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Research Article

Sonochemical Degradation of Pharmaceutical Wastewater

This study presents the influence of the addition of additives such as activated carbon, carbon tetra chloride, hydrogen peroxide, and potassium dichromate on ultrasonic reduction of pharmaceutical wastewater chemical oxygen demand (COD) under laboratory conditions. The addition of activated carbon increased the % COD reduction whereas the combined addition of activated carbon and H_2O_2/CCl_4/$K_2Cr_2O_7$ was found to show higher reduction. Among the various combinations investigated, the combined addition of activated carbon and CCl_4 was found to be the best combination. However, the environmental and health problems associated with these chemicals limit the applicability of the process in an industrial level. Further investigation with this system showed that the initial pH and initial COD have significant influence on the removal rate. The data obtained were fitted with first order and Langmuir–Hinshelwood kinetic models. The values of the rate constants obtained indicated that the pharmaceutical wastewater can be treated efficiently by the proposed methods.

Keywords: Activated carbon; Additives; Kinetics; Pharmaceutical wastewater; Sonolysis

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1 Introduction

The pharmaceutical industrial wastewater contains a wide variety of chemicals and products such as anesthetics, disinfectants, salt, anti-clotting agent, analgesic, antibiotics, vitamins, syrups, and tablets. Solid waste from pharmaceutical industry comprises of expired or rejected medicine, spent solvent, damaged bottles, and packaging materials. The composition of wastewater generated depends mainly on the type of process and size of the industry [1]. Pharmaceutical industry wastewater is highly polluted with very high chemical oxygen demand (COD), total solids (TS), colloidal solids, toxicity, and odor [2–5]. Worldwide, half of the total amount of pharmaceutical wastewater produced is discarded without any specific treatment [6].

The techniques reported to be effective to treat the recalcitrant industrial effluent are based on advanced oxidation process (AOP) [7]. The AOPs such as Fenton oxidation [8], photo-oxidation [9], ozonation [10], oxidation by direct attack of oxidants, and electrochemical methods [11] are efficient in destructing refractory pollutants. Such techniques generate highly reactive hydroxyl radicals that oxidize a broad range of organic pollutants non-selectively [12]. Among the various AOPs, sonolysis is an emerging method due to its numerous advantages [13].

Sonochemical decomposition of organic pollutants is due to the formation and collapse of high-energy cavitation bubbles, which results in an enormous increase in temperature and pressure [14]. This phenomenon destructs the organics present through pyrolytic cleavage and also generates oxidative species [15, 16]. On the other hand, the sonochemical destruction of pollutants may be increased by the addition of additives such as activated carbon [17], Fenton's reagent [18], ozone [16], CCl_4 [19], and H_2O_2 [20]. However, in the literature the influence of combined addition of these additives has not been given much attention. Therefore, the main aim of the present study was to investigate the influence of the addition of combined additives (activated carbon, H_2O_2 plus activated carbon, CCl_4 plus activated carbon and $K_2Cr_2O_7$ plus activated carbon) on the sonochemical degradation of pharmaceutical wastewater under laboratory conditions. It should be noted that CCl_4 and $K_2Cr_2O_7$ are toxic and carcinogenic chemicals. Thus, the use of such chemicals for the treatment of wastewater in an industrial level may create associated problems and hence, the practical applicability of the processes presented is limited.

2 Materials and methods

2.1 Materials

Activated carbon and H_2O_2 were purchased from Rankem (New Delhi); CCl_4 and $K_2Cr_2O_7$ were obtained from SRL (Mumbai). The reagents used such as ferrous ammonium sulphate, potassium dichromate, sulphuric acid (98%), silver sulphate, and mercuric sulphate were purchased from Rankem.

2.2 Wastewater

Pharmaceutical industry wastewater was obtained from the central effluent treatment plant facility available at industrial estate,

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Abbreviations: COD, chemical oxygen demand; **AOP**, advanced oxidation process.

Table 1. Characteristics of pharmaceutical wastewater

Parameters	Value
COD (g/L)	10.933
pH	9.2
Total solids (ppm)	60 680
Dissolved solids (ppm)	40 280
Suspended solids (ppm)	20 400

Chennai, India and was stored in a deep freezer. The important characteristics of the effluent are presented in Table 1.

2.3 Sonicator

All experiments were carried out with tank type sonolyzer operating at a frequency of 30 kHz. The tank was made up of stainless steel and the bottom of the tank was fitted with an ultrasonic transducer. The reactor was provided with timer and temperature indicator.

2.4 Experimental

For all sonication experiments, 1 L of pharmaceutical wastewater was loaded into the sonicator and was subjected to sonication for the desired period. To study the influence of addition of activated carbon, H_2O_2, CCl_4, and $K_2Cr_2O_7$ on the reduction of COD, 1 L of wastewater was sonicated with a desired additive for the desired time. The control experiment was carried out without any additives. The effect of addition of activated carbon was studied by varying the concentration as 1, 1.5, 2, 2.5, and 3 g/L and the optimum concentration was achieved based on the maximum % COD reduction. The combined effect of H_2O_2 and activated carbon (2 g/L) was studied by varying the H_2O_2 concentration as 100, 250, 500, 1000, and 1200 mg/L and the combined effect of CCl_4 and activated carbon (2 g/L) was studied by varying the CCl_4 concentration as 50, 100, 250, and 500 mg/L. The effect of $K_2Cr_2O_7$ in the presence of activated carbon was studied by varying its concentration as 100, 250, 500, and 1000 mg/L. The optimum additive concentration and the best combination were achieved based on the maximum % COD reduction.

In the present study, for the best combination, the effect of initial pH and initial COD on % COD reduction was studied by varying the initial pH from 6 to 9 and the initial COD as 10.9, 9.5, 8.0, 7.3, 6.5, and 5.1 g/L. Samples (2 mL) were withdrawn at a 1-min interval and were centrifuged at 6000 rpm for 10 min. Then, the supernatant was subjected to COD determination.

2.5 Analytical methods

The pH of the sample was measured with a digital pH meter (Elico) and the COD was determined by the open reflux method [21]. Total suspended solids, total dissolved solids, and total solids were measured by standard methods [21].

3 Results and discussion

3.1 Sonolysis

The effect of sonication time on the % COD reduction is shown in Fig. 1 and the % reduction observed after 60 min was about 41%. As can be seen from Fig. 1, the prolonged application of ultrasound did not affect the COD reduction considerably. This may be due to the formation of products which could not be destroyed further or may be due to the lack of oxidants ($OH^{\bullet}$ and H_2O_2) availability. The same trend was reported for the ultrasonic treatment of the dye Basic blue 41 [20]. However, the degradation can be further improved by sonicating the wastewater with some additives.

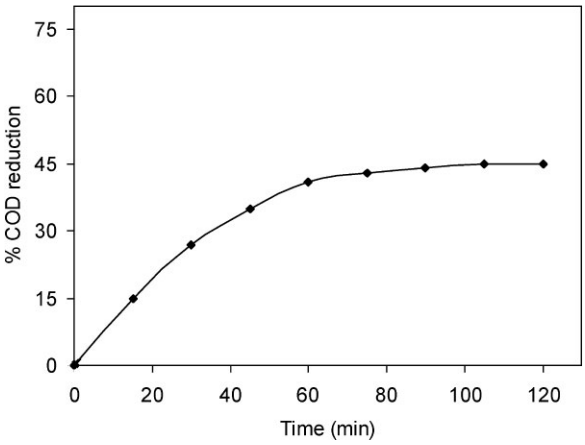

Figure 1. Effect of sonication time on % COD reduction.

3.2 Effect of additives

3.2.1 Effect of activated carbon

The effect of addition of activated carbon on % COD reduction was studied and the results obtained are shown in Fig. 2. In the concentration range studied, 2 g/L of activated carbon was found to be the optimum. The addition of 2 g/L of activated carbon showed about 60% COD reduction after 120 min irradiation, whereas the reduction was only 45% when the sonolysis was carried out without activated carbon (Fig. 1). It can be seen that the % COD reduction increased due to the addition of activated carbon. The adsorption of organic molecules by the activated carbon reduces the amount of dissolved organics, which in turn considerably reduces the COD. Moreover,

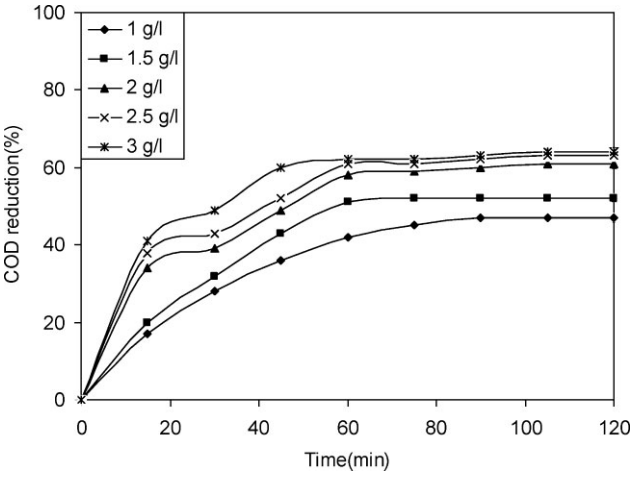

Figure 2. Effect of sonication time on % COD reduction at various concentrations of activated carbon.

the activated carbon acts as a catalyst for the oxidation of organics and hence, the adsorbed organics are oxidized efficiently [17, 22].

3.2.2 Effect of H_2O_2

The combined effect of H_2O_2 and activated carbon (2 g/L) on the % COD reduction was studied at various concentrations of H_2O_2 and the results obtained are shown in Fig. 3. The increase in the concentration of H_2O_2 increased the % COD reduction considerably. With the addition of 250 mg/L of H_2O_2, 79% COD reduction was obtained and a further increase in H_2O_2 concentration did not affect the % COD reduction. The self decomposition of H_2O_2 enhanced the formation of hydroxyl radicals during the sonolytic treatment and is responsible for the oxidation of organic contaminants present in the wastewater [23]. The increase in concentration beyond the optimum concentration leads to the formation of more hydroxyl radicals, whereas the formation of $HO_2^{\bullet}$ and H_2O_2 cause detriment to the degradation due to scavenging action [24]. Therefore, 250 mg/L of H_2O_2 were considered as an optimum level for the treatment of pharmaceutical wastewater.

3.2.3 Effect of CCl_4

The effect of CCl_4 addition with 2 g/L of activated carbon on the % COD reduction was studied and the results obtained are shown in Fig. 4. The %COD reduction increased with an increase in time and with the concentration of CCl_4. The optimum concentration was found to be100 mg/L, which gave a 75% COD reduction. Even though the increase in CCl_4 concentration from 100 to 500 mg/L increased the COD reduction; the results observed after 60 min were not significant. The following reactions are known to occur during sonolysis of CCl_4.

$$H_2O + \xrightarrow{h\nu} {}^{\bullet}H + {}^{\bullet}OH$$

$$CCl_4 + {}^{\bullet}H \rightarrow HCl + {}^{\bullet}CCl_3$$

It can be noted that CCl_4 is a hydrogen atom scavenger and controls the recombination reaction between hydrogen atoms and hydroxyl radicals. Moreover, it is a hydrophobic organic compound and is prone to enter into the cavitation bubbles and thereby undergoes degradation by pyrolytic cleavage [19].

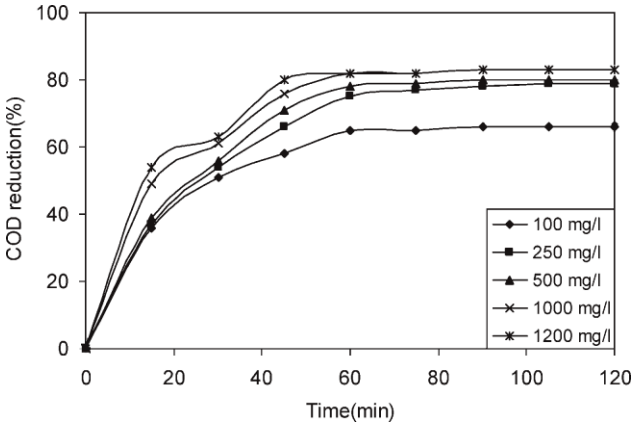

Figure 3. Effect of sonication time on % COD reduction at various concentrations of H_2O_2 with activated carbon (2 g/L).

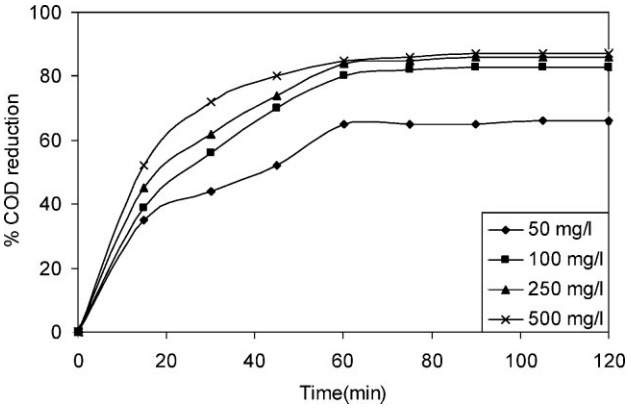

Figure 4. Effect of sonication time on % COD reduction at various concentrations of CCl_4 with activated carbon (2 g/L).

3.2.4 Effect of $K_2Cr_2O_7$

The effect of $K_2Cr_2O_7$ in the presence of activated carbon on the % COD reduction was studied and the variation of % COD reduction with time is shown in Fig. 5. The maximum % COD reduction of about 68% was observed at a $K_2Cr_2O_7$ concentration of 1000 mg/L [23]. The observed % COD reduction was less mainly due to the influence by the pH of the effluent and in the present study the degradation was carried out at a natural pH of the wastewater (pH = 9.2). The complete oxidation of organics with $K_2Cr_2O_7$ is only possible under acidic conditions and hence, a lower % COD reduction was observed even at higher concentrations of $K_2Cr_2O_7$.

3.2.5 Comparison studies

The effect of sonication time on the % COD reduction in the presence of various additives with activated carbon (2 g/L) is shown in Fig. 6. From the results, it is evident that the addition of activated carbon resulted in 61% COD reduction. The % COD reduction observed with the addition of H_2O_2 (250 mg/L), CCl_4 (100 mg/L), and $K_2Cr_2O_7$ (1000 mg/L) in the presence of activated carbon were 79, 83, and 68%, respectively. It can be seen, that the combined addition of CCl_4 and activated carbon was found to give a maximum % COD

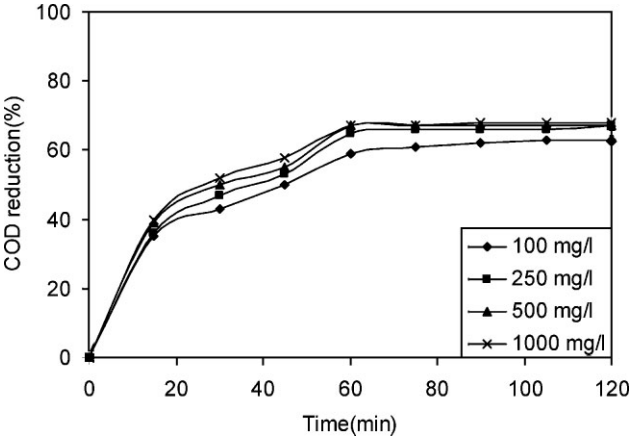

Figure 5. Effect of sonication time on % COD reduction at various concentrations of $K_2Cr_2O_7$ with activated carbon (2 g/L).

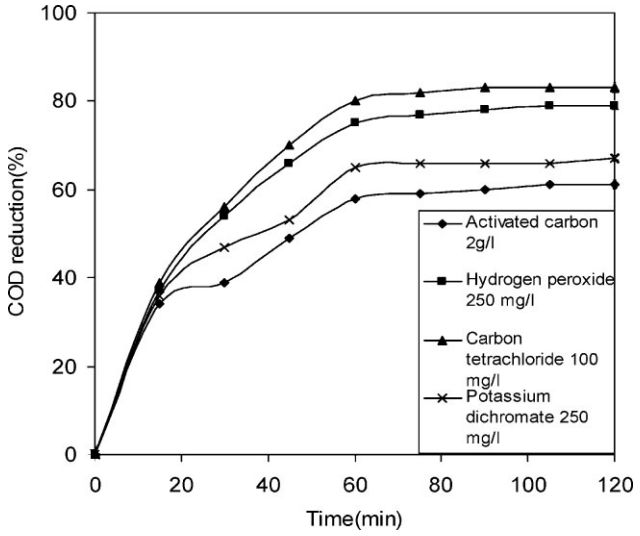

Figure 6. Effect of sonication time on % COD reduction in the presence of various additives with activated carbon (2 g/L).

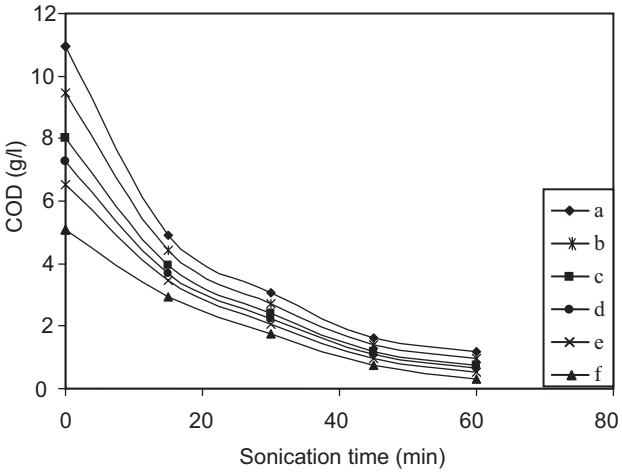

Figure 8. Effect of sonication time on % COD reduction at various initial COD in the presence of CCl_4 (100 mg/L) and activated carbon (2 g/L); (a) 10.9 g/L, (b) 9.5 g/L, (c) 8.0 g/L, (d) 7.3 g/L, (e) 6.5 g/L, and (f) 5.1 g/L.

reduction and hence, the detailed investigation was carried out with 2 g/L of activated carbon and 100 mg/L of CCl_4.

3.3 Studies with activated carbon and CCl_4

3.3.1 Effect of pH

The influence of initial pH on the sonochemical degradation of pharmaceutical wastewater in the presence of activated carbon (2 g/L) and CCl_4 (100 mg/L) was studied by varying the pH as 6, 7, 8, and 9. The results obtained are shown in Fig. 7 and the maximum % COD reduction was observed at low pH levels.

3.3.2 Effect of initial COD

The influence of initial COD on the % COD reduction was studied and the results are shown in Fig. 8. The % COD reduction rate was found to decrease with an increase in initial COD of the effluent. This may be attributed to the increase in organics load and insufficient production of oxidizing agents. So, it is evident that the initial COD has significant influence on the treatment process.

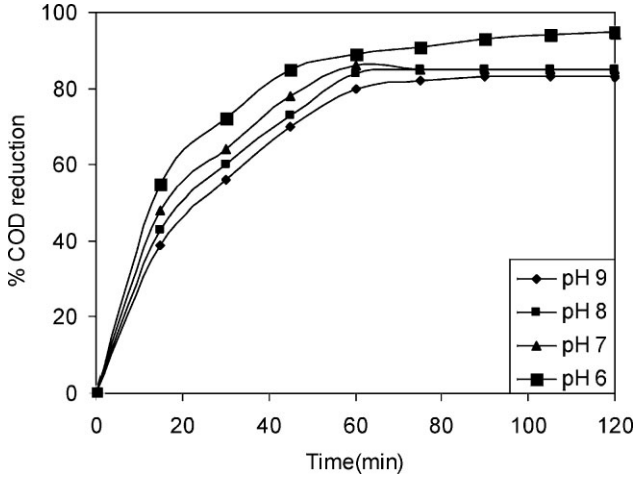

Figure 7. Effect of sonication time on % COD reduction at various pH in the presence of CCl_4 (100 mg/L) and activated carbon (2 g/L).

3.4 Kinetics study

3.4.1 Models

The sonochemical degradation of pharmaceutical wastewater was carried out with activated carbon and activated carbon in combination with additives such as H_2O_2, CCl_4, and $K_2Cr_2O_7$. The results obtained were analyzed with pseudo first order (Eq. (1)) and Langmuir–Hinshelwood kinetic models (Eq. (2)) [25]:

$$\ln \frac{[\mathrm{COD}]_t}{[\mathrm{COD}]_0} = -kt \tag{1}$$

where $[\mathrm{COD}]_0$, $[\mathrm{COD}]_t$, t and k are the initial COD, the COD at time t (min), the sonolysis time, and the rate constant, respectively.

$$r_{\mathrm{COD}} = \frac{k_0[\mathrm{COD}]}{1 + K_0[\mathrm{COD}]} \tag{2}$$

The parameters k_0 and K_0 can be evaluated by rearranging the Eq. (2) as:

$$\frac{1}{r_{\mathrm{COD0}}} = \frac{1}{k_0}\left(\frac{1}{[\mathrm{COD}]_0}\right) + \frac{K_0}{k_0} \tag{3}$$

The values k_0 and K_0 were obtained from the slope and intercept of the plot between the inverse of initial rate ($1/r_{\mathrm{COD0}}$) and inverse of initial COD ($1/[\mathrm{COD}]_0$).

3.4.2 Comparison of additives

The values of pseudo first order rate constants obtained for various combinations are presented in Table 2. It was observed that the rate constants increased with an increase in concentration of additives. Higher values of constants were observed for the combination of activated carbon and CCl_4.

Table 2. Rate constants for various additives

Concentration (g/L)	k (min^{-1})	R^2
Activated carbon		
1.000	0.0097	0.98
1.500	0.0123	0.99
2.000	0.0153	0.91
2.500	0.0168	0.88
3.000	0.0189	0.83
H_2O_2 + activated carbon (2 g/L)		
0.100	0.0193	0.92
0.250	0.0240	0.99
0.550	0.0265	0.99
1.000	0.0304	0.97
1.200	0.0321	0.98
CCl_4 + activated carbon (2 g/L)		
0.050	0.0178	0.94
0.100	0.0271	0.99
0.250	0.0309	0.99
0.500	0.0349	0.94
$K_2Cr_2O_7$ + activated carbon (2 g/L)		
0.100	0.0160	0.89
0.250	0.0182	0.93
0.500	0.0194	0.91
1.000	0.0200	0.90

3.4.3 Kinetics of combined effect of activated carbon and CCl_4

The best achieved combination was subjected to further investigate the effect of initial concentration on % COD reduction. The initial COD was varied as 10.9, 9.5, 8.0, 7.3, 6.5, and 5.1 g/L. The change in COD with respect to sonolysis time was recorded and in turn rate constants were determined. The values obtained are given in Table 3. The sonochemical degradation of pharmaceutical wastewater was found to follow the Langmuir–Hinshelwood kinetics ($R^2 = 0.99$) and the k_0 and K_0 values obtained were 0.0230 min^{-1} and 3.68×10^{-5} L/mg, respectively.

3.5 Practical relevance and limitations

The treatment of pharmaceutical wastewater by the proposed methods may appear practically irrelevant and uneconomical. The pharmaceutical wastewater is known to contain complex organics and non-biodegradable compounds and those should be converted into biodegradable compound before subjected to biological treatment. The conversion of such compounds can be achieved using these methods very easily. Therefore, the presented methods can be employed as pretreatment techniques and such treated effluent can be subjected to biological treatment. This approach definitely will improve the efficiency of the treatment plant and also will reduce the operating costs. The major limitation of this study is the toxic effect of additives used. For example, CCl_4 present in the treated water may migrate into the atmosphere in a matter of days and may produce some ill effects. The presence of hydrogen peroxide causes corneal damages in eyes, whitening and bleaching of skin and ingestion of H_2O_2 causes irritation to the upper gastrointestinal tract. High doses of $K_2Cr_2O_7$ interfere with nerve impulses and affect heart functioning. Therefore, after the treatment the water should be checked for the presence of these additives and accordingly necessary action must be taken to remove excess amount present. The other limitation is the separation and recycling of activated carbon.

Table 3. Rate constants for carbon tetrachloride (100 mg/L) and activated carbon (2 g/L) at various initial COD

Initial COD (g/L)	k (min^{-1})	R^2
5.067	0.04316	0.98
6.533	0.04294	0.99
7.267	0.04206	0.99
8.000	0.04175	0.99
9.467	0.04076	0.99
10.933	0.03830	0.99

4 Conclusions

The influence of addition of activated carbon and activated carbon in combination with H_2O_2, CCl_4, and $K_2Cr_2O_7$ on sonochemical degradation of pharmaceutical industry wastewater was studied. A maximum % COD reduction (83%) was observed with the addition of CCl_4 (100 mg/L) and activated carbon (2 g/L). The % COD reduction was strongly influenced by the initial pH and a better reduction was observed at pH 6 for the best combination. The data obtained were found to follow pseudo first order kinetics and higher rate constant values were observed for the combined addition of CCl_4 (100 mg/L) and activated carbon (2 g/L). The data obtained with the best combination were found to fit well with the Langmuir–Hinshelwood kinetic model. The proposed methods can be used as a pretreatment for destructing complex organic molecules into simpler molecules, which can be further treated easily with conventional biological treatment. However, the toxic nature of the additives used in the present study restricts the practical applicability of the methods presented.

The authors have declared no conflict of interest.

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