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Solar driven degradation of 4-chlorophenol

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Abstract

The feasibility of the Photo–Fenton reaction with sunlight as irradiation source was tested with model waste waters (4-chlorophenol) in different weather conditions and at two sites. The degradation rate was found to decrease with rising length of path in experiments in a glass basin with a volume of up to 20 l in Vienna. In a compound parabolic collector (CPC) at the Plataforma Solar de Almería increasing the amount of the iron catalyst proved to accelerate the degradation while the degradation rate decreased with rising initial pollutant concentration.

Keywords: Photo–Fenton reaction; Solar Photo–Fenton; Degradation of 4-chlorophenol; AOPs; Waste water treatment

1. Introduction

1.1. Fenton and Photo–Fenton reactions

Although the oxidising power of the combination of Fe^{2+} and H_2O_2 (i.e., the Fenton reaction, cf. Eq. (1)) has been known for more than 100 years [1], the fact that the reaction can be enhanced by UV/Vis irradiation ($\lambda < 580\,\mathrm{nm}$) was found out only a few years ago [2–7]. The so-called Photo–Fenton reaction (Eq. (2)) produces additional hydroxyl radicals and leads to a reduction of the photocatalyst by the irradiated light. Only a very simplified description is given in Eqs. (1) and (2), for a detailed discussion of the rather complex reaction cycles refer to [8].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + OH^\bullet \qquad (2)$$

Recent papers question the role of the hydroxyl radical as responsible species for the degradation steps [9] and suggest Fe(IV) species instead. The possibility of applying solar light instead of artificial light for the Photo–Fenton reaction has been suggested in literature [10,11]. This substitution would dramatically lower the costs of the process and thus provide a major step towards industrial application. A task of this work is to demonstrate, that degradation with the Photo–Fenton method is not only possible in direct sunlight, but also in shadowy places and even in winter.

Fig. 1 shows the solar emission spectrum, absorption spectra of a 4-chlorophenol (4-CP) degradation experiment and an Fe(III)-solution. 4-CP has been chosen as the model pollutant because the degradation mechanism and kinetics of the common toxicant is well known [12,13]. As a rule of thumb the amount of irradiated solar energy can be considered to be 600–700 $\mathrm{W/m^2}$ in Almería and Vienna. The major difference though are the number of sunny hours per year (3000 in Almería, 2000 in Vienna) [14,15].

Solar emission starts at 300 nm, the very same wavelength where the absorption of a mixture of hydrogen

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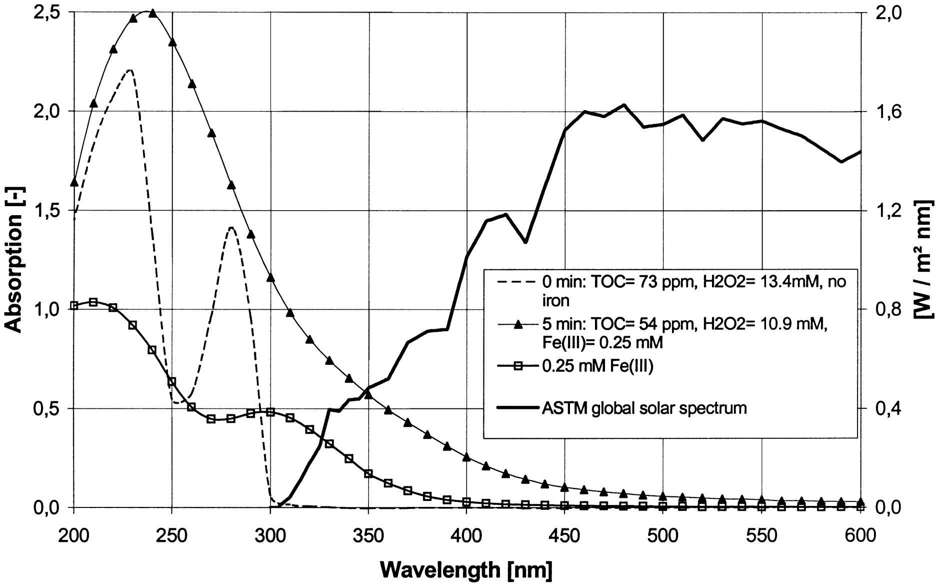

Fig. 1. Solar emission spectrum, absorption spectra of a 4-chlorophenol degradation experiment and an Fe(III)-solution; solid line: ASTM global solar spectrum; broken line: $t=0$ min, TOC = 73 ppm, $c(H_2O_2) = 13.4$ mM, no iron; triangles: $t=5$ min, TOC = 54 ppm, $c(H_2O_2) = 10.9$ mM, $c(Fe^{3+}) = 0.25$ mM; squares: solution containing only $Fe_2(SO_4)_3$, $c(Fe^{3+}) = 0.25$ mM, which is almost identical to a spectrum at the end of the experiment.

peroxide and 4–chlorophenol stops. The addition of iron causes a decisive shift of the absorption towards higher wavelengths, far into the visible range. It can also be seen, that the most important wavelengths for solar Photo–Fenton are in the UV-A range between 300 and 400 nm, where emission and absorption are both strong.

This absorption shift of Fe^{3+} in organic complexes has also been reported in literature [16].

2. Experimental

4-Chlorophenol (4-CP), hydrogen peroxide, ferrous sulphate, sodium hydroxide and sulphuric acid (all p.a.) were obtained from Merck and were used as received. The solvent was distilled water. The amount of iron was determined by colorimetry of the Fe(II)/1,10-phenanthroline complex. Fe(III) was reduced with ascorbic acid to determine the total amount of iron. The analysis was carried out by a Shimadzu photometer (UV-160A) at a wavelength of 510 nm. Iodometric titration was used for the determination of the actual hydrogen peroxide content [17]. Total organic carbon measurements (TOC) were carried out by using a Shimadzu TOC-Analyser 5000 equipped with an autosampler ASI-5000. The pH was measured by means of a WTW pH-Meter 537 equipped with a pH combination electrode E56. In Vienna, light intensity was measured with a Kipp and Zonen CC20 radiation indicator with pyranometer CM3, spectral range from 305 to 2800 nm. In Spain global UV (300–400 nm) irradiance was recorded by a Kipp and Zonen CUV3 detector, inclined 37° like the reactor modules.

At the PSA a CPC (compound parabolic collector) reactor (mounted inclined by 37°, 3 m^2 aperture area, $2 \times 60°$ aperture angle, concentration factor approximately 1, total area 9 m^2, 108 l illuminated volume) was used [18]. 250 l waste water were circulated from a storage tank through the collectors in batch mode. Irradiation times were calculated as $t_R = V_R t_T V_T^{-1}$ where t_T is the total time elapsed, V_R the illuminated reactor volume and V_T the total volume.

In Vienna the experiments were carried out in a 60 cm × 70 cm × 6 cm glass basin, which was situated outdoors. The walls and the bottom were covered with aluminium foil to reflect the sunlight back into the

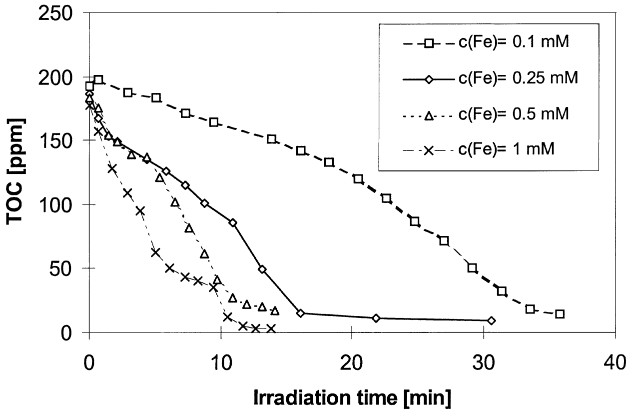

Fig. 2. Influence of the iron concentration on the degradation; CPC; $V=250\,l$; c_0 (4-CP) = 3 mM; c_0 (H_2O_2) = 45 mM.

solution and thereby optimise the use of sunlight. A glass plate could be placed on top of the basin to simulate an apparatus which prevents possible stenches and minimises evaporation losses. Magnetic stirring of the solution was applied. As the total volume of the solution was exposed to the sunlight, irradiation time equals total experiment time ($V_R = V_T$).

The experiments were carried out in unbuffered aqueous solutions without regulation of temperature. Ferrous sulphate and 4-CP were also added and pH adjusted to 2.8 by addition of concentrated sulphuric acid. An excess (115%) of the stoichiometric demand of H_2O_2 was added at the beginning of the experiment ($t=t_0$). At defined intervals samples were taken and the following parameters were measured: TOC, pH, temperature and contents of iron and H_2O_2. The temperature wasn't regulated but closely monitored. In all cases the change of temperature was similar and approached ambient temperature.

3. Results and discussion

3.1. Experiments at the PSA

At first the influence of the iron concentration on the degradation performance has been investigated. As the iron acts as a catalyst in the Photo–Fenton reaction, the degradation rate should increase with rising amount of iron added. This effect is clearly visible in Fig. 2. The flattening in the curve with c(Fe) = 1 mM is caused by a lack of peroxide in the last part of the experiment. Therefore, further hydrogen peroxide was added and the reaction continued. Thereby, complete mineralisation of 4-CP was achieved.

The 2.5-fold amount of iron decreases the half-life of the TOC from 24 to 10.5 min (43%), a further doubling of catalyst concentration leads to reduction to 7 min (66%), and after a final doubling the half-time is merely 4.2 min (60%). The percentile reduction factors support the linear growth which has been suggested in a previous work [19]. The degradation rate does not increase indefinitely but reaches a maximum at the optimum iron concentration. Further addition of iron does not increase the degradation rate. The limit of catalyst concentration depends on the type of waste water and the length of path in the reactor used. During the experiments performed at the PSA the optimum concentration has not been found.

The other series of experiments was conducted to study the influence of the 4-chlorophenol concentration on the degradation in order to judge the applicability of concentrating methods (e.g., reverse osmosis) before Photo–Fenton treatment. The advantage of these methods is a saving of process water which could be vital in arid countries.

An increase of the initial pollutant concentration results in two antagonistic effects. On the one hand, the higher concentration of peroxide and organic substrate should lead to a higher probability of collision of the reactant molecules. On the other hand the higher concentration of radical scavengers should diminish the degradation rate. The role of inorganic anions (in this case carbonate, hydrogencarbonate chloride and

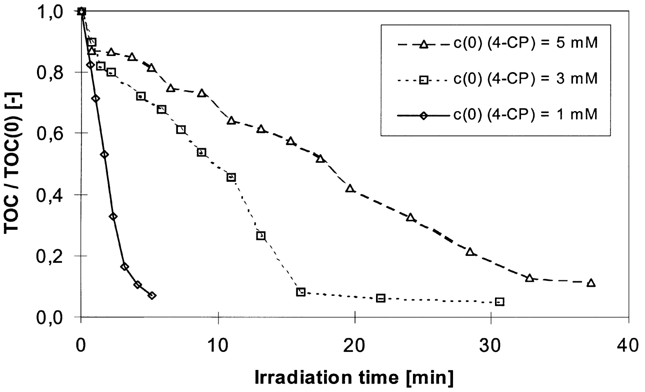

Fig. 3. Influence of pollutant concentration on degradation; CPC; $V=250\,l$; c_0 (Fe^{2+}) = 0.25 mM; c_0 (H$_2$O$_2$) = 15* c_0 (4-CP) (75, 45 and 15 mM, respectively).

sulphate) as radical scavengers and their effect has been reported in literature [20]. The concentration of sulphate is constant and depends only on the amount of iron added as ferrous sulphate. As carbonates and chloride are degradation products, their concentration increases along the experiments with rising amount of pollutant. A further fact that has to be taken into consideration is the self-degradation of hydrogen peroxide, which increases with rising concentration. The degradation rates were calculated for a TOC-removal of 50%: 8.9 ppm TOC/min (5 mM 4-CP), 9.8 ppm TOC/min (3 mM 4-CP), 14.7 ppm TOC/min (1 mM 4-CP). The predomination of the slowing effects can also be seen in Fig. 3. A study dealing with the influences of the catalyst and the pollutant concentration on the degradation of pesticidal waste water is published in another article in this issue [21].

3.2. *Results of the experiments in Vienna*

In Table 1 information of the experiments in Vienna is given: the volumes and corresponding layer thickness are presented and whether the experiments have been conducted in direct sunlight or in shadow (i.e., shadow of a building). The value given for the power density is the average of three values, measured at the beginning, middle and the end of the experiment.

All experiments were conducted to investigate the influence of the layer thickness on the degradation of 4-chlorophenol. The volume of the solution was varied from 2 to 20 l in order to obtain lengths of path from 0.5 to 5 cm. Apart from the length of path, the intensity of the irradiating sunlight is of importance, and whether the reaction solution is exposed directly to the sunlight or in a shadowy position.

Table 1
Summary of the experiments in Vienna

Run	Sunlight Condition	(Wh/m^2)	Volume (l)	Layer thickness (cm)
1	direct	518	2	0.5
2	direct	717	4	1
3	direct	555	8	2
4	direct	623	12	3
5	direct	176	16	4
6	direct	544	20	5
7	shadow	224	2	0.5
8	shadow	110	4	1
9	shadow	106	8	2
10	shadow	137	12	3
11	shadow	98	16	4
12	shadow	88	20	5
13	direct	675	4	1
14	direct	498	4	1
15	shadow	89	4	1
16	shadow	99	4	1
17	shadow	65	8	2

The achieved results are summarised in Fig. 4 which depicts the experiments in direct sunlight and Fig. 5 showing the experiments in shadow. In Table 2 the reaction rates (calculated for a TOC removal of 80%) have been compiled and the layer thickness is repeated for convenience.

The experiments in direct sunlight (Fig. 4) show alike degradation curves from 2 to 12 l with an exceptionally quick performance of Run 2, which can be explained by the high amount of irradiated energy. To

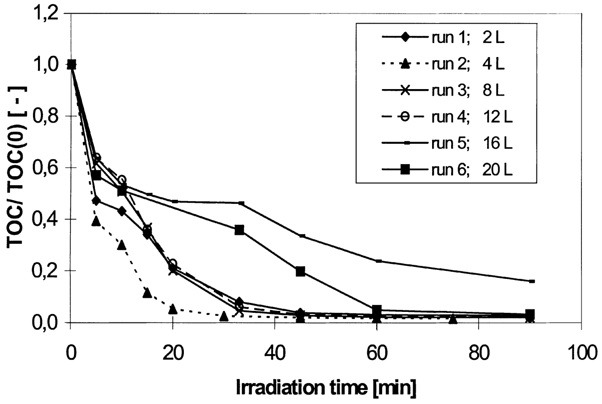

Fig. 4. Degradation in direct sunlight; basin, c_0 (4-CP) = 3 mM; c_0 (Fe^{2+}) = 0.75 mM; c_0 (H_2O_2) = 45 mM; Runs 1, 2, 3, 4, 5, 6: V = 2, 4, 8, 12, 16, 20 l, respectively.

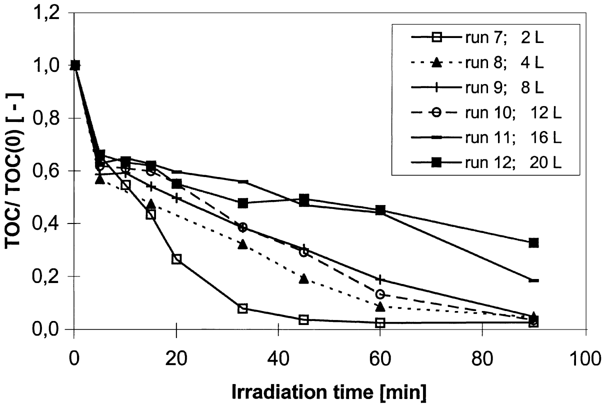

Fig. 5. Degradation in shadowy conditions; basin, c_0 (4-CP) = 3 mM; c_0 (Fe^{2+}) = 0.75 mM; c_0 (H_2O_2) = 45 mM; Runs 7, 8, 9, 10, 11, 12: V = 2, 4, 8, 12, 16, 20 l, respectively.

Table 2
Degradation parameters of experiments with different layer thickness

Run	Layer thickness (cm)	Degradation rate (ppm TOC/min)
1	0.5	10.1
2	1	13.4
3	2	9.1
4	3	8.5
5	4	2.0
6	5	3.6
7	0.5	8.3
8	1	3.7
9	2	2.8
10	3	3.0
11	4	1.9
12	5	1.6

explain the differences in performance of the experiments, especially that of Run 5, the third column (irradiation energy/m^2) of Table 1 has to be taken into consideration. The value is by large the lowest of the sunny experiments, which means that the sky was partly overcast on that day. Thus, degradation was slow.

The expected trend is, of course, that the degradation rate dwindles with increasing volume since the available number of photons needed for the reduction of the iron catalyst is limited. The course of the shadowy experiments agrees with this thesis. In comparison to the runs in direct sunlight, the degradation rates are lower than the experiments with the same volume. The rates though do not include the volume of the solution and the irradiated energy.

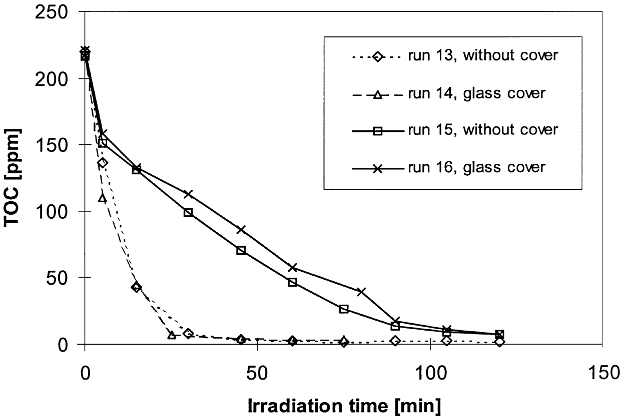

Fig. 6. Experiments with and without covering glass plate under different sunlight conditions; basin; $V = 4$ l; c_0 (4-CP) = 3 mM; c_0 (Fe^{2+}) = 0.75 mM; c_0 (H_2O_2) = 45 mM; Runs 13 and 14: direct sunlight; Runs 15 and 16: shadow; Runs 14 and 16: covering glass plate; Runs 13 and 15: without covering glass plate.

The amount of solar energy in direct light is approximately five times as much as in shadowy conditions. The actual runtimes are only half the amount in direct sunlight. Focusing on the experiments with 8 and 12 l, respectively, the influence of the degraded volume becomes apparent. The two experiments in direct sunlight performed equally good in terms of degradation grade (90% in 30 min) and rate (cf. Table 2 and Figs. 4 and 5). Likewise the degradation grade was 90% after 80 min for the runs in shadow.

The change in volume from 8 to 12 l (+50%) corresponded to an increase of the amount of degraded TOC from 3.46 g/h in Run 3 (8 l) to 4.96 g/h in Run 4 (12 l) and from 1.35 g/h in Run 9 (8 l) to 2.13 g/h in Run 10 (12 l), respectively.

Fig. 6 presents a comparison of a pair of experiments (Runs 14 and 16) with covering glass plate to a pair without (Runs 13 and 15). The idea was to find out whether the loss of sunlight significantly influences the degradation. One experiment of each pair was carried out under shadowy conditions, the other one in direct sunlight. The latter (indicated by a broken line) are 3.75-times quicker. No significant influence of the covering plate could be detected. The cut-off effect of the glass plate is cancelled by the fact that the emission of the sunlight below 300 nm is neglectable. The absorption by the glass plate seems to be insufficient to decrease the degradation rate.

In the Figs. 4–7 the influence of the dark reaction can be noticed in the first phase of the experiments where the degradation of the pollutant is caused by the hydrogen radicals generated by iron(II) and hydrogen peroxide. After 5 min all Fe^{2+} is oxidised and has to be reduced by solar irradiation, otherwise the degradation will stop.

All the previous experiments have been carried out in summer. As the ability of year-round operation would pose a great advantage, a test run was conducted in mid-January. Subject of investigation was primarily whether degradation is still possible in a low temperature, low intensity of sunlight environment.

The broken line in Fig. 7 resembles this experiment, comparing it to a summer experiment in direct sunlight (Run 4) and one in shadow (Run 10). With Run 17 as reference the degradation is 5.8-times quicker in Run 4 and 1.8-times faster in Run 10.

The considerable slower degradation in winter is due to the lower intensity of sunlight (10% of direct sunlight, 61% of shadowy conditions) and lower temperature (12–13°C less than in summer). Still, even under these unfavourable circumstances solar driven degradation of 4-chlorophenol has been achieved.

4. Conclusions

Variation of path-length was attempted to find out the optimum layer thickness of the solution and thus acquire information for the construction of a bigger reactor. According to the degradation performances

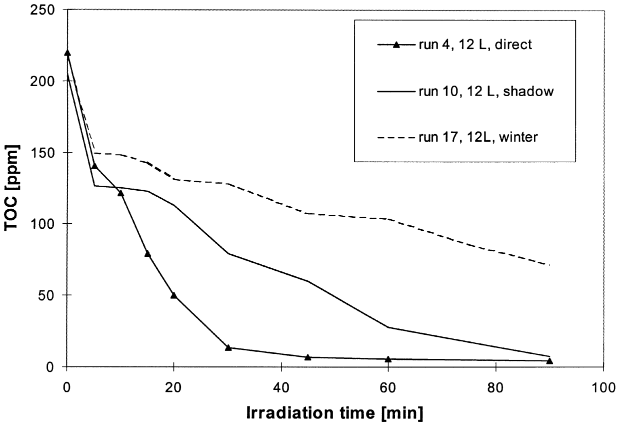

Fig. 7. Comparison of different seasons (winter, summer); basin, c_0 (4-CP) = 3 mM; c_0 (Fe^{2+}) = 0.75 mM; c_0 (H_2O_2) = 45 mM; V = 12 l; Run 4: direct sunlight, summer; Run 10: shadow, summer; Run 17: shadow, winter.

the optimum length of path was 3 cm in direct sunlight, while it was only half a centimetre under shadowy conditions. Furthermore, it has been proved that satisfying degradation is possible with thick irradiated layers. In the given case the mineralisation of 4-CP is still efficient at 5 cm, which is an important result for future constructions of larger scale.

The experiments with increasing initial amount of pollutant have clearly shown that application of concentrating methods and thereby a saving of process water before Photo–Fenton treatment is possible which provides a major advantage of the method in arid countries. Summarising the work in a final statement it has been found that natural sunlight is a powerful driving force for the Photo–Fenton reaction, the application of which is possible in a year-round operation.

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