Electrochemically Enhanced Fenton's Reaction

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Fenton reaction is often used for the treatment of industrial wastewaters polluted by a toxic and difficult to remove compounds where other methods as emulsion breaking chemical precipitation, or advanced chemical processes fail. To this category belong phenols, polychlorinated aromatic hydrocarbons, amines, mercaptans, and stable chemical complexes containing heavy metals at different concentrations and sometimes even radioactive isotopes. These wastewaters can cause severe damage to the environment, so their removal has a high priority. The principle of Fenton's reaction is based on radical oxidation of the difficult to remove compounds realised by the application of oxidising reagent catalysed by the addition of metallic cations as an oxidant is frequently used hydrogen peroxide, ozone, or chloride lime which allows production of the hydroxyl radicals. As a catalyst, Cu^+, Ti^{3+} or Cr^{2+} can be successfully employed, but most commonly, Fe^{2+} cations are used.

The contribution of this paper is an adding of Fe^{2+} ions by dissolution of the electrodes. The advantage of this method consists of indirect adding of Fe^{+2} from solid phase which eliminates the need of dosing of the Fe in the form of the solution ($FeSO_4$, $FeCl_2$, $FeCl_3$, $Fe_2(SO_4)_3$ …) causing secondary pollution and an increase of salinity. This technology avoids unnecessary salts addition essential in cases, with problems of high salinity of the wastewater. To realise this process in the industrial scale, profound knowledge of the electrocoagulation and/or electroflotation is indispensable, especially for scale-up. This paper brings knowledge about the electrochemical background and technological approach for successful design for required volume flow. Based on our results, some details of suitable reactor types and its scale-up is presented in brief overview revealing suitability for selected cases.

1. Introduction

The objective of this paper was to provide an overview of wastewater treatment based on Fenton's reaction for engineering application in pilot-scale or full-scale.

Methods based on the Fenton's principle belong to the advanced oxidation processes (AOPs) group, methods which generate hydroxyl radicals. These can be created by chemical reactions, electrochemically or UV radiation. AOP methods are broadly examined, but in most of the cases, they are performed just in laboratory scale in beakers, just a minimal number in a larger scale (Poza-Nogueiras V. et al., 2018). They are an excellent choice as a preliminary treatment before biological treatment, which would fail because of toxic matter (Vorontsov, A.V., 2018).

Electro-Fenton's processes can be distinguished into four categories depending on the origin of the Fenton's reagents. First one is defined by the generation of both reagents electrochemically from the reactions at the electrode's surfaces. Another option is employing a sacrificial electrode as the source of iron ions while hydrogen peroxide is dosed externally. The third category contains externally dosed catalyst and hydrogen peroxide generated by oxygen sparging cathode. Last defined option uses the electrochemical cell for production of the hydroxyl radicals and cathodic reduction for regeneration of iron ions (Gümüs D., Akbal F., 2016).

Following selected reactions occurs within electro-Fenton's reaction process of the second type (Kubo D., Kawase Y., 2018):

Evolution of ferrous ion from the iron anode

$$Fe \rightarrow Fe^{2+} + 2e^-$$ (1)
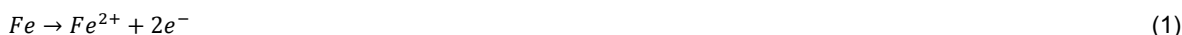
Fenton's reaction in acidic solution

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$$ (2)

Fenton-like reaction – decomposition of H_2O_2

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$ (3)

oxidation of Fe2+ to Fe3+ under acidic conditions

$$Fe^{2+} + O_2 + 4H^+ \rightarrow Fe^{3+} + 2H_2O$$ (4)

generation of O_2 at the anode

$$2H_2O \rightarrow O2 + 4H^+ + 4e^-$$ (5)

generation of H_2 at the cathode

$$2H^+ + 2e^- \rightarrow H_2.$$ (6)

Even though Fenton's reaction is well-known for more than one hundred years, the exact processes of the creation of $HO^{\bullet}$ radicals were not exactly described (Vorontsov, A.V., 2018). Nevertheless, the fundamental equation, for control of the whole process can be presented. Faraday's law validity was verified experimentally with the real wastewaters.

$$m = \frac{M}{z \cdot F} \cdot I \cdot t$$ (7)

Where: m – weight of dissolved metal [g]; I – electric current [A]; t – electrolyzing time [s]; M – molecular weight of metal [g/mol]; z – number of electrons exchanged in oxidation/reduction reaction [-]; F – Faraday´s constant (96,485 C/mol).; Q – charge loading [C].

The disadvantage of Fenton's, electro-Fenton's and photo-Fenton's reactions is the condition of pH of the solution in the acidic area, e.g. reaction has the best efficiency around value pH 3. Optimal pH supporting the Fenton's reaction is mentioned in almost all articles the same. Low pH leads to side-reactions with hydrogen and higher pH cause precipitation of the Fe into complexes such as Fe(OH)2 (Guan W. et al., 2018). Reaction in the higher pH (neutral or alkaline) is much slower or not provide good efficiency (Poza-Nogueiras V. et al., 2018). Precipitation of ferric species is the main reason for the lower efficiency of the classical Fenton's reaction and photo/Fenton's reaction. Total contaminant mineralisation is difficult for Fenton's reaction because Fe creates stable complexes. These can be destroyed by UV radiation (Vorontsov, A.V., 2018). Photo-Fenton's reaction often has higher efficiency than Fenton's or electro-Fenton's reaction, but has longer residence time extensively. Also, working conditions of neutral pH or higher bring considerably lower efficiency (Jiang Z. et al., 2019).

Currently appeared researches in utilisation chelating agents to enable Fenton's reactions in a broader range of pH. Chelating agents showed up great results in the area above pH 3, but they have some serious problems. Organic chelating agents are toxic, and research of the inorganic ones did not finish yet. Another restriction represents its price (Zhang Y., Zhou M., 2019). Nevertheless, the utilisation of chelating agent EDTA-Fe(III) enabled almost total decomposition of malachite green with solution pH 7 (Hu Y. et al., 2018).

Nowadays the heterogeneus electrodes from various materials able to recycle and without the disadvantage of the amount of the sludge created are possible to employ in the electrochemical process. They allow running of the treatment even in the neutral or alkaline range of pH. Nevertheless, the best results of separation efficiency achieve again close around the pH 3 (Ganiyu S.O et al., 2018). Though, working in the pH in higher range would spare following pH adjustment to the area pH 7 – 9 for further treatment. Heterogenous electrodes are made from mainly iron oxides, clays, silicates, zeolites, nanoparticles (Poza-Nogueiras V. et al., 2018). Recycled catalyst had almost the same separation efficiency as a fresh one, but the reduction of COD dropped considerably. Preparation of the catalyst is quite time-consuming, and its recycling needs high temperatures and grinding afterwards (Sruthi T. et al., 2018).

Interesting experiments of electro-Fenton's reaction with on-site production of both reagents were successfully carried out. The sacrificed electrode was the source of the Fe ions, meanwhile for hydrogen peroxide generation was utilised gas-diffusion-electrode (GDE) specialised on hydrogen peroxide production. Reagents

were not dosed externally in this case, but pH should be again adjusted to the pH 3, where was the most efficient (Kubo D., Kawase Y., 2018). However, electrodes made from rare metals, which are often very efficient are divided from full industrial utilisation by complicated manufacture together with a high price (Liu X. et al., 2018). Initiation to the industrial scale might take some time. Because of these findings seems to be the most industrially applicable electro-Fenton's process with a sacrificed electrode as a source of the iron ions and externally dosed hydrogen peroxide. The material of the electrode should be iron with the known composition to prevent secondary pollution.

Important factors influencing the efficiency of electro-Fenton's reaction are pH value, the concentration of hydrogen peroxide and current density. Increasing current density cause rising of the efficiency up to a certain point where current density stops to have an influence on the further increase or due to side-reactions have the opposite effect, and efficiency starts to decline. Increasing of the hydrogen peroxide dosage has a favourable effect on separation efficiency up to a point, from which its further increase has no influence (Guan W. et al., 2018).

2. Experimental

For the evaluation of fundamental data for the pilot-scale and full-scale reactor were performed experiments in laboratory-scale. All measurements were performed in the glass beaker with a solution volume of 1.5 l in the configuration seen in Figure 1. Mixing in the cylindrical vessel equipped with four plastic baffles ensured impeller (CVS 69 1020) with six blades to homogenise the batch. The pH was monitored by the pH probe (DULCOTEST PHEX 112 SE) placed next to the redox potential probe (DULCOTEST RHEX-Pt-SE) opposite the mercury thermometer. These quantities are essential for the following wastewater treatment (biological treatment or disposal).

The model wastewater consisted of demineralised water and phenol ($0.5 \ g \cdot l^{-1}$) which was the object of the removal. Iron sulphate was dosed into the solution as the source of Fe^{2+} ions in the case of classical Fenton's reaction. Electrode pairs were constituted by the sacrificed iron anode and the cathode made of titanium in case of an electrochemically enhanced reaction. An iron anode (m = 0.261 g) was dissolved (employed current density 408.16 $A.m^{-2}$) during the reaction time – equal to Fe^{2+} in iron sulphate utilised within the classical Fenton reaction. The conductivity of model wastewater was intentionally increased by potassium chloride (c = 1.0 $g \cdot l^{-1}$).

Experiment procedures were initiated by lowering the pH by sulfuric acid to value pH 3 where Fenton's reaction is the most efficient. Subsequently dosed hydrogen peroxide provided free hydroxyl radicals and started the reaction with concurrently added iron ions. The hydrogen peroxide was consumed entirely after the predetermined reaction time (15 minutes). Model wastewater was then alkalized by a water solution of calcium hydroxide, which caused the Fe^{2+} precipitation. Following filtration was accelerated by a water solution of anionic flocculant Sokoflok 16. Described redundant iron removal together with possible redundant hydrogen peroxide decayed in alkali background improved the accuracy of COD measurement. The COD was afterwards measured by fast Kubel`s method.
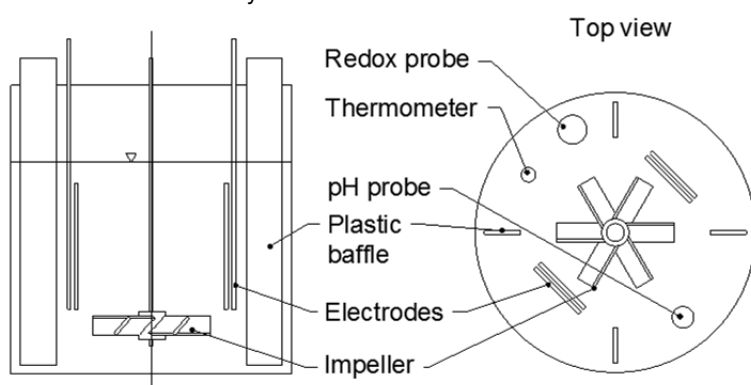

Figure 1: Scheme of experimental equipment.

3. Experimental results

Classical Fenton's reaction was performed for determination of the optimal dosage of hydrogen peroxide and for following comparison with the electrochemically enhanced reaction. COD was measured as a benchmark of applicability for following wastewater treatment, indicating acceptable decomposition of the pollutants.

Classical Fenton's reaction followed the results of the other authors – rising dosage of the hydrogen peroxide helps to decompose impurities up to a certain point as seen in Figure 2. The further increase does not improve removal efficiency or can cause a drop in separation efficiency.
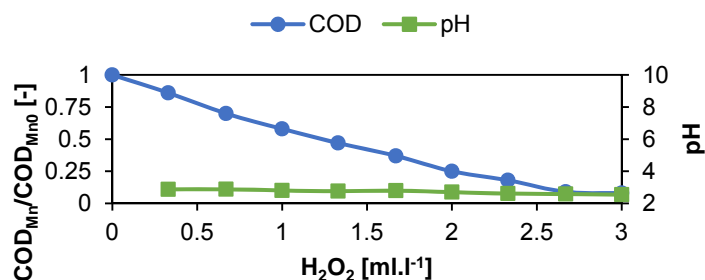

Figure 2: Classical Fenton's reaction process – H_2O_2 dosage dependence on the removal of Phenol (0.50 g·l^{-1}).

The timing of the hydrogen peroxide release was examined. The efficiency of the process was lower with five minutes postponement of hydrogen peroxide dosage after the experiment beginning compared to the concurrent dosage of both reactants, as seen in Figure 3. The current density was held constant during both experiments. The study of different dosing modes of the reagents showed the importance of the continual dosing. Gradual addition brought the best efficiency in comparison with the instant release of the compounds in a single step (Gümüs D., Akbal F., 2016). Electro-Fenton's process with the continuous dosage of the hydrogen peroxide can offer excellent control over the timing to fulfil this demand.
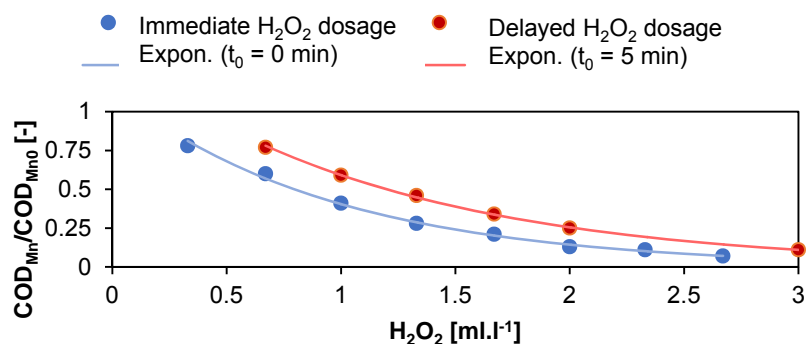

Figure 3: Electrochemical Fenton's reaction – H_2O_2 dosage timing influence on Phenol removal (0.50 g·l^{-1}).

The experiment of electrochemical Fenton's reaction was performed in two setups - with one or with two pairs of electrodes. When one pair of electrodes was used, the anode and the cathode were placed 14 cm from each other on the opposite sides of the vessel. In the case of two pairs of electrodes, the electrode gap was 1.8 mm. The electrode gap should be adequately smaller considering the linear dependence between the distance between the electrodes and the electrical resistance, to keep power losses as low as possible.
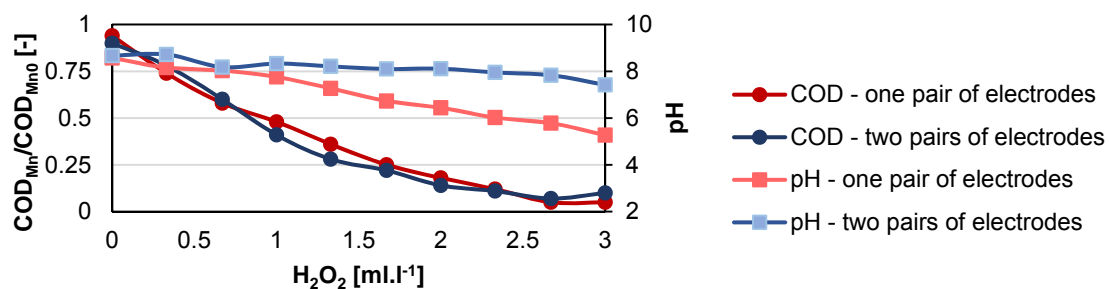

Figure 4: Electrochemical Fenton's reaction – dependence of electrodes arrangement.

The comparison of COD results shows that the usage of the two pairs of electrodes is more convenient than using a single pair of electrodes placed inappropriately from the point of reducing the losses as seen in Figure 4.

Iron ions dosed electrochemically can save loads of sulphates or other salts potentially added to the wastewater in the form of the chemicals. Considering the typical dosage of the most used sulphate – $FeSO_4$, in the range 2 – 4 g/l, chemical way brings additional 1,264 – 2,528 g of SO_4 into every litre of the treated wastewater.

4. Electrochemical cell design

The design of the electrochemical cell and its scaling up can be tricky. Laboratory-scale experiments have entirely different demands from the real industrial-scale processes. Processes with smaller volume flows can be treated in small batches like the one proposed in the experimental part, but continual apparatus seems to be more practical for large industrial flows.

The critical point of the design has shown to be the placement of the electrodes. Laying the electrodes on the bottom of the chambers seems to be right in terms of enabling the created floccules to rise with the ascending bubbles generated at the electrodes, but such design has its limits. With rising volume flow grows demands for the area of the electrodes in the reactor, considering constant current density, the same as in the laboratory scale experiments. The bottom of the chamber cannot fulfil the needs for the required electrodes area for rising electrode surface. The amount of iron must be delivered proportionally to the experimental dosage and current density. In an industrial scale, there is another issue to deal with. Electrodes in the industrial scale must be easy to maintain and replace to reduce or better to avoid the shutdown. Such requirements are easily fulfilled by vertically placed electrodes which can be arranged into compact units. They are accessible from the top for replacing or cleaning.

As mentioned before, the electrode gap has a significant influence on the utilised power source. The distance between the electrodes should be rather small for reducing the electrical losses, however, should not be unduly narrow, causing clogging the gaps by the sludge. Careful design can allow the requisite flow velocity and obviate the need for stirring the batch.

The bubbles generated on the electrodes surface help lifting the floccules on the water surface. The limiting factor for the free rise of the bubbles is the distance from the water surface. There are significant hydrodynamic forces on the bubbles below one-meter depth, creating the resistance against ascension.

The necessity of the sludge treatment facility must be reminded. The amount of the created sludge can be separated by ranking or by suction from the treated wastewater surface and/or by scraping from the bottom in case of heavy aggregates.

The concept of the electrochemical chamber was designed based on the concerns written above as seen in Figure 5. The apparatus is combined with an additional electroflotation chamber, which based on our experience can considerably accelerate the separation. Wastewater effluent is directly supplied with hydrogen peroxide feed for the avoidance of the other mixing. The stream then continues to the main area with the electrodes. The designed geometry forces the suspension to pass between the electrodes allowing the created floccules to be carried by the stream and by the generated bubbles. The scraper removes part of the formed sludge, elevated by electroflotation on the surface. Meanwhile, the solution flows into the second chamber where separation continues. In the second chamber is separated the remaining amount of the sludge and treated wastewater leaves the equipment for further treatment or back to the technology.

1 - Wastewater feed
2 - Hydrogen peroxide feed
3 - Sacrificed electrodes
4 - Sludge scraper
5 - Sludge drainage
6 - Permanent electrodes
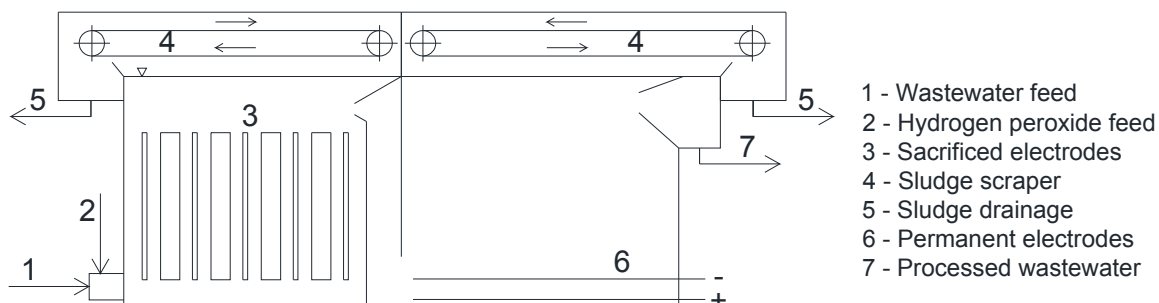7 - Processed wastewater

Figure 5: Design of chamber for a continuous process of electrochemically enhanced Fenton's reaction.

5. Conclusions

The continuous dosage of metallic ions in the case of electro-Fenton's reaction brings advantages in the form of higher removal efficiency in comparison with classical Fenton's reaction. Faraday's law can easily control continual dissolution of ferrous ions for simple regulation of the reaction. Moreover, hydrogen peroxide consumption is lower with an electrochemical way in comparison with Fenton's reaction, by our experience, which was also registered by other researchers (Sruthi T. et al., 2018). On the surface of the electrodes is generated highly reactive nascent oxygen, helping with better quick pollutant decomposition. Essential quantities for the industrial-scale design which have to be experimentally discovered are chiefly: dosage of the reagents, current density, the distance between the electrodes, the amount of the sludge created and volume flow of the wastewater.

Many impurities are complex compounds or can combine with other types of pollutants often causing unpredictable results, especially in the pharmaceutical industry (Kubo D., Kawase Y., 2018). Another problem can happen with the wastewater containing cyanides after lowering the pH under specific value which causes the development of the hydrogen cyanide gas. For this reason, preliminary experiments in the laboratory including a detailed analysis of the effluent and released gasses are highly recommended. Wastewater containing toxic matter can be favourable to process separately and after the concentration of the solution to stabilise into the form non-leachable by water or to burn it in the form of dry matter.

Acknowledgements

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