

Treatment of Pesticide Wastewater by Physicochemical and Fenton Processes

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The process of pesticide removal from industrial wastewater using which chemical, vacuum-chemical and Fenton's reactions have been analyzed. Fenton process is attractive alternative to conventional oxidation processes in effluent treatment of recalcitrant compounds. The aim of this study is to evaluate the efficiency of chemical, vacuum and Fenton processes for the reduction of chemical oxygen demand in wastewaters from pesticide industry. In this study wastewater from pesticide industry was used. Whereas in the chemical procedure $[\text{Ca}(\text{OH})_2]$ and $[\text{KMnO}_4]$, the chemical oxygen demand removal efficiency is 94.9 %; in the vacuum- $[\text{Ca}(\text{OH})_2]$ + $[\text{KMnO}_4]$ system (with 250 mg/L $[\text{KMnO}_4]$, 1 mL H_2SO_4 , 5 mg/L polyelectrolyte and 2000 mg/L CaOH application) this efficiency was 97.8 %; and a 99.8 % KOI removal efficiency was obtained by the Fenton process (the optimum ratio of $[\text{Fe}^{2+}]$ to $[\text{H}_2\text{O}_2]$ was 1:1.56 (mM/mM), at pH 3.0).

Key Words: Pesticide, Industrial wastewater, Physicochemical treatment, Fenton process, Chemical oxygen demand removal.

INTRODUCTION

The most important portion of contamination due to pesticide is observed in agricultural areas and in surface waters that come from agricultural areas. An important quantity of pesticide is released from pesticide production plants. Pesticides usually have direct adverse effect on the living organisms. These compounds are toxic and carcinogenic in nature even at low concentration¹. Along with municipal point sources and industrial discharges, urban stormwater runoff has been identified as a primary source of pollution of surface waters with pesticides². The process of pesticide removal from industrial wastewater is of great importance because of well known pesticide

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resistance to microbial degradation and its ability of accumulation in the environment as well as possible carcinogenic and mutagenic properties³. The main causes of surface water and groundwater contamination are industrial discharges and agricultural activities.

Currently the reactors which are used in pilot scale and on which researches are made are parabolic trough reactors, fixed bed reactors and double-skin sheet reactor. Even though the current reactors have advantages of their own, they also have process, toxicity and efficiency disadvantages⁴. Other processes include: chemical coagulation, photo-oxidation, sedimentation, filtration, adsorption⁵. In these processes, partial elimination of pesticides is achieved and the efficiency of pesticide removal or degradation is heavily dependent on the chemical nature of the pesticides being treated⁶ in addition to the mechanism of the treatment process itself.

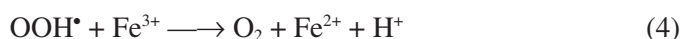
The oxidation system based on the Fenton's reagent has been used for the treatment of both organic and inorganic substances. Fenton's chemistry uses hydrogen peroxides (H₂O₂) and iron salts where the effectiveness of H₂O₂ is improved by iron through generation of highly reactive hydroxyl radicals. The iron acts as a catalyst in the process. Iron typically occurs naturally in the subsurface or may be added in small concentrations. If the hydroxyl radical is the key intermediate, the initiation step would be⁷:



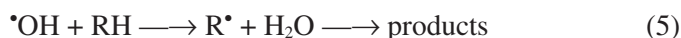
Afterwards, $\bullet\text{OH}$ radicals may either oxidize another Fe²⁺ to Fe³⁺ (termination step):



or they may give reaction with H₂O₂ (propagation step):



Also, the $\bullet\text{OH}$ radical may oxidize other species (substrate) present in solution:



In comparison to other oxidation processes, such as UV/H₂O₂ process, costs of Fenton oxidation are quite low⁸. Fenton oxidation has been used for different treatment processes because of its ease operation, the simple system and the possibility to work in a wide range of temperatures⁹. Hydroxyl radicals are powerful oxidizing reagents with an oxidation potential of 2.33 V and exhibits faster rates of oxidation reactions as compared to that using conventional oxidants like hydrogen peroxide or KMnO₄⁷.

We report in this paper the results obtained during removal of pesticides from industrial wastewater by chemical oxidation, chemical oxidation + vacuum application and Fenton process. The vacuum process was used to

determine if pressure has any effect on pesticide decomposition. It was used to specify the effects of chemical oxidation on the pesticide increase efficiency. Fenton process is an attractive alternative to conventional oxidation processes in effluent treatment of recalcitrant compounds. The aim of this study is to evaluate the efficiency of all used process for the reduction of chemical oxygen demand (COD) in wastewaters from pesticide industry.

EXPERIMENTAL

Wastewater was supplied by pesticide industry located in Turkey as 24 h composite samples. Chemical oxygen demand (COD) concentration in effluent was 11.400 mg/L. All chemicals used for Fenton were at least reagent grade and obtained from Merck. Chemicals used for the Fenton experiments were hydrogen peroxide (35 % w/w, Merck), ferrous sulphate hepta hydrate (Merck), sodium hydroxide pellets (Merck), potassium permanganate (Merck) and sulphuric acid (Merck). Hydrated lime [Ca(OH)₂] was used in flocculation step were purchased as commercial. Distilled water was used to prepare the desired concentration of solutions.

Chemical oxidation-Coagulation process: In this process first there is a chemical oxidation with KMnO₄ and then coagulation with Ca(OH)₂ and addition of polyelectrolyte. The pH of the wastewater is 7.6. The pH level has to be decreased to 2-3 for the effective chemical oxidation of the complex organic materials dissolved in water. The pH level of the wastewater was set by H₂SO₄ (6 N). After the setting of the pH level, steady amounts of of KMnO₄ (250 mg/L) and polyelectrolyte (10 mg/L) were used to determine the Ca(OH)₂ dose (from 250 to 2500 mg/L). After determining the optimum Ca(OH)₂ dose varying doses of KMnO₄ (from 250 to 2500 mg/L) were used. The reaction time was set as 0.5 h. After the chemical oxidation the pH level was set to 8-9 by using NaOH (6 N) to be able to reach the coagulation conditions. After all these processes are over the mixing process is stopped and COD removal efficiencies were determined after 1 h of precipitation.

Vacuum method: This was used to determine if pressure has any effect on the degradation of the pesticides or not. After the preparation of the samples, pressure was applied on them. The vacuum time was 5-25 min. In the vacuum process a vacuum pump of 1 kW power was used. In the samples subjected to pressure the best COD removal conditions have been applied.

Fenton process: The Fenton process serves both oxidation and coagulation functions in this study. The following parameters of Fenton's reaction were examined and optimized at pH 3: Fe²⁺ concentration, H₂O₂ concentration. Magnetic stirrers (Chiltern, HS31) were used to ensure mixing

at a constant rate during all experiments. Oxidation experiments were run at constant room temperature (20 ± 1 °C), 500 mL glass beakers that were continuously stirred for up to 0.5 h at a constant rate of 90 rpm, after initiation of the Fenton process. For that purpose, first the pH of the freshly prepared effluent solution was adjusted to 3.0 by using 6 N H_2SO_4 ¹⁰. Afterwards, proper amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added to the reaction solution as the ferrous iron source. The reaction was assumed to start with the addition of H_2O_2 . After the selected reaction time, usually set as 0.5 h for the preliminary optimization experiments, the experiment was ceased with the addition of 6 N NaOH as to increase the pH to around 9, to precipitate ferrous iron out as solid $\text{Fe}(\text{OH})_3$.

Calcium hydroxide was used in flocculation step as coagulants. Chemical coagulants were added and mixed for 2 min under rapid mixing condition (100 rpm). The solution was mixed at slow flocculation (30 rpm) for 0.5 h after rapid mixing. Residual COD and pH of supernatant were measured after settling for 1 h. The coagulations were conducted by varying the initial pH (8-9) and the coagulant concentration. The procedure was shown in Fig. 1.

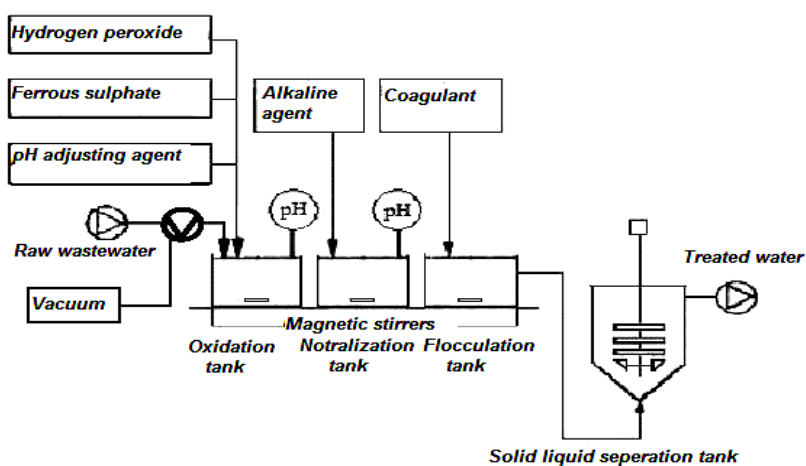


Fig. 1. Treatment flowsheet for chemical oxidation-coagulation process, vacuum application, fenton's reagent

Analytical methods: Residual H_2O_2 results in an increase in COD concentration. Thus, previous to the COD determination, it was necessary to remove it. After a settling period of 1 h, samples were kept in an oven at 50 °C for 0.5 h to remove the interference of residual H_2O_2 on the COD measurement¹¹. The presence of residual H_2O_2 was checked by H_2O_2 test strips (Macherey-Nagel).

All samples were filtered through 0.45 μm membrane filters (purchased from Whatmann) to remove iron prior to analyses. COD was determined in accordance with Standard methods (closed reflux, titrimetric method No. 5220C)¹². pH was measured by using a pH-meter (multimeter 314i, WTW Germany).

RESULTS AND DISCUSSION

Chemical oxidation-coagulation process

In the first phase the H_2SO_4 , KMnO_4 and polyelectrolyte were held constant and the optimum $\text{Ca}(\text{OH})_2$ dose was determined by applying different dosages of $\text{Ca}(\text{OH})_2$. The COD removal efficiencies obtained are given in Fig. 2. The KMnO_4 dose was determined by keeping this optimum $\text{Ca}(\text{OH})_2$ dose constant. The best COD removals and the results of this study are given in Fig. 3. The optimum $\text{Ca}(\text{OH})_2$ dose was determined by keeping the polyelectrolyte constant and trying different $\text{Ca}(\text{OH})_2$ doses.

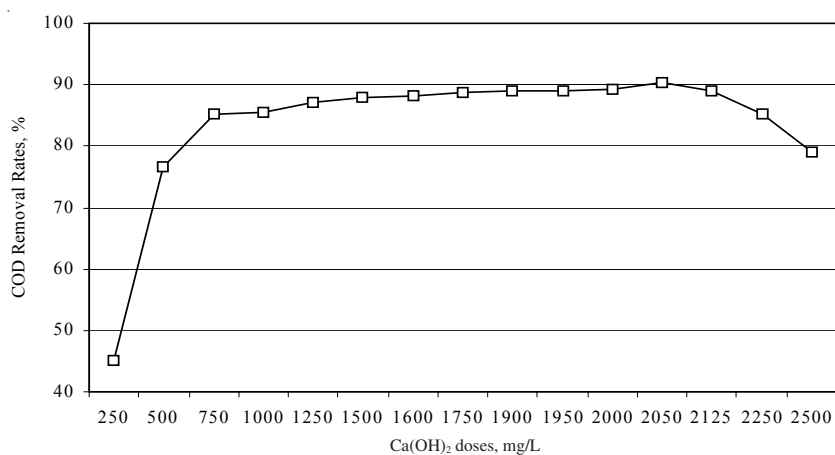


Fig. 2. Chemical oxygen demand (COD) removal efficiencies obtained at varying $\text{Ca}(\text{OH})_2$ doses

The sample pH was determined to be 7.6. Because the pH value is very high the pH of the solution was adjusted by using H_2SO_4 . After the adjustment of the pH level 250 mg/L KMnO_4 and 10 mg/L polyelectrolyte was added. Finally varying doses of lime was added.

By looking at the sample specifications and the results in Fig. 2, the optimum kireç dose was determined to be 2050 mg/L. A 90.6 % COD removal efficiency was obtained at a $\text{Ca}(\text{OH})_2$ dose of 2050 mg/L. At this kireç dose a study was made for the KMnO_4 dose.

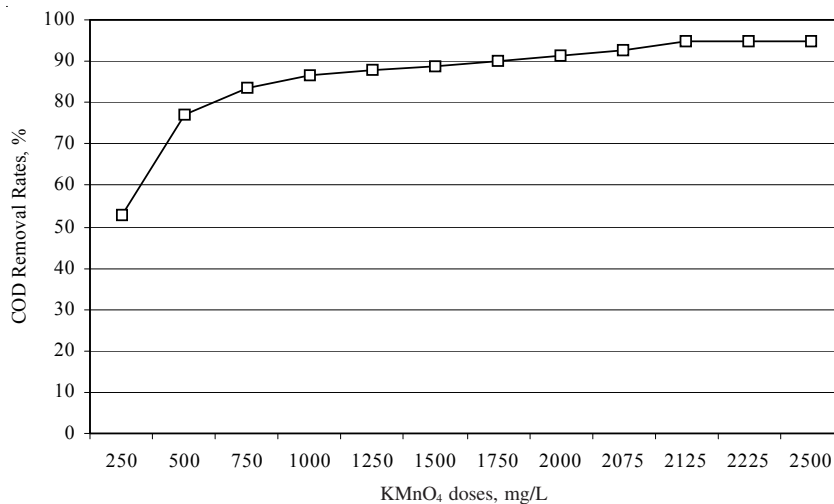


Fig. 3. KOI Values determined for differing doses of KMnO₄

After setting the pH value of the sample to 3 varying doses of KMnO₄ were added. The best kireç dose obtained in the previous study and a constant Ca(OH)₂ (2050 mg/L) and polyelectrolyte (10 mg/L) level was used at pH 3.

In this study where a 2125 mg/L of Ca(OH)₂ was held constant the most suitable KMnO₄ dose was determined to be 2125 mg/L (94.9 % COD removal efficiency). Similar values were obtained at KMnO₄ doses of 2125, 2250 and 2500 mg/L.

Vacuum-chemical methods

We used the vacuum method thinking that the degradation of the pesticides would be faster. A vacuum was applied on the sample inside a closed box by a vacuum pump of 1 kW power for 5, 10, 15, 20 and 25 min. Optimum chemical doses obtained by the chemical method were applied to each sample on which vacuum was applied. The chemical method conditions were Ca(OH)₂ (2050 mg/L), KMnO₄ (2125 mg/L) and polyelectrolyte (10 mg/L) at pH 3.

In the vacuum method it was observed that after 15 min of application the pesticides were decomposed with an efficiency of 16.5 % and this made a further addition to COD removal (Fig. 4). In the vacuum + chemical method after 15 min of vacuum application a 97.8 % COD removal efficiency was obtained with the chemical method-Ca(OH)₂ (2050 mg/L), KMnO₄ (2125 mg/L) and polyelectrolyte (10 mg/L) at pH 3.

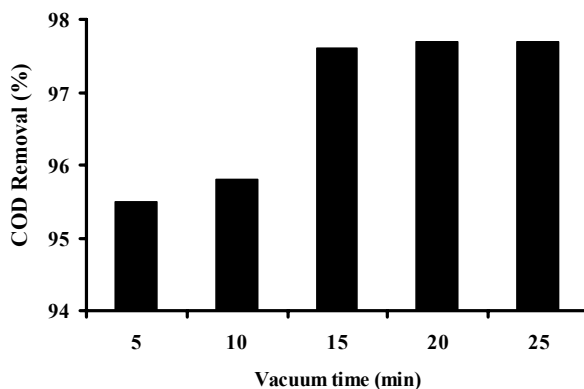


Fig. 4. Chemical oxygen demand (COD) removal efficiencies for differing vacuum times

Fenton process

In order to determine the optimum initial H_2O_2 concentration, a set of experiments was carried out for wastewater for which the concentration of H_2O_2 was progressively increased while maintaining the concentration of Fe^{2+} constant at an arbitrary value of 1600 mM. All experiments were carried out for 0.5 h of reaction time and at an initial pH of 3. The hydrogen peroxide concentrations studied were in the range of 150-2000 mg/L. The optimum H_2O_2 concentration was determined as 1300 mg/L. After this, 1500 mg/L $\text{Ca}(\text{OH})_2$ and 10 mg/L polyelectrolyte was added and NaOH was added until the pH became 8 for precipitation conditions. Per cent COD removal efficiencies obtained after Fenton's treatment of wastewater at varying initial H_2O_2 concentrations are presented in Fig. 5. Therefore, H_2O_2 should be added at the optimal concentration to achieve the best degradation.

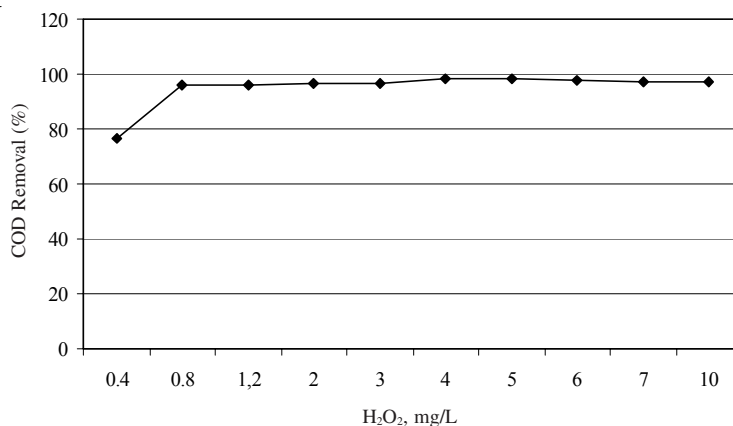


Fig. 5. Chemical oxygen demand (COD) removal rates for differing doses of H_2O_2

Role of pH in Fenton reaction must be determined. The COD degradation of model substances by Fenton treatment as a function of pH are shown in Fig. 6. The experiments were carried out a pH range from 2 to 4 (Fig. 6). The results clearly indicate that the extent of degradation decreases with the increase in pH value for pH 2-4. This demonstrates that the most effective pH value for degradation of the selected model substrates by Fenton treatment is 3. At acidic pH values, it has been shown that H_2O_2 decomposes to produce OH^\bullet radicals. For pH values above 4, the degradation strongly decreases because at higher pH values iron precipitates as ferric hydroxide.

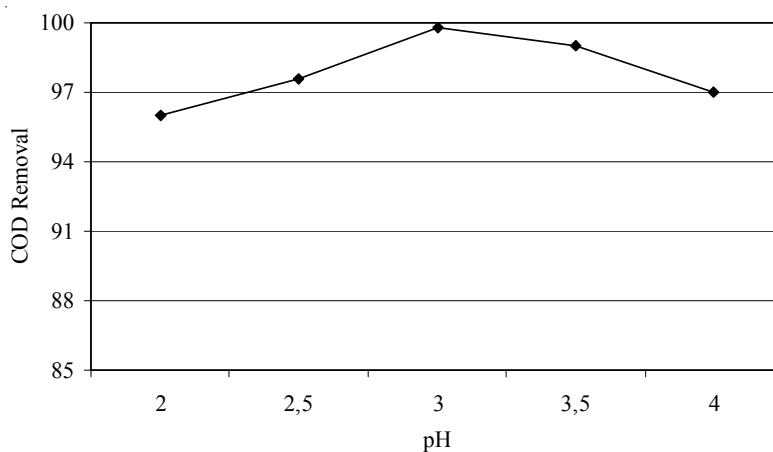


Fig. 6. Chemical oxygen demand (COD) removal efficiencies for differing pH values

For Fenton pH was set to 3, in the flocculation-coagulation process this value has to be high for $Ca(OH)_2$ efficiency (pH 8-9). For this, apart from the conditions described above the H_2O_2 dose was set to 1300 mg/L and studies were made at differing pH values (Fig. 7). A maximum COD degradation (99.8 %) was obtained with the Fenton treatment within 0.5 h at last pH 8.4 (Fig. 7) and 1600 mg Fe^{2+} /L (Fig. 8). The pH value has a decisively effect on the oxidation potential of OH^\bullet radicals because of the reciprocal relation of the oxidation potential to the pH value¹⁰.

The oxidation processes were repeated at the optimum operating conditions for the degradation of the mixture of the used model substances to represent the real wastewater effluent from a pesticide-producing company. The oxidation efficiency of the Fenton reaction is at a maximum when the pH value is between 2-5 and the H_2O_2/Fe^{2+} ratio is 1:1. The mechanism of this reaction was tested for a wide range of enzymatic reactions¹³ and reactions of organic compounds.

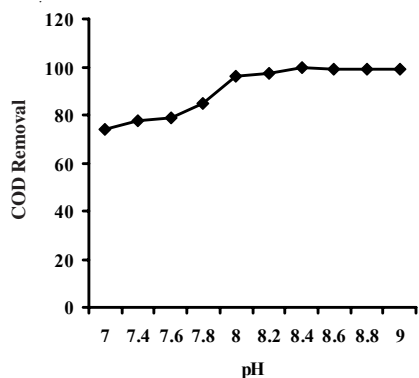


Fig. 7. Chemical oxygen demand (COD) removal efficiencies for differing pH values

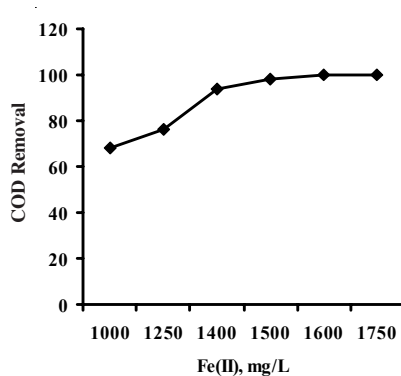


Fig. 8. Chemical oxygen demand (COD) removal efficiencies for differing Fe(II) doses

For the decomposition of a 50 mg/L Dichlorvos containing aqueous solution by sunlight effect and in the presence of a photocatalyzer in sunny and cloudy days was found to be differing between 76.49-93.20 and 45.14-85.77 % when left under the sun for 2.5 h¹⁴. In the filtration study of pesticides containing organochlore with the Fenton process an efficiency higher than 90 % was obtained. The optimum Fe²⁺/H₂O₂ ratio was determined to be 1/3 and 1/2 when the pH value is between 3.0-3.5. In this study, CaO was used as a coagulant³. Stearman *et al.*¹⁵ used the wetland system in pesticide removal studies. In a period of two years different pesticide types were filtrated in wetland cells (pool) with an efficiency between 63.2-82.0 %. In studies made with lignocellulosic materials efficiencies close to those of studies with granulated active carbon (12-96 %) were obtained¹⁶. The examined Fenton's reaction was found to be very efficient for removing pesticides from industrial wastewater. The best removal efficiency was achieved for fenitrothion (from 98.5 to 100.0 %) and chlorfenvinphos (from 97.1 to 100.0 %)³.

In the study, we analyzed the pesticide industry wastewater. Three different methods were used to filtrate the pesticide material that is very polluting. Two of the methods used to remove pesticide are chemical and one is physico-chemical. In laboratory scale studies, good efficiencies were obtained for all the three methods. In the first method, H₂SO₄ and KMnO₄ and in the second method H₂O₂ and FeSO₂ were used as chemicals. The second method of vacuum + chemical increased the efficiency by 16.5 % compared with the first method. In the Fenton process a better COD removal efficiency was obtained with a lower chemical usage compared with those of the first and second methods. Where the KOI removal efficiency is 94.9 % in the

first method, a COD removal efficiency of 99.8 % was obtained with the vacuum + chemical method. In the Fenton method the COD removal efficiency was 99.8 %.

The pesticide that causes toxic effect on both aerobic and anaerobic biological systems caused inhibition for these types of processes. Researchers obtained some positive results for wetland systems also called filtration in the field. However not knowing the treatment duration and the results of continuous feeding poses some unknown values for this system. Whereas in chemical filtration when continuity and efficiency are taken into account, the only problem is slurry.

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