REMOVAL OF ANTIBIOTIC RESIDUE FROM AQUEOUS SOLUTION BY ADVANCED OXIDATION PROCESS

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ABSTRACT

Advanced oxidation processes are low-cost, highly efficient, and eco-friendly technologies in the removal of organic pollutants in wastewater using hydroxyl radicals for oxidation. Hydroxyl radicals possess high oxidation potential and can react with organic compounds, resulting in the complete mineralization of these compounds into carbon dioxide, water, and inorganic salt or their conversion into other compounds. The present investigation deals with the removal of tetracycline from water using simulated ultraviolet radiation and hydrogen peroxide, assessing the effect of operational parameters like the solution's initial pH, retention time, hydrogen peroxide dosage in terms of chemical oxygen demand (COD) removal from the standard aqueous solution of tetracycline. Results indicate that alkaline conditions and larger hydrogen peroxide dosage negatively affect the degradation. The removal efficiency of 68 % was achieved at 150 min of batch reaction under optimum conditions: pH = 4, and a dose of hydrogen peroxide of 0.3 ml per 100 ml of the solution to be treated. At optimum conditions, LC-MS/MS (liquid chromatography tandem mass spectrometry) analysis results showed a reduction in initial concentration of aqueous solution of tetracycline. Photocatalytic degradation followed pseudo-first-order kinetics with the rate constant (k) of 0.0061 min^{-1}. Photocatalysis based on hydrogen peroxide is effective in the degradation of tetracycline in an aqueous solution and can be applied as a pretreatment of hospital wastewater containing tetracycline residues.

Keywords: *organic contaminant, tetracycline, AOP, COD*

INTRODUCTION

To prevent the infections caused by the pathogenic microorganisms, different types of antibiotics are used. Antibiotics are low to medium-molecular-weight compounds exhibiting various chemical and biological properties. This is important for chemotherapeutic and prophylactic purposes and is also used as feed additives to promote growth and improve feed efficiency in animals [1]. Antibiotics can kill and also inhibit the growth of pathogenic bacteria. [2]. However, pharmaceutical residues are widespread and occasionally found in surface water with inherent bioactive properties, while water preservation is a matter of debate and argument among policymakers [3].

Antibiotics are a class of pharmaceutically active compounds with high usage and consumption all over the world [4]. Large amounts of antibiotics are daily used for patient care and control of infections in hospitals. These antibiotics are excreted through the feces and urine of the patient and reach liquid waste [5]. In addition to wastewater, biofilms are also investigated in drinking water from river bank filtrate to estimate the occurrence of resistant bacteria and their resistance genes, thus indicating possible transfer from wastewater and surface water to the drinking water supply network [6].

The occurrence of antibiotic residues in sewage treatment plants poses a problem due to the reasons such as increased risks to human health from the development of antibiotic-resistant microorganisms if antibiotics are present in sub-lethal concentrations of the pathogen in the sewage [7]. The occurrence of antibiotics in the aquatic environment has raised concern regarding their potential impact on drinking water quality [8]. Antimicrobial resistance (AMR) is an emerging worldwide threat [9]. Therefore, antibiotic residue is considered as public health hazard [10].

However, many antibiotics with different structures have been found in the environment that are regarded to have poor biodegradability and may affect living organisms. Several physico-chemical, biological, and advanced techniques were evaluated to treat water containing contaminants such as antibiotics, and their efficiency depends on the type of contaminants to be degraded and related operating parameters [11]. Antimicrobial drugs are among the most commonly used medications in the world. Tetracycline is a widely used antibiotic for human and animal therapy due to its broad-spectrum activity, high effectiveness and reasonable cost [12]. The indications for treatment with tetracycline include pneumonia, bone and joint infections, infectious disorders of the skin, sexually transmitted and gastrointestinal infections. However, tetracyclines become a serious threat to the environment because of its overuse by humans and veterinarians and weak ability to degrade. Tetracycline can accumulate along the food chain, causing toxicity to microbial community, encouraging the development and spread of antibiotic resistance, creating threats to drinking and irrigation water and disrupting microbial flora in the human intestine [13].

Advanced oxidation processes (AOPs) are used to treat water contaminated with organic pollutants that cannot be treated using conventional techniques such as filtration, coagulation, and biological degradation due to their chemical stability and low biodegradability [14]. In comparison with other conventional treatment methods, photocatalytic processes are regarded to be low-cost methods. AOPs use generated hydroxyl radicals which oxidize a wide variety of organic molecules [15]. The AOP process using UV/H_2O_2 has proven its ability to degrade various pollutants including pesticides, phenolic compounds, and antibiotics [16].

Tetracyclines are important, broad-spectrum antibiotics that prevent bacterial growth by inhibiting protein synthesis. This large class includes compounds with bacteriostatic activity and a wide range of uses from gram-positive and gram-negative bacterial infections to those caused by a protozoan parasite and intracellular organisms [17]. Therefore, an investigation of AOP-based treatment method for the degradation of the antibiotic residue of tetracycline is carried out to suggest a promising treatment method which is a more practical, convenient, low cost, faster, and easier technique for degrading antibiotics to protect the environment and human health than other conventional methods.

MATERIAL AND METHODOLOGY

Chemicals and antibiotics used for the experiment

Analytical grade hydrogen peroxide (H_2O_2) 30 % (W/W) and tetracycline hydrochloride were purchased from HI Media. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were purchased from Qualigens Fine Chemicals Pvt. Ltd.

Preparation of aqueous solution of tetracycline

The standard antibiotic aqueous solution of 10 mg/L was freshly prepared in double distilled water and stored at 4 °C for further use.

Experimental procedure

An experiment was carried out by using the batch method [18]. The effect of various parameters such as reaction time, pH, and dosage of H_2O_2 on COD reduction efficiency was studied. Initially, COD of stock solution of 10 mg/L were determined. In the batch method, 100 ml aliquot of the tetracycline solution of known concentration was agitated with a dosage of H_2O_2 varying from 0.1 to 0.5 mL. A reaction time of 30 min to 150 min was used. Total 25 experimental sets were used in triplicate to find out efficiency at various dosage and time. After getting the results from the first setup, pH was adjusted using 1 N H_2SO_4 and 1N NaOH at optimum conditions of 150 min, and 0.3 ml of hydrogen peroxide. The total 5 experimental sets in triplicate were used to find out optimum pH. Thereafter, the mixture was subjected to UV radiation with a wavelength of 354 nm using UV lamp inside the laminar air flow. After completion of the preselected time, samples were taken out and filtered through Whatman no. 42 filter paper for COD determination.

COD reduction efficiency

Both the initial and the final COD after completion of experiment were determined using the standard method [19]. pH measurements were done with a pH meter.

COD reduction efficiency was calculated using the following formula [20]:

$$\text{COD reduction efficiency (\%)} = \frac{C_o - C_f}{C_o} \cdot 100 \quad (1)$$

where C_o is the initial COD reading, and C_f is the final COD reading.

Analytical method

The final concentration of the treated aqueous solution at optimum conditions of 0.3 ml hydrogen peroxide, 150 min, and pH = 4 was investigated using LC-MS/MS equipment.

LC-MS/MS analysis was carried out on liquid chromatography-mass spectrometer, model: HPLC 1260Infinity, 6460 QQQ. The mass spectrometer was operated in electrospray positive ionisation mode. Capillary voltage - 2000 V, drying gas temperature - 350 °C, drying gas flow - 13 L/min and nebulising gas pressure - 0.276 MPa were used. Mobile phase consisted of 0.1 % formic acid in ultra-pure water (eluent A) and 0.1 % formic acid in acetonitrile (v/v) (eluent B).

RESULT AND DISCUSSION

The experiment was used to determine the influence of various experimental conditions such as reaction time, hydrogen peroxide dosage, and pH of the solution on the removal of tetracycline which was measured in terms of COD reduction (%). Table 1 shows the experimental matrix and the response factors, corresponding to the tetracycline degradation at various reaction times. Experimental conditions were made variable to establish the conditions that favour the highest COD reduction; it is necessary to evaluate the effect of each parameter. These results could be associated with the interactions between radical species generation and the eventual tetracycline oxidation [21].

Effect of H_2O_2 dosage

The addition of H_2O_2 is a well-known procedure and in many cases it leads to an increase in the rate of photocatalytic degradation [22]. To investigate the effect of hydrogen peroxide dosage on the reaction, experiments were performed by varying this parameter in the range of 0.1 to 0.5 ml of hydrogen peroxide per 100 ml of solution to be treated along with UV irradiation. Table 1 illustrates the effect of H_2O_2 dosage on tetracycline degradation in terms of COD removal. The dosage of 0.1 to 0.5 ml at various reaction times resulted in an increase in COD reduction from 0.1 to 0.3 ml of H_2O_2 dosage, and then at 0.4 ml of H_2O_2 dosage it remained constant. With further increase in the dosage up to 0.5 ml, COD removal was decreased.

Degradation at lower H_2O_2 dosage was presumably due to direct photolysis of H_2O_2 by UV light which can generate hydroxyl radicals. Another mechanism which may partially contribute to the rate improvement is one in which H_2O_2 is suggested to be a better electron acceptor than oxygen [23]. An increase in hydrogen peroxide dosage promotes a higher antibiotic elimination, possibly due to a greater generation of hydroxyl radicals from the decomposition of hydrogen peroxide [24]. However, if the hydrogen peroxide initial amount is very high, an inhibitory effect takes place, a situation that can be attributed to the scavenging of hydroxyl radicals due to the excess of hydrogen peroxide [25], as presented in equation (2). Hydrogen peroxide can react with •OH generating the hydroperoxyl radical (HO_2•), which is a weaker oxidizing agent, reducing the number of available hydroxyl radicals for pollutant removal [26].

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \qquad (2)$$

The above reaction indicates that larger hydrogen peroxide doses could negatively affect the formation of •OH under the experimental conditions evaluated in this study.

Effect of reaction time

The reaction time for the AOP should be as short as possible to avoid high power consumption, which represents about 60 % of the total running cost when using an energy source. However, if the fixed retention time is too short, the intermediates remaining in the solution could still be structurally similar to initial bio-recalcitrant compounds and therefore not biodegradable [27]. The efficiency of AOP depends mainly upon the formation and scavenging of the hydroxyl radicals which vary depending on the provided retention time [28].

Figure 1 shows the effect of retention time on the COD removal rate. The obtained results show that the tetracycline degradation in terms of COD reduction increases with the time from 30 min to 150 min for all preselected doses of hydrogen peroxide. The results reveal that the optimum retention time for the tetracycline degradation is 150 min as it has shown the highest efficiencies that lower retention times.

Table 1. Effect of H_2O_2 dosage on COD reduction efficiency

Sr. No	Reaction time (min)	Initial COD (mg/l)	COD reduction (%) for various H_2O_2 dosage				
			0.1 ml	0.2 ml	0.3 ml	0.4 ml	0.5 ml
1	30	330	23.9 ± 0.2	25.8 ± 0.3	29.7 ± 0.1	29.4 ± 0.3	24.8 ± 0.8
2	60	330	28.2 ± 0.2	35.2 ± 0.2	41.2 ± 0.1	40.2 ± 0.6	32.7 ± 0.6
3	90	330	32.4 ± 0.3	41.8 ± 0.2	50.6 ± 0.5	50.6 ± 0.1	41.5 ± 0.9
4	120	330	45.2 ± 0.4	48.5 ± 0.3	59.4 ± 0.2	58.5 ± 0.5	50.9 ± 0.5
5	150	330	50.3 ± 0.1	53.3 ± 0.1	62.1 ± 0.2	61.2 ± 0.8	59.7 ± 0.3

* values are presented as mean ± SD (n = 3)

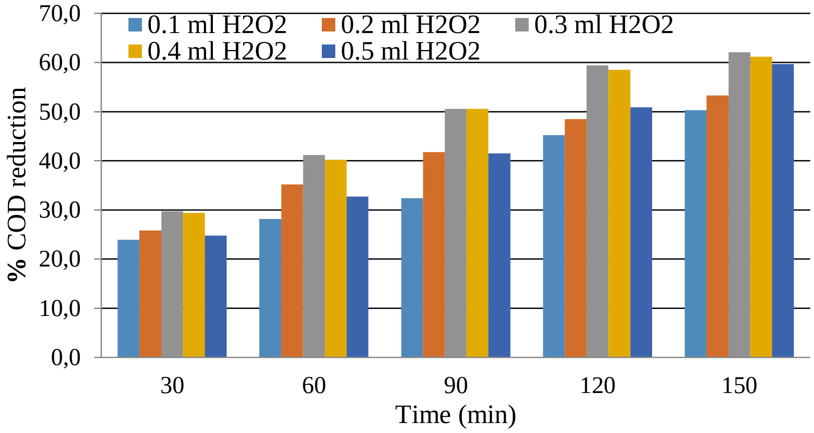

Figure 1. Effect of retention time on COD reduction efficiency

Effect of pH

The pH value influences the generation of hydroxyl radicals and hence the oxidation efficiency. To determine the optimum pH, experiments were conducted by varying the pH in the range 2 - 10. The experimental conditions were: 100 ml of tetracycline stock solution of 10 mg/L, retention time of 150 min and H_2O_2 dosage was 0.3 ml. The value of pH has s significant effect on the oxidation potential of •OH because of the reciprocal relation of the oxidation potential to the pH value [27].

Substantial decrease in COD removal efficiency was observed in correlation with the increasing pH value. It may be due to several reasons such as the fact that at a pH value greater than 7, a rapid decrease in COD reduction was also observed. This is due to a rise in pH which makes the solution alkaline. As H_2O_2 is unstable, it decomposes in alkaline conditions to give O_2 and H_2O and consequently losses its oxidizing capacity [29]. The optimum initial pH for Fenton-like oxidation should be < 4.5. Many investigations have indicated that the optimum pH for the degradation of pollutants decreases with increasing pH value > 3 [30].

The obtained result shows that the optimum pH value for the degradation of tetracycline with optimum retention time and H_2O_2 dosage is 4 (Figure 2). At pH = 4, the COD reduction efficiency has achieved the highest degradation, which is 68 % efficient.

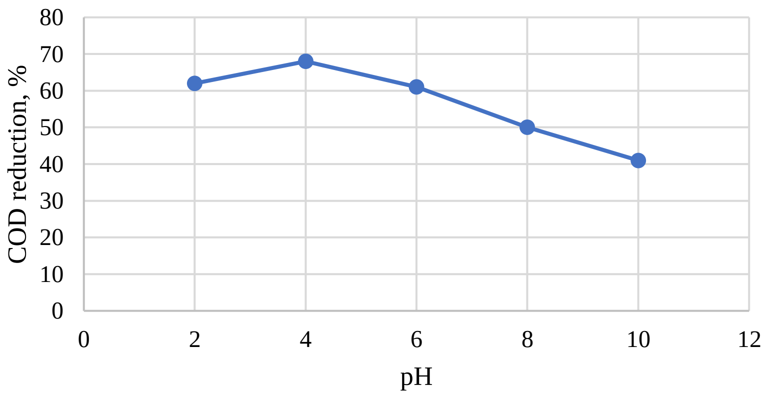

Figure 2. Effect of pH on COD reduction efficiency

Analysis using LC-MS/MS

Qualitative and quantitative analysis was done for the residue of tetracycline and the results represent that there is the decrease in the concentration of antibiotic residue from the initial concentration of 10 mg/L. Figure 3 reveals the results that the final concentration after treatment was 1265.6 ng/l. Figure 4 represents the peak obtained on LC-MS/MS after detection of tetracycline compound.

Table 2 shows the final concentration of tetracycline residue after AOP at optimum conditions.

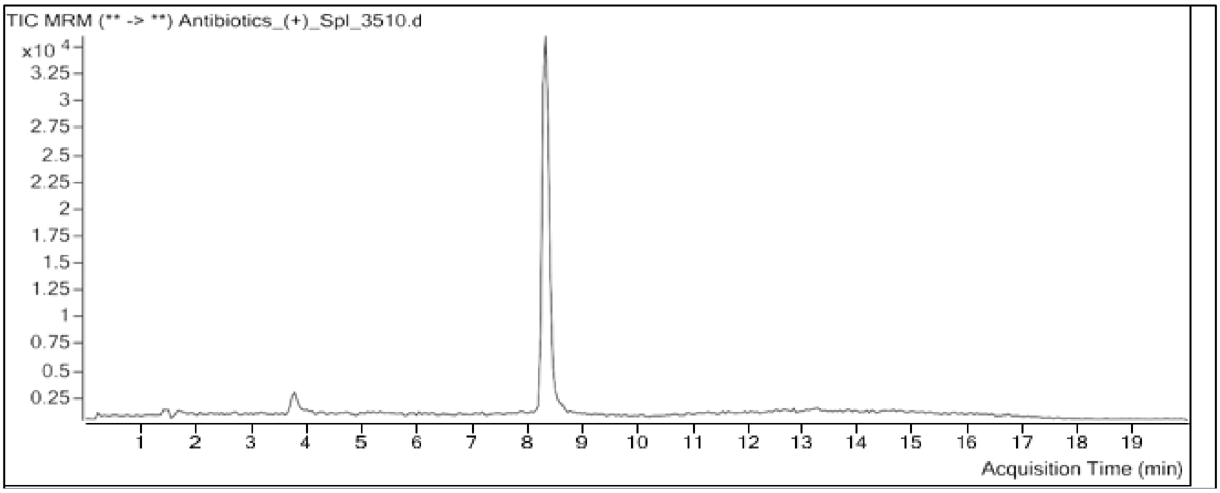

Figure 3. Chromatogram of tetracycline antibiotic residue using LC-MS/MS

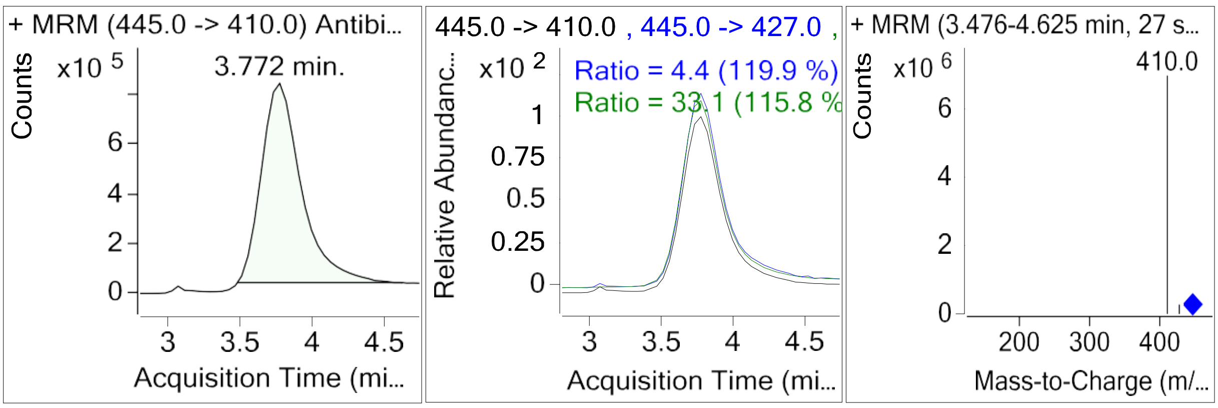

Figure 4. Compound graphics for tetracycline

Table 2. Quantitative results obtained by LC-MS/MS

Quantitation results		
Compound	Final concentration	
Tetracycline hydrochloride	1265.6	ng/l

Kinetics of photocatalytic degradation

To investigate the kinetics of photocatalytic degradation of the tetracycline antibiotics in an aqueous solution, experiments were conducted under optimum operating conditions. The approach was to find out whether photocatalysis degradation of tetracycline follows pseudo-first-order kinetics used by [31] and [32].

The pseudo-first-order kinetics can be represented using a simple expression, such as the following equation [30]:

$$\ln\left(\frac{C_t}{C_o}\right) = -\,k \cdot t \qquad (3)$$

where k is the pseudo-first-order rate constant, t is the irradiation time in min, C_o is the initial concentration of tetracycline in aqueous solution and C_t is the residual concentration of a pollutant at time t. By plotting the graph using the above equation, the rate constant (k) was determined from the slope of the straight line. Photocatalytic degradation followed pseudo-first-order kinetics (Figure 5) with rate constant (k) of 0.0061 min^{-1} and R^2 (correlation coefficient) value of 0.9387 for COD removal.

CONCLUSION

In the current work, various experimental conditions such as time, pH, and amount of H_2O_2 were examined using the batch method at room temperature and COD removal rate as a standard for assessment. In AOP using UV and hydrogen peroxide, experimental conditions have great influence. It is found that efficiency increases with respect to the dosage of hydrogen peroxide until the achievement of equilibrium and then it remains constant, but if excessive H_2O_2 is used for AOP, then that may result in negative effects. Obtained results show that efficiency increases with respect to time from 30 min to 150 min. It is also found that the highest efficiency is achieved at pH = 4. The optimum operating conditions for degradation of the tetracycline antibiotics in an aqueous solution containing 10 mg/L were: hydrogen peroxide dosage = 0.3 ml per 100 ml of the solution to be treated, retention time = 150 min, and pH value = 4. Under these optimum conditions, 68 % COD removal was obtained. Results are verified by using LC-MS/MS for the sample which is treated at optimum conditions, and it has been revealed that the concentration of antibiotic residue decreased. Finally, it is recommended to apply the used treatment method (AOP) in the treatment of wastewater containing organic compounds since it is a user-friendly and low-cost method.

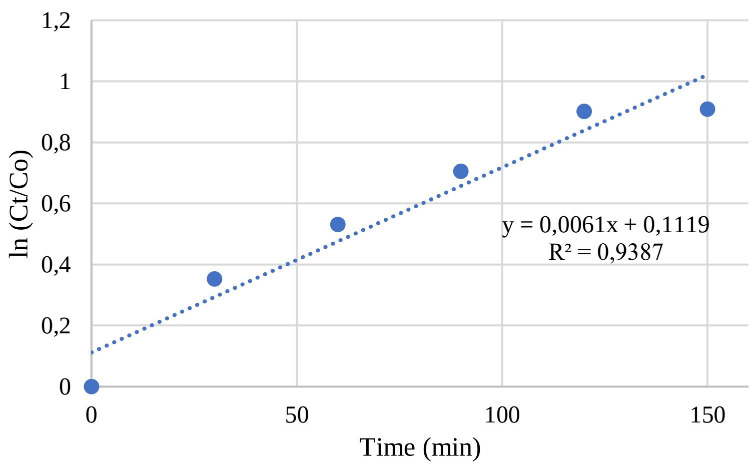

Figure 5. Kinetics of photodegradation in terms of COD removal

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