-1}$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad (3)$$

$$Fe^{3+} + R\bullet \rightarrow Fe^{2+} + R^+ \quad (4)$$

Several studies have demonstrated, that the best oxidation efficiency is achieved when neither H_2O_2 nor Fe^{2+} is overdosed, so that the maximum amount of OH• radicals is available for the oxidation of organics.[9] Many authors suggested Fe^{2+} to H_2O_2 mass ratio to be optimal at 1 to 10, but it must be optimised for particular wastewater to minimize scavenging effects.[9] For pharmaceutical wastewaters usually Fe^{2+}/H_2O_2 mass ratio from 1/2 to 1/10 is found to be the most effective one.[5]

The Fenton reaction has a short reaction time among all advanced oxidation processes and it has other important advantages. Iron and H_2O_2 are cheap and non-toxic, there is no mass transfer limitations due to its homogenous catalytic nature, there is no energy involved as catalyst and the process is easily to run and control. It has been widely used for treatment of highly polluted textile and paper mill wastewaters, as well as pharmaceutical wastewaters.[5,6,9]

Substantial quantities of pharmaceuticals are used in human and veterinary medicine. They are often not metabolised by the body after administration. Depending upon their excretion rate, they are released into the effluent and reach sewage treatment plant. If they are not degraded, they could enter the environment, where little is known about their fate and effects. They usually have two characteristics, which declare them as environmental hostile: they are stable and biologically effective.[10] For these reasons optimisation of production processes and effective end-of pipe treatment is necessary to avoid broad contamination of receiving environment due to the pharmaceutical industry.

The aim of our work was to study the biotreatability of heavily polluted pharmaceutical fermentation broth as well as application of Fenton oxidation for effective pretreatment.

Materials and Methods

Wastewater

The same sample of the waste fermentation broth was used for all of the experiments. It was produced in the pharmaceutical factory, during biosynthesis of active substances for human medicine. Remained broth was random grab sampled from the effluent of the reactor and it is afterwards mixed (0.7 vol%) with other wastewaters from the factory. Formed effluent is then released into sewerage system leading to municipal wastewater treatment plant. Due to this dilution the highest expected volumetric load of the investigated fermentation broth in biological treatment plant is 0.042 vol%.

Physico-chemical analysis of the wastewater

pH, BOD_5[11] (Biochemical Oxygen Demand), COD[12] (Chemical Oxygen Demand), DOC (Dissolved Organic Carbon), IC[13] (Inorganic Carbon) (Shimadzu TOC 5000A Analyser, 1998), nitrogen as Kljeldahl nitrogen[14], ammonium nitrogen[15] (Kjeltec Auto Analyser FOSS Tecator, 1998), NO_2^--N and NO_3^--N and PO_4^{3-}-P[16] (DIONEX 120, 2000) were determined in fresh raw sample of the broth prior to toxicity and biodegradability testing, as well as treatment experiments. The same parameters were also determined in the influent and effluent of the pilot laboratory wastewater treatment plant. COD[12] measurements were used to determine removal efficiency of organics during chemical oxidation in Fenton process.

Toxicity testing

Raw broth toxicity was determined using two different toxicity tests. We determined the inhibition of oxygen consumption by activated sludge, using low (100 $mg_{VSS}\cdot L^{-1}$) concentration of the inoculum – activated sludge.[17] Addition of toxic concentration of the wastewater (as 5, 10 and 50 vol%) results in a decrease in the oxygen consumption rate. Oxygen concentration was followed up to 180 minutes at 20±1 °C. The percentage inhibition of the oxygen consumption was estimated by comparison of oxygen consumption rate ($mg\cdot L^{-1}\cdot min^{-1}$) in the test mixture with a control containing no test material. Finally percentage of inhibition was plotted versus logarithm of wastewaters' concentration (vol%) to determine EC (Effective Concentration) values.

Above mentioned toxicity test was accomplished using non-adapted inoculum. Its source was laboratory treatment plant with 8.3 L of aeration basin, sludge retention time was 9–11 days, and hydraulic retention time was 6–7 hours. The plant was fed with synthetic municipal wastewater, constituted of 130 $mg\cdot L^{-1}$ of peptone, 0.9 $mg\cdot L^{-1}$ of P as KH_2PO_4, 70 vol% of distilled water and 30 vol% of domestic sewage. The same activated sludge was also used in biodegradability assessment test.

We performed additional acute toxicity test on raw fermentation broth with freeze-dried luminiscent bacteria *Vibrio fischeri* (DR. LANGE LUMIStox, 2001).[18] It was also used for monitoring changes in toxicity of the sample during biological and chemical treatment.

Biodegradability testing

Biodegradability of the sample was determined by applying standardized method where oxygen consumption during biodegradation of diluted raw broth has been measured.[19] The same method was also used for checking biodegradability of the effluent from pilot biological treatment plant, as well as after Fenton oxidation experiment.

Initial concentration of the raw broth in biodegradability test (0.1 vol%) was chosen on the basis of toxicity test with measurement of inhibition of oxygen consumption. Biodegradability assessment tests with effluent from biological pilot plant as well as chemically treated broth were performed with non-diluted samples.

Experiments were conducted in a closed respirometer Micro Oxymax, Columbus Instruments, USA, 1996. As inoculum non-adapted activated sludge from a laboratory wastewater treatment plant was used. Its concentration in measuring chamber was 30 $mg_{VSS}·L^{-1}$. Temperature was maintained at 20±1 °C. All tests were run in 250 mL duplicates. Nitrification of the sample was prevented by addition of 4 $ml·L^{-1}$ of alilthiourea (1 $g·L^{-1}$). Abiotic degradation of wastewater was evaluated under the same conditions simultaneously without inoculation. Biodegradation curves were plotted as % of degradation versus time to read out lag phase (time in days to reach 10% degradation) and maximal level of biodegradation (D_m, %) and to calculate the rate of biodegradation as rate constant k_1 (day^{-1}).[20] We simplify the calculations neglecting changes in biomass yield and data fit the first order kinetics. In Equation 1, c corresponds to the concentration of the substance ($mg·L^{-1}$), which in our case was expressed as oxygen consumption in particular time interval t (Day). In fact, we have many organics degrading according to different rates with overall (pseudo)first order kinetics.[21]

$$-\frac{dc}{dt} = k_1 c \qquad \text{eq (1)}$$

$$\ln\left[1-\frac{D_t}{100}\right] = -k_1 t \qquad \text{eq (2)}$$

For calculation of rate constants, Equation 1 was modified to Equation 2, to enable direct calculation of degradation rate constants (k_1, day^{-1} or min^{-1}) from degradation levels (Dt, %).[22]

Biological pilot treatment plant

Biological treatment of the diluted fermentation broth was run out in laboratory aerobic wastewater treatment plant. Aeration basin of the unit had a volume of 8.3 L and the volume of the secondary clarifier was 2.2 L. The start-up influent was synthetic municipal wastewater as described for the unit, used for cultivation of inoculum for toxicity test. 4 days after, 0.01 vol% of the broth was added and operation of the plant was followed for 19 days. Then the broth load was increased to 0.02 vol%, causing intensive sludge bulking within 2 days. The treatment unit collapsed due to the washout of the activated sludge.

Table 1. Process parameters during the start-up procedure and during plant operation.

Process parameters	Start-up	Operation
Influent flow ($L·day^{-1}$)	22.0 (±2.0)	27.3 (±1.3)
Sample concentration in the influent (vol%)	/	0.01
Hydraulic retention time (h)	9.0 (±0.7)	7.3 (±0.3)
Sludge volume index ($mL·g^{-1}$)	88 (±13)	70 (±9)
$COD_{influent}$ ($mg·L^{-1}$)	130 (±12)	190 (±5)
Sludge concentration ($g_{VSS}·L^{-1}$)	3.2	3.5 (±0.3)
Biomass loading rate ($g_{COD}·g_{VSS}^{-1}·day^{-1}$)	0.10 (±0.03)	0.18 (±0.02)
Volumetric loading rate ($g_{COD}·L^{-1}·day^{-1}$)	0.34 (±0.07)	0.63 (±0.04)

/…No sample was added.

Start-up and operational parameters for the wastewater treatment plant are presented in Table 1. Temperature of the system was maintained constant (20±2 °C), diffused aeration assured at least 2 $mg·L^{-1}$ of dissolved oxygen. DOC, IC and temperature of the system were checked daily, while COD, BOD_5, pH, sludge volume index and concentration of activated sludge were monitored periodically during 19 days of the experiment. Toxicity of the influent and effluent was determined once during the experiment.

Fenton oxidation experiments

Experiments were performed using 500-times diluted broth sample (0.2 vol%). Wastewater samples were filtered through black ribbon to remove solids and pH was adjusted to 4.0 (±0.2) before chemical oxidation experiments. A 150 mL sample was placed into 500 mL Erlenmayer flask, which was submerged in a temperature controlled water bath to attain desired constant temperature (40/45 °C). $FeSO_4$, p.a. was added to attain selected Fe^{2+} concentrations (0.2/0.3/0.4 M). Finally, Fenton reaction was started with addition of H_2O_2 (30% w/v, p.a.) to achieve concentrations 2.0/2.5/3.0/3.5 M. The reaction is fast and exothermic: initial temperature was among 40 and 45 °C, so we conducted our experiments at 40 and 45 °C. The aqueous solution of Fenton reagent and diluted broth was stirred during the reaction period up to 35 minutes. Samples were redrawn at 5, 10, 20 and 30 minutes and COD was determined immediately. Prior to COD analysis 1M NaOH was added to stop the oxidation at pH = 12 (±0.2). To eliminate the excess H_2O_2, the sample was boiled for 10 minutes and then allowed to cool to room temperature. It has been filtered afterwards to remove the formed ferric hydroxide and COD was determined.

Results and Discussion

Characterization of fermentation broth

Main physico-chemical characteristics of the raw sample are presented in Table 2. The value of soluble COD (124,500 mg·L^{-1}) was extremely high, but BOD_5/COD ratio was not too low (0.40) to achieve good biological treatment under appropriate conditions.

At the same time, sample appeared to be not very toxic. It was not toxic to mixed culture of activated sludge according to measurement of inhibition of oxygen consumption up to 50 vol%, while 30minEC_{20}, based on bioluminescence inhibition was 0.48 vol% and 30minEC_{50} was 1.11 vol%. Wastewater should not inhibit microorganisms at concentrations applied in biodegradability assessment test or in pilot treatment plant (0.1/0.01/0.02 vol%).

Table 2. Physico-chemical analysis of the raw pharmaceutical broth.

Parameter	Value
pH	6.9 (±0.1)
COD (mg·L^{-1})	124,500 (±11,200)
DOC (mg·L^{-1})	40,200 (±500)
IC (mg·L^{-1})	400 (±8)
BOD_5 (mg·L^{-1})	49,400 (±2,700)
N-organic (mg·L^{-1})	3,200 (±800)
N-NH_4^+ (mg·L^{-1})	245 (±66)
N-NO_3^- (mg·L^{-1})	27 (±1)
P-PO_4^{3-} (mg·L^{-1})	141 (±78)
Cl^- (mg·L^{-1})	51 (±2)

Results of the ready biodegradability assessment test are presented in Figure 1.

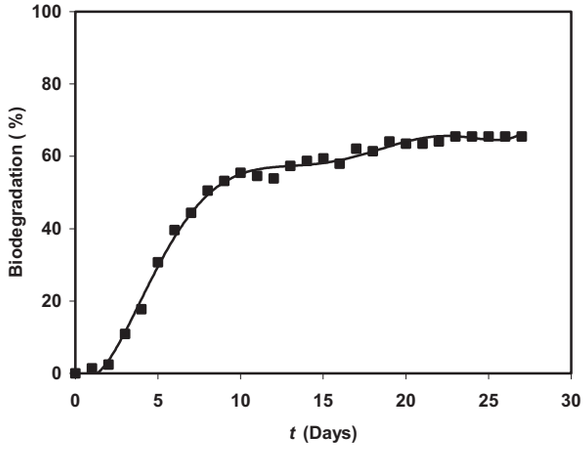

Figure 1. Biodegradation of diluted raw fermentation broth (0.1 vol%) in ready biodegradability assessment test.

Initial COD of the sample was 125 mg·L^{-1}. Wastewater degraded 65%, what was higher than expected on the basis of BOD_5/COD ratio (40%) due to the better conditions and longer incubation period. It also degraded rapidly, k_1 = 0.12 day^{-1} (r^2 = 0.98), lag phase was 3 days. Abiotic elimination reached 2% (± 2%) and it was neglected. We predicted good biotreatability of the diluted broth in biological pilot treatment plant. Reference compound sodium acetate degraded 65% in 14 days confirming validity of the biodegradability assessment test.

Biological treatment of fermentation broth

The aerobic biological pilot plant was running for 24 days. We allowed 3 days for starting-up, then 0.01 vol% of the wastewater has been added for the next 19 days to achieve constant operational parameters. Then 0.02 vol% of the wastewater was added, resulting in immediate increase of SVI (990 mL·L^{-1}) and washout of activated sludge. After 2 days sludge concentration dropped to 0.5 g·L^{-1} and experiment has been terminated.

Average DOC, IC and COD values during the constant operation of the treatment unit are presented for the influent and the effluent in Table 3. Average treatment efficiency according to COD was 82% and 76% according to DOC. Degradation rate constants based on COD measurements were 5.63 day^{-1} and 4.69 day^{-1} according to DOC measurements (Equation 2), respectively. They were much higher as measured in ready biodegradability assessment test (0.12 day^{-1}). Reduction of inorganic carbon (IC) indicated nitrification of the nitrogen components, what has also been confirmed by nitrogen mass balance (Table 4).

Table 3. Average COD, DOC and IC values of the influent (0.01 vol% of the sample) and the effluent of the pilot biological treatment plant during constant operation period (19 days).

Parameter	Value	
	Influent	Effluent
COD (mg·L^{-1})	190 (±5)	34 (±6)
DOC (mg·L^{-1})	95.1 (±13.6)	22.4 (±5.4)
IC (mg·L^{-1})	69.6 (±14.3)	23.9 (±5.9)

DOC removal in % versus time is presented in Figure 2. DOC removal showed slight decrease from initial 86% to final 74%, indicating minor impact of the wastewater to the activated sludge system. In spite of the fact, that raw fermentation broth was non-toxic to *Vibrio fischeri* up to 0.48 vol% (30minEC_{20}), diluted broth (0.01 vol%) at the influent of the pilot plant expressed high toxicity: 30minEC_{20} was 0.86 vol% and 30minEC_{50} was 4.43 vol%. Increased toxicity was probably a consequence of synergistic effect among the sample and dilution medium (municipal sewage and nutrient solution).

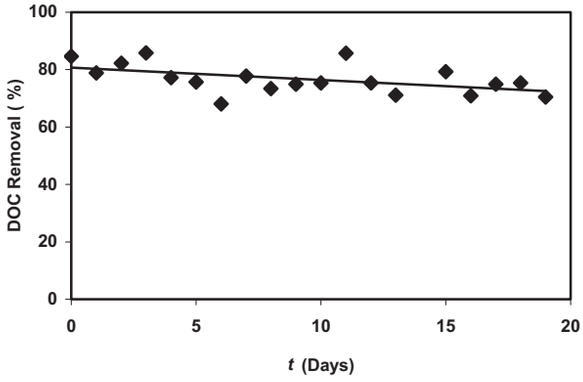

Figure 2. Treatment efficiency according to DOC removal of diluted sample (0.01 vol%) in biological pilot treatment plant.

This could be one of the reasons for decreasing treatment performance of the unit. After biological treatment, wastewater effluent had no toxic impact to luminiscent bacteria.

Table 4. Concentration of nitrogen components in the influent and effluent of biological pilot plant during constant operation (19 days).

Parameter	Influent	Effluent
N-organic ($mg \cdot L^{-1}$)	(±4.5)	0.1
N-NH_4^+ ($mg \cdot L^{-1}$)	52.0 (±19.4)	1.5
N-NO_2^- ($mg \cdot L^{-1}$)	/	1.0
N-NO_3^- ($mg \cdot L^{-1}$)	1.8 (±0.2)	36.1

/…Analysis was not accomplished.

Concentration of organic and ammonium nitrogen decreased (99%/97%) during biological treatment, while concentration of nitrate N increased significantly, confirming nitrification processes.

Chemical treatment of fermentation broth

COD removal rate in Fenton oxidation experiments under different conditions is presented in Figure 3 (the first set of experiments) and Figure 4 (the second set of experiments). In all the cases more than 90% of final COD removal was achieved in first 10 minutes of reaction, what has also been reported by other authors.[5] That is important for the pretreatment of an industrial wastewater, because it can be accomplished quickly without a need for large treatment reactors. Degradation rate constants (Equation 2) were comparable in the first set of four experiments, where Fe^{2+} and peroxide concentrations were varied in the mass ratio Fe^2/H_2O_2 from 1/5 to 1/6. This range has been selected for our investigation on the basis of literature data for comparable pharmaceutical broth.[5] k_1 varied from 0.019 to 0.030 min^{-1} and they were not depended upon concentrations of H_2O_2 or Fe^{2+} and their mass ratio.

As could be seen from Figure 3, the highest COD removal efficiency (as COD removal in %) in the first set of experiments was achieved after the highest addition of reagents (0.4 M Fe^{2+} and 3.5 M H_2O_2, with mass ratio Fe^{2+}/H_2O_2 was 1/5): 26%. It was only 2% higher than in oxidation experiment with 0.3 M Fe^{2+} and 3.0 M H_2O_2 (mass ratio Fe^{2+}/H_2O_2 was 1/6), so we assumed that higher concentrations of both reagents would not improve treatment efficiency enough to be economically acceptable. Selected Fe^{2+}/H_2O_2 mass ratios (1/5 or 1/6) seemed to be not effective enough for tested fermentation broth. At the same time, addition of hydrogen peroxide could not be increased over 3.5 M due to a violent reaction with a quick boiling of the sample. Water bath was unable to maintain required temperature and the system overheated up to 65 °C. Although some different strategies to add the hydrogen peroxide carefully were tested, no reliable results could be obtained from these experiments. This experiment, although not conducted under controlled circumstances, confirmed low impact of the temperature to oxidation of the sample. Temperature showed no positive effect on the final COD removal efficiency (18% COD removal at 45 °C in comparable experiments with 2 M and 2.5 M H_2O_2 at 40 °C), but the reaction rate was the highest at 45 °C: $k_1 = 0.030\ min^{-1}$ (Equation 2).

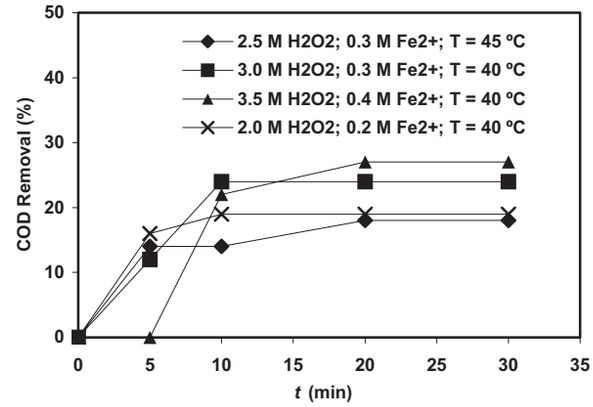

Figure 3. Treatment efficiency according to COD removal of diluted sample (0.2 vol%) in Fenton oxidation experiments (the first set of experiments).

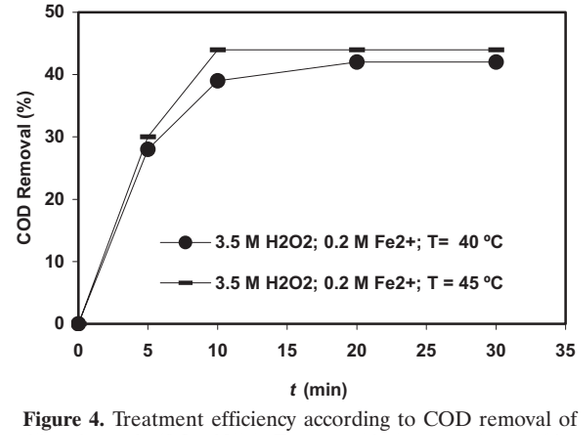

Figure 4. Treatment efficiency according to COD removal of diluted sample (0.2 vol%) in Fenton oxidation experiments (the second set of experiments).

The second set of experiments was conducted at the mass ratio Fe^{2+}/H_2O_2 of 1/11 at the same temperatures: 40 and 45 °C (Figure 4). Final levels of degradation were comparable (42%/44%) and much higher than in the first set of experiments (Figure 3). Degradation rate constants k_1 were also higher (0.049 min^{-1} at 40 °C and 0.058 at 45 °C), confirming impact of the temperature on the reaction rate but not to final removal rate. Due to the fast oxidation of the sample (final DOC removal was achieved practically within the first 10 minutes of experiments), we assumed that reaction at higher temperature is unnecessary and economically unacceptable.

We investigated the sample, which has showed the highest, 44% COD removal efficiency (0.2 M Fe^{2+} and 3.5 M H_2O_2; Fe^{2+}/H_2O_2 mass ratio was 1/11, Figure 4), determining its toxicity to *Vibrio fischeri* as well as its biodegradability. After chemical treatment diluted broth (0.2 vol%) was not toxic to luminiscent bacteria, as raw broth was non-toxic prior to chemical oxidation. At the same time, Fenton process enhanced biodegradability of the sample. Its maximal level of biodegradation reached 82% (65% in the case of untreated broth) and it also degraded more rapidly (k_1 = 0.17 day^{-1}) in comparison with untreated broth (k_1 = 0.12 day^{-1}), with negligible abiotic elimination.

Conclusions

A study on selection of appropriate treatment techniques of complex fermentation pharmaceutical broth has been conducted. Fermentation broth was highly polluted (COD value of 124,500 $mg \cdot L^{-1}$), with BOD_5/COD ratio 0.4. Biological treatment was the first choice for broth treatment due to its cost-effectiveness and environmental acceptability. At the same time, in preliminary ready biodegradability assessment test, diluted broth degraded 65% as well it was not toxic to mixed bacterial culture of activated sludge. Effectiveness of biological treatment was studied in pilot plant, where satisfactory average 76% of COD removal was obtained, as well as effective nitrification up to 0.01 vol% of broth in municipal wastewater. At higher broth load (0.02 vol%) pilot plant has collapsed due to the washout of bulked activated sludge. Additional pretreatment using Fenton oxidation has been considered to enhance biotreatability. Fenton process has been optimised using different concentrations of Fe^{2+} and H_2O_2. The highest removal of organics reached 44% (0.2 M Fe^{2+} and 3.5 M H_2O_2 at 40 °C). Broth toxicity was not affected at investigated conditions, while increased biodegradability of the diluted broth up to 82% has been detected. A further investigation will be focused on biological treatment of the produced pretreated broth to design a complete treatment for the waste broth under study.

Acknowledgements

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Povzetek

Namen našega dela je bil preučiti možnost biološkega čiščenja fermentacijske odpadne brozge in ugotoviti smiselnost uporabe Fentonovega oksidacijskega procesa kot ene izmed možnosti (pred)čiščenja te močno obremenjene brozge. Odpadno farmacevtsko brozgo smo najprej želeli čistiti v biološki čistilni napravi, saj je bila kljub visoki obremenitvi z organskim onesnaženjem (KPK = 124.500 $mg \cdot L^{-1}$), dobro biološko razgradljiva. V izbirnem testu za določanje lahke biorazgradljivosti se je znatno razredčena odpadna brozga razgradila 65%, obenem pa tudi ni bila znatno strupena niti na mikroorganizme aktivnega blata niti ne na luminiscenčne bakterije *Vibrio fischeri*. Simulacija biološkega čiščenja odpadne fermentacijske brozge v pilotni biološki čistilni napravi je bila uspešna le pri nizkih obremenitvah reaktorja z odpadno brozgo (0,01 vol%, 76% čiščenje glede na DOC), medtem ko se je pri višjih obremenitvah sistem porušil zaradi izplavljanja napihnjenega aktivnega blata. Zato smo surovo odpadno brozgo obdelali po Fentonovem postopku v šaržnem reaktorju. Postopek smo optimirali z različnimi koncentracijami Fe^{2+} soli, vodikovega peroksida, pri različnih temperaturah (40 in 45 °C) ter zadrževalnih časih (do 30 min). Dosegli smo 44% učinek čiščenja glede na KPK, obenem pa se je povečala lahka biorazgradljivost tako obdelane fermentacijske brozge. Fentonova oksidacija preiskovane brozge se je izkazala kot dovolj učinkovita metoda (pred)čiščenja, zato smo nadaljnje raziskave usmerili v študij sposobnosti biološkega čiščenja tako obdelane fermentacijske brozge.