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Original Article

Utilization of Activated Carbon Catalyzed Ozonation (ACCO) for Removal of Ciprofloxacin and Vancomycin from Hospital Wastewater

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Abstract

Background: Hospital wastewater is considered by health and environmental researchers due to the presence of various hazardous chemical contaminants such as residual of antibiotics and other drugs. The conventional treatment processes are not able to complete removal of them, and could lead to the entry of these compounds into the environment. Then, we aimed to analyze and evaluate the removal of ciprofloxacin and vancomycin antibiotics from hospital wastewater.

Methods: The effect of antibiotic concentration and reaction time was investigated on the performance of single ozonation (SOZ) and activated carbon catalyzed ozonation (ACCO). In addition, COD and BOD of the effluent, antibiotics degradation kinetics and mathematical modeling were determined. Solid phase extraction columns (SPE) and high-performance liquid chromatography (HPLC) methods were used to extract and measure the intended antibiotics, respectively.

Results: The results of this study showed that degradation of both antibiotics follow pseudo-first order kinetic. SOZ was able to eliminate 6 mg/L of vancomycin and ciprofloxacin within 45 and 65 min, respectively. Due to the synergistic effect of activated carbon on ozonation, ACCO significantly reduced the degradation time to 20 and 25 minutes, respectively. BOD/COD ratio at the outlet of ACCO process increases from 0.2 in raw wastewater to 0.4 in treated wastewater, which could be appropriate for biological treatment.

Conclusion: ACCO could be considered an efficient process for degradation of antibiotics in hospital wastewater.

Keywords: Catalyzed ozonation; Antibiotic; Hospital wastewater; Activated carbon

Introduction

Personal care products and pharmaceuticals are among the emerging contaminants increasingly observed in water resources. The adverse effect of these compounds in the aquatic environment has been approved (1, 2). Several authors have documented residual of pharmaceutical compounds in the environment (3-5). Antibiotics are the most widely used and frequently prescribed ones among the pharmaceuticals (6). Development of antibiotic resistant bacteria have raised a great concern in recent years due to the exposure to the residual of antibiotics in the environment (7).

Hospital wastewater is one of the major sources of antibiotics secretion to the environment due to the high consumption of antibiotics for treatment of infectious diseases (8, 9). Therefore, recently many researchers are interested in the removal of drug compounds from hospital wastewater.

Although biological processes are commonly used for wastewater treatment, but degradation of antibiotics by microbial population is not well documented (10, 11). In addition, biological reactors could lead to the proliferation of the resistant microbial species. Physical processes such as adsorption do not degrade the contaminants, and they are only transferring the contaminant from the aquatic to the solid phase. In addition, adsorbent regeneration is the other limiting factor (12).

Several oxidizing agent such as ozone, hydrogen peroxide, and chlorine dioxide have been used for degradation of wide range of contaminants (13). High reaction rate along with the high mineralization of the wide range of organic contaminants are the main advantages of oxidation methods for wastewater treatment as compared with the conventional methods (14).

Ozone has highest oxidation potential (E°= 2.07eV) among the conventional oxidizing agents leading to the direct reaction with organic compounds (15, 16). However, partial oxidation of contaminants, poor mass transfer rate, and low solubility and stability in the aqueous solutions and thus high treatment cost are the most limitative factors for S. Then, SOZ could not completely mineralize organic compounds (17). In order to overcome the above-mentioned problems, ozone-based advanced oxidation processes such as UV/O_3, O_3/H_2O_2, and ACCO have recently been developed (18-20). In ACCO, a solid catalyst is added to the ozonation reactor to gain the controlled decomposition of ozone and formation of hydroxyl radical which is a strong oxidizing agent (20).

We aimed to investigate the efficacy of ACCO process for degradation of antibiotics from the real hospital wastewater samples. Vancomycin and ciprofloxacin were selected as model antibiotics in the preset study. The effect of antibiotic concentration in SOZ and ACCO processes, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) reduction of the wastewater and the kinetics of pollutants degradation were investigated, and finally mathematical models were developed for degradation of the antibiotics.

Materials and Methods

Material and chemical reagents

The analytical grade of vancomycin and ciprofloxacin were obtained from a local pharmaceutical company and prepared standard solutions. Wastewater samples were taken from Emam Reza Hospital, Tabriz, Iran. In order to investigate the feasibility of the suggested process for antibiotics removal, different concentrations of vancomycin and ciprofloxacin (1.5, 3.0, 4.5 and 6.0 mg/L) were prepared with spiking calculated amount from the standard solutions into the wastewater samples.

Experimental apparatus and procedure

The schematic diagram and details of the reactors and experimental set up has been presented in our previous published study (15). The experiments were conducted in two columns with 2.5 m height and 4.6 cm inner diameter. One of the columns was filled with 3-liter activated carbon and the wastewater was fed from the top for ACCO. The other column was used for SOZ. The ozone generator in the present study was able to generate 5.0 ± 0.2 g/h that was equipped with an oxygen generator (Type CFS-1, New Life Elite oxygen concentrator, Airsep Corporation Company, USA). The generated ozone was continuously fed to the bottom of the reactors by a ceramic diffuser at a constant flow rate of one L/min.

The removal of vancomycin and ciprofloxacin along with COD and BOD were evaluated using SOZ, adsorption and ACCO processes. Removal efficiency was calculated using Eq. [1].

$$\text{RE } (\%) = \frac{C_0 - C_1}{C_0} \times 100 \quad [1]$$

Where, C_0 is the initial concentration of target pollutants, and C_1 is the final concentration in the effluent.

The kinetic of antibiotics degradation for the processes was calculated using the pseudo-first order reaction kinetic (Eq. [2]).

$$ln\left(\frac{C_t}{C_0}\right) = -kt \quad [2]$$

Where, k is the reaction rate constant for SOZ and ACCO process.

Stability tests

The prepared samples of antibiotic were used at the same day, but stability of each analyte was confirmed at low and high and short –term storage at room temperature. The storage time was lower that4 h).

Extraction and measurement of vancomycin and ciprofloxacin

Due to the presence of wide variety of interferences in the real wastewater samples, direct measurement of residual pharmaceutical compounds is not feasible. For this purpose, in most studies, the method of solid phase extraction columns (SPE) is used. The SPE method for separation of vancomycin and ciprofloxacin from the real wastewater sample is an efficient and feasible method. Therefore, extraction of the antibiotics was carried out by SPE columns similar to the method reported in Golet EM, et al. (21) and our previous study (24). The SPE columns used in this study were CHROMABOND®EASY (C18) made by the German company MACHEREY-NAGEL.

Analytical procedure

The antibiotics were detected in wastewater samples by a high-performance liquid chromatography (HPLC) equipped with a UV detector (Agilent Co., USA) at wavelength of 240 and 280 nm, respectively, for vancomycin and ciprofloxacin using a C18 column (Restek Co.: 250 mm × 4.6 mm ID ×5 µm particles). SPE columns are commonly used for pre-concentration, purification and extraction of pharmaceuticals from wastewater samples (9, 22). The extraction method of vancomycin and ciprofloxacin were as follow: the SPE columns were washed with 5 ml methanol, and then 5 ml of deionized water. After that, 250 ml of sample was passed through the columns at a flow rate of 3 ml/min. The column was washed with 6 ml of water/methanol (95:5, v/v). Then, the columns dried by the vacuum pump for 10 minutes. The target compounds were eluted in 5 ml of methanol into 10 ml glass vials. Afterward, the extracted solution was dried to a volume of approximately 0.5 ml using nitrogen gas at 45 °C. Finally, the solute was added in one ml of water/methanol mixture (10:90, v/v) for injection into HPLC.

The mobile phase for determination of vancomycin was a mixture of acetate buffer and acetonitrile containing 0.1% acid formic at 85:15 (v/v%) injected at the flow rate of 0.8 mL/min. The mobile phase for determination of ciprofloxacin was a mixture of acetonitrile/water (20/80 v/v%) which was injected to the column at a flow rate of 0.8 ml/min.

BOD and COD of the samples were measured using the standard methods for examination of water and wastewater (23). All the experiments were conducted in duplicate and the average values have been reported.

Method validation

Linearity, precision, and accuracy

At least five measuring points were used in each curve to evaluate the calibration curve and the linearity criterion. In this study, for each of the ciprofloxacin and vancomycin, seven measuring points with concentrations of 0.5, 1, 2, 5, 10, 15 and 20 mg /l were used to draw the calibration curve and determine the amount of linearity. Correlation coefficients of >0.9946 and 0.9972 were obtained for ciprofloxacin and vancomycin, respectively. Precision and accuracy for the concentration of the calibration points (n = 7) of below 15% were considered. The calibration diagrams of vancomycin and ciprofloxacin are shown in Fig. 1.

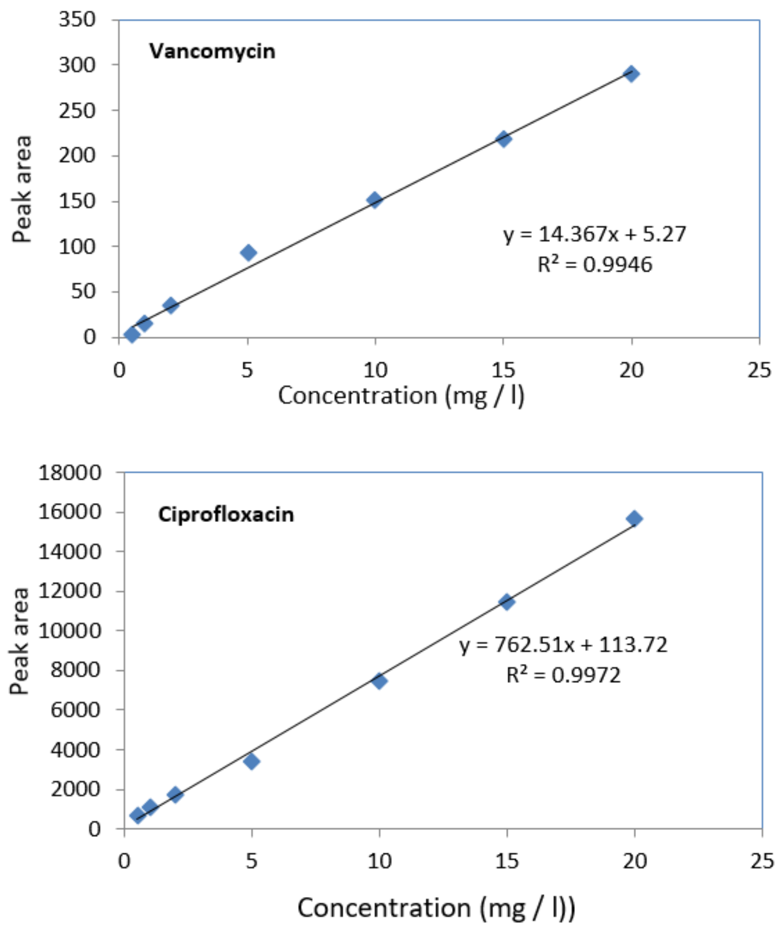

Fig. 1: Vancomycin and ciprofloxacin calibration curves

Table 1 shows the characteristics of the calibration curves plotted for vancomycin and ciprofloxacin. The values of limit of quantification (LOQ) and detection (LOD) are also given in this table.

Table 1: Characteristics of the calibration curves

Medicinal composition	*Correlation coefficient (R^2)*	*Intercept*	*Slope*	*Concentration range (mg/L)*	*LOD (mg/L)*	*LOQ (mg/L)*
vancomycin	0.9946	5.27	14.367	0.5-1	1.1	3.6
ciprofloxacin	0.9972	113.7	762.51	0.5-1	0.44	1.49

Recovery percent of the analytes

In order to determine the recovery percentage of the extraction process, certain amounts of antibiotics were dissolved in the wastewater samples and were extracted using SPE columns. The concentration of vancomycin and ciprofloxacin were measured by HPLC. The values of recovery percentages are presented in Table 2.

The recoveries were calculated using the equation below:

$$\% \text{ Recovery} = \frac{C_{spiked} - C_{measured}}{C_{spiked}}$$

A recovery of more than 50% was considered as the required sensitivity.

Table 2: The peak area obtained from standard samples and recovery percentage SPE of vancomycin and ciprofloxacin

Antibiotic	*Prepared concentration (mg / L)*	*Peak area*	*Concentration in the extracted sample (mg / L)*	*Recovery percentages (%)*
Vancomycin	0.5	13.00	0.31	62
	1.0	15.14	0.64	64
	2.0	35.10	1.31	66
	5.0	93.00	3.42	68
	10.0	151.70	7.14	71
	15.0	217.60	11.50	77
	20.0	290.00	15.60	78
Ciprofloxacin	0.5	706.2	0.36	72
	1.0	1139	0.73	73
	2.0	1738	1.50	75
	5.0	3407	3.90	78
	10.0	7463	8.10	81
	15.0	11481	12.60	84
	20.0	15656	17.7	89

Mathematical modeling of oxidation processes

The least square regression method (independent variables product) was used for each pollutant using EViews software version 6001. Effect of the independent variables such as contact time and antibiotic concentration on the removal efficiency of each pollutant were evaluated with the model.

Results

Single ozonation (SOZ)

In order to determine the contribution of ozone in the suggested catalyzed ozonation, ACCO, removal of vancomycin and ciprofloxacin were investigated in a separate single ozonation reactor, SOZ. Different concentration of vancomycin and ciprofloxacin (1.5, 3.0, 4.5, and 6.0 mg/L) were prepared using hospital wastewater and introduced to the reactor, and after ozonation, individual samples were taken at different time intervals. Fig. 2 and 3 show the kinetic model and removal rate of vancomycin and ciprofloxacin by SOZ, respectively.

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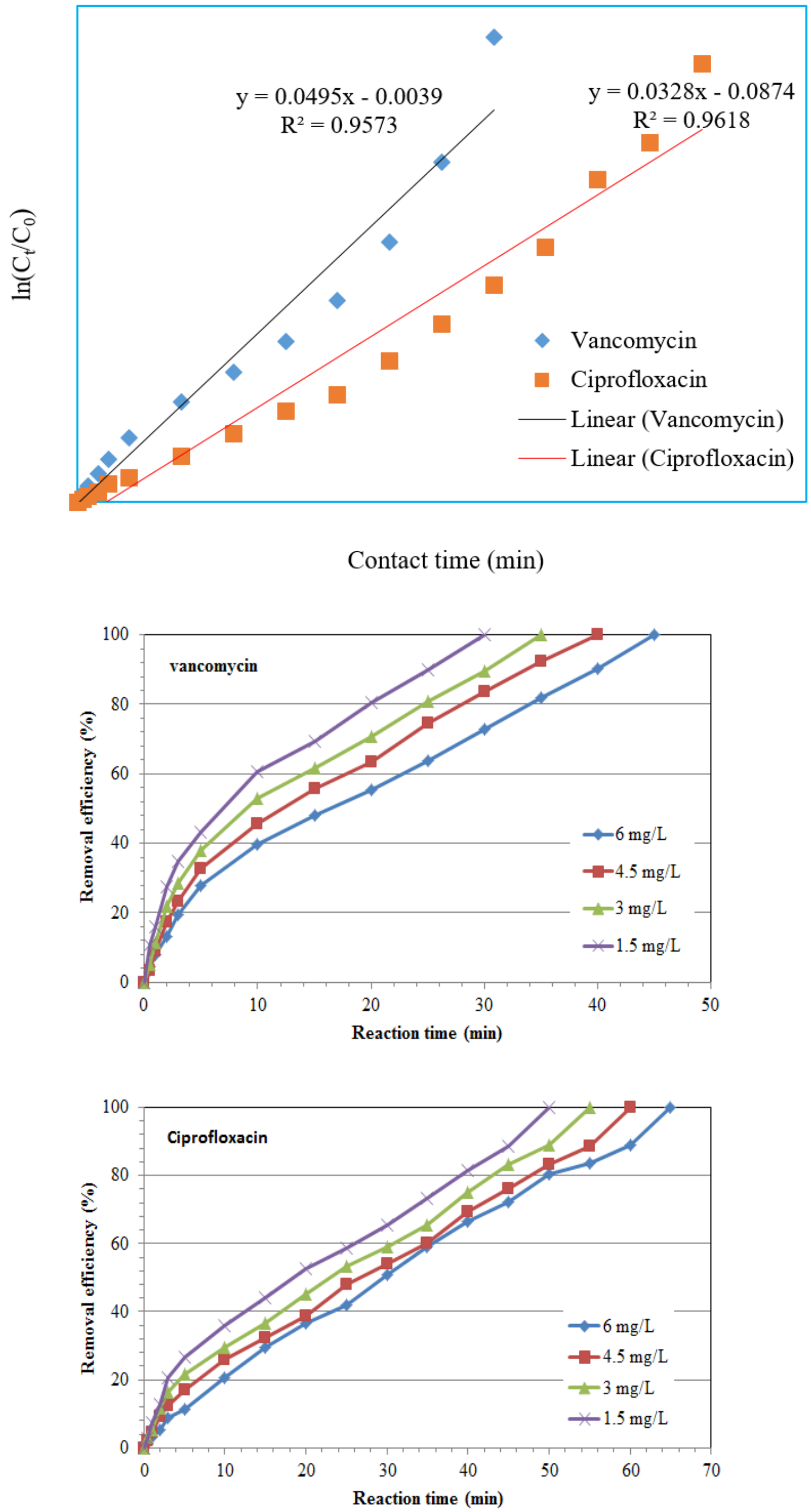

Fig. 3: Removal of vancomycin and ciprofloxacin by SOZ process

Adsorption of antibiotics on to activated carbon

Fig. 4 shows the rate of varying concentration of antibiotics adsorption on activated carbon without ozonation. As shown, the adsorption of vancomycin and ciprofloxacin are increasing rapidly in the first 10 minutes of the reaction time.

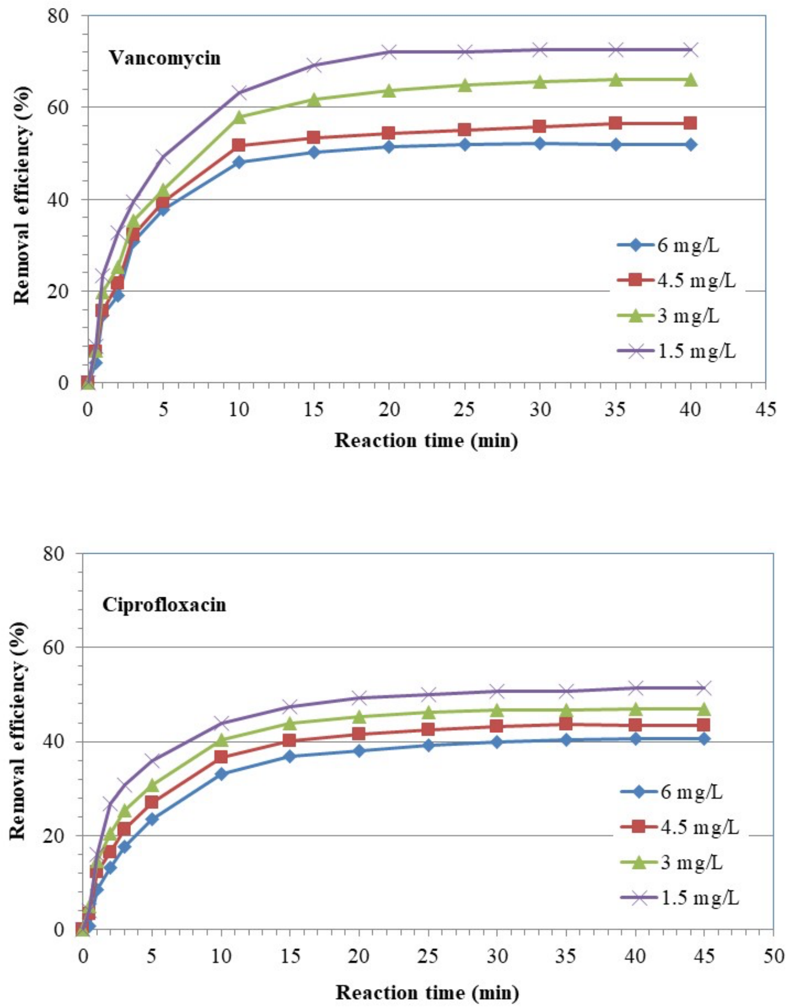

Fig. 4: Adsorption of vancomycin and ciprofloxacin on activated carbon

Activated carbon catalyzed ozonation (ACCD)

In order to distinguish the deference in the performance of single and catalyzed ozonation processes, activated carbon was added to the ozonation reactor. In this way, different concentrations of vancomycin and ciprofloxacin were examined in the process. Fig. 5 and 6 show the kinetic model and removal rate of vancomycin and ciprofloxacin by ACCO process, respectively. As shown in Fig. 6, ozonation in the presence of activated carbon leads to a significant improvement in the performance of the process in the removal of the antibiotics.

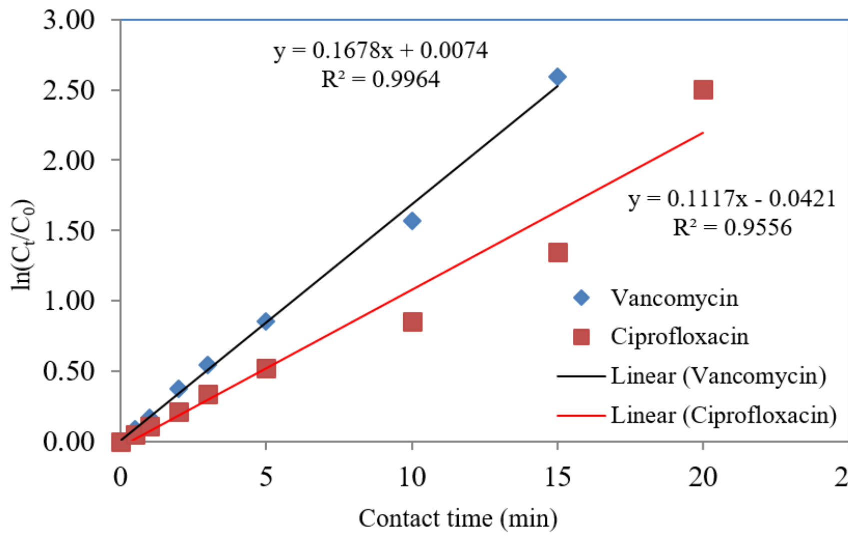

Fig. 5: First-order kinetic model in the removal of vancomycin and ciprofloxacin by ACCO

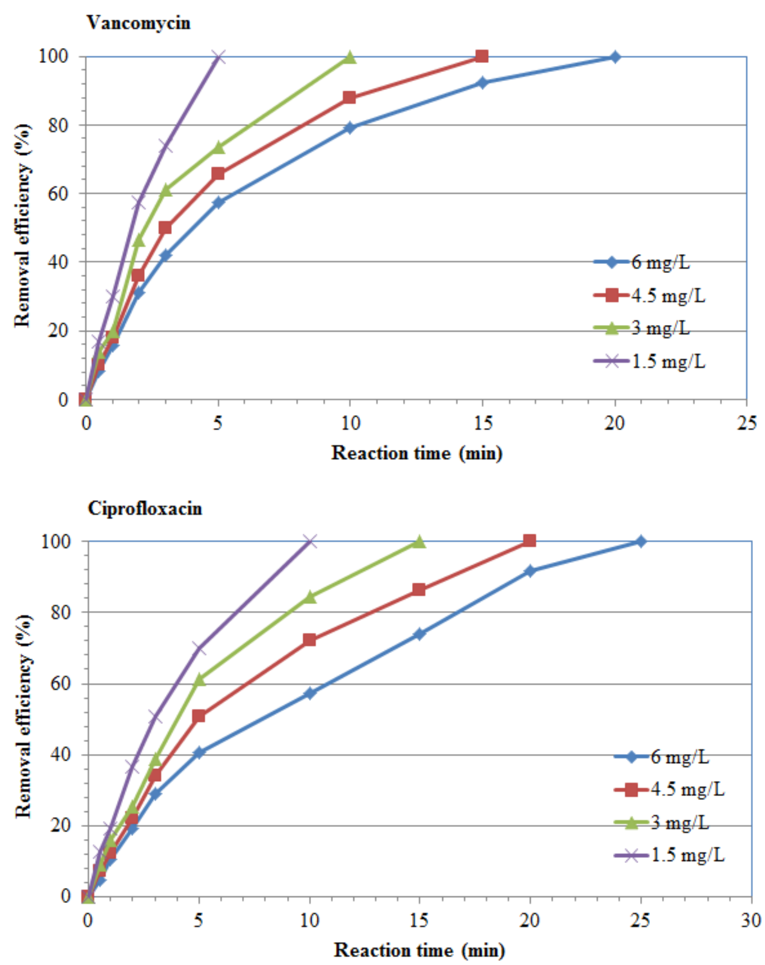

Fig. 6: Degradation of vancomycin and ciprofloxacin by ACCO

COD and BOD reduction

Because of complex matrix of the real wastewater samples, it was not possible to investigate the final by products of antibiotics degradation in the present study. However, in order to see the mineralization rates of the wastewater organic compounds, COD and BOD of the effluents from three investigated processes were measured. Fig. 7 shows the results of BOD and COD removal by SOZ, adsorption and ACCO.

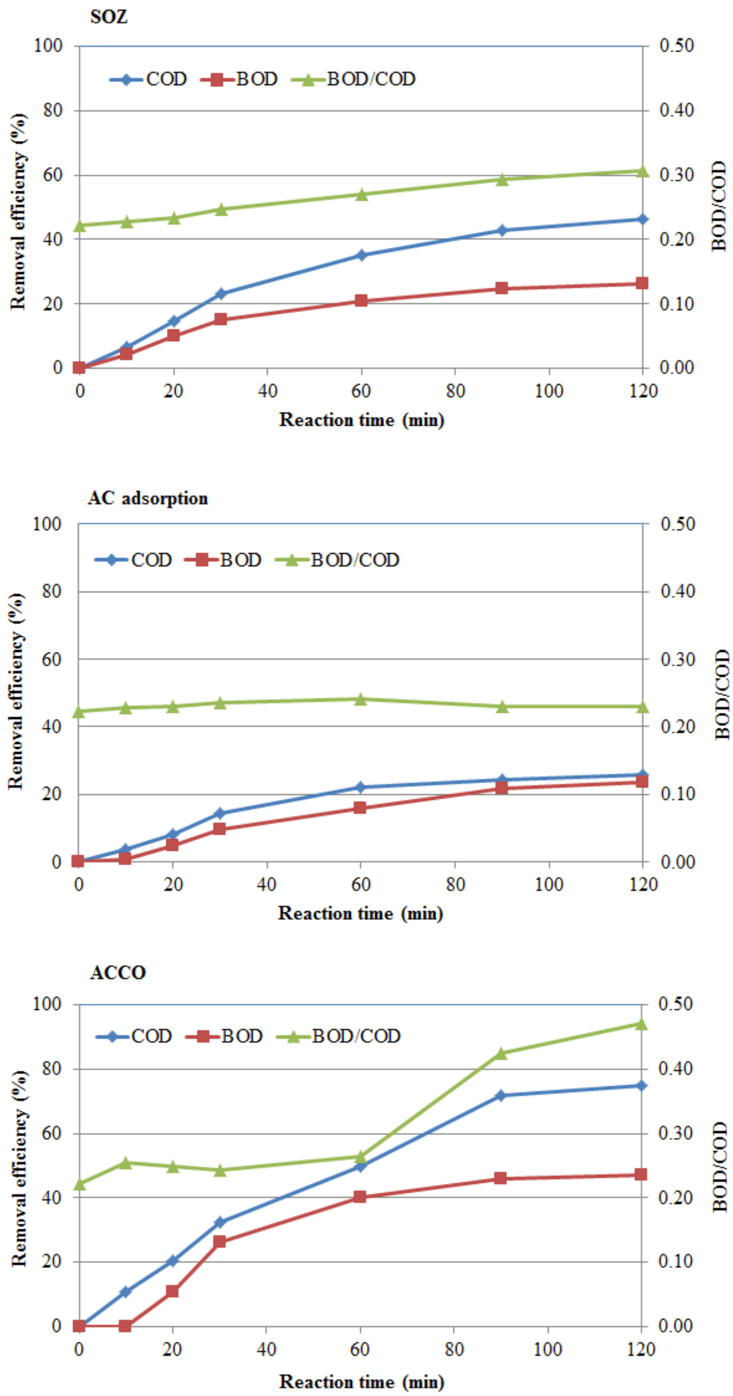

Fig. 7: COD and BOD reduction of hospital wastewater by SOZ, AC adsorption, and ACCO

Kinetics of degradation

Table 3 shows the pseudo-first order kinetic model constants. As shown in table 3, the reaction rate constants in ACCO is more than SOZ, which is confirming the synergistic effect of ozonation and adsorption process. It was found that, reaction rate constants in ACCO is 5.5 times more than SOZ.

Table 3: Reaction rate constant of vancomycin and ciprofloxacin degradation by ACCO and SOZ

Antibiotic	*Concentration (mg/L)*	*ACCO*		*SOZ*		k_{ACCO}/k_{SOZ}
		k_{app}	R^2	k_{app}	R^2	
Vancomycin	6.0	0.167	0.99	0.049	0.95	3.4
	4.5	0.210	0.99	0.061	0.96	3.4
	3.0	0.278	0.98	0.067	0.97	4.1
	1.5	0.454	0.99	0.082	0.98	5.5
Ciprofloxacin	3.46	0.111	0.95	0.032	0.96	6.0
	3.85	0.131	0.99	0.034	0.95	4.5
	5.10	0.189	0.99	0.037	0.95	3.0
	5.83	0.239	0.99	0.041	0.96	1.5

Abbreviations: ACCO, activated carbon catalyzed ozonation; SOZ, single ozonation

Mathematical modeling

Mathematical modeling of the SOZ, adsorption and ACCO of antibiotics degradation were investigated to find the best equation for predicting the results of suggested processes for antibiotic degradation in the real wastewater. Table 4 is summarizing the best equations for predicting the performance of the processes. All the equations are in the following format:

$$RE = (C_1 \times B) + (C_2 \times D) + C_3 \quad [3]$$

Where C_1 is the concentration constant, B is the antibiotic concentration at time D, and C_3 is a constant coefficient. Based on the mathematical equations in Table 4, vancomycin and ciprofloxacin degradation could be predicted at different concentrations and time intervals.

Table 4: Mathematical modeling of antibiotics removal

Antibiotic/Process	*Mathematical equation*	R^2
Vancomycin/SOZ	$RE = (-4.50 \times B) + (2.31 \times D) + 34.14$	0.95
Ciprofloxacin/SOZ	$RE = (-3.13 \times B) + (1.59 \times D) + 20.08$	0.98
Vancomycin/adsorption	$RE = (-3.47 \times B) + (1.14 \times D) + 40.78$	0.68
Ciprofloxacin/adsorption	$RE = (-2.31 \times B) + (0.87 \times D) + 27.92$	0.71
Vancomycin/ACCO	$RE = (-6.46 \times B) + (5.66 \times D) + 51.95$	0.78
Ciprofloxacin/ACCO	$RE = (-5.88 \times B) + (4.68 \times D) + 40.81$	0.87

Discussion

Extraction and measurement of vancomycin and ciprofloxacin

As mentioned, higher recovery rates were obtained in the present study (78.0% for vancomycin and 88.5% for ciprofloxacin). Golet EM, et al. have measured the fluoroquinolone antibiotics in the municipal wastewater samples, they also used the solid phase extraction method for this purpose and reached the recovery rates of 80% (21). In our previous study we also investigated the recovery of vancomycin and imipenem from real wastewater using SPE method and the recovery rate of 80% was obtained (24). The recovery rates of pharmaceutical at low concentrations are smaller than higher concentrations The findings were compatible with previous studies (24).

Single ozonation (SOZ)

The results of the study show that single ozonation process could eliminate 6.0 mg/L of vancomycin and ciprofloxacin at 45 and 65 minutes, respectively. With regard to adsorption process, the maximum adsorption efficiency was obtained 52.0% for vancomycin and 40.5% for ciprofloxacin.

Yargeau V, et al. investigated degradation of sulfamethoxazole by ozonation process, they reported complete degradation of 80 mg/L of sulfamethoxazole after 4.5 min ozonation. This difference in reaction times could be due to the differences in the structure of compounds and variety and oxidation form of chemicals found in the matrix (25). In another study ozonation process was used for degradation of diclofenac from synthetic wastewater that reported 98% degradation of 4 mg/L of diclofenac at 40 min ozonation, but, only 10% mineralization has been reached (26).

Adsorption on activated carbon

The use of catalytic ozonation process due to the production of hydroxyl radicals by combination of ozonation and adsorption resulted in improved process performance whereas complete removal of 6 mg/L vancomycin and ciprofloxacin was reached at 20 and 25 minutes, respectively.

Vancomycin and ciprofloxacin adsorptions were completed up 10 min reaction time. This is because, in the earlier times of process, there are more active sites on the surface of activated carbon. Later, the active sites on the surface of activated carbon are occupied by the antibiotics and the other organic compounds present in the wastewater. Therefore, the removal efficiency of antibiotics remained approximately constant at higher reaction times. Also, there was a reduction in removal efficiency of antibiotics by increasing the concentration of antibiotics This was in accordance with the findings of similar studies (14, 27).

Activated carbon catalyzed ozonation (ACCO)

As the results of this study showed, ozonation in the presence of activated carbon leads to a significant improvement in the performance of the process in the removal of antibiotic compounds. In ACCO process, activated carbon plays an initiating and promoting role in breakdown of ozone to $HO^{\bullet}$ and/or the adsorption of contaminants on the catalyst surface and then continually reaction with the oxidizing agents (28). Therefore, the influence of activated carbon adsorption in the overall performance of ACCO process could not be ignored, and the removal of antibiotic interacts with adsorption and oxidation jointly.

COD and BOD reduction

As results showed, after 2 h of ozonation in SOZ, 41% and 26% reduction was achieved in COD and BOD of the wastewater, respectively. BOD/COD ratio is an important factor in wastewater treatment methods selection. BOD/COD ratio in raw wastewater was 0.2. After ozonation, the ratio reached to 0.3. Therefore, SOZ is able to increase the biodegradability of wastewater by oxidizing some portion of COD.

There was a slight reduction in BOD and COD of wastewater after the adsorption process. About 25% and 23% COD and BOD reduction was achieved, respectively, after 120 min. In the adsorption process, organic compounds are only transferred from the aqueous phase to the solid phase, and there is no degradation and conversion of organic compounds. Therefore, BOD/COD ratio remained constant after adsorption process.

In ACCO, 75% of COD reduction and 47% of BOD reduction were reached after 120 min of reaction time. The results show that some parts of organic compounds are degraded and mineralized by ACCO. This is due to the synergistic effect of ozonation on activated carbon, which is as the result of radical generation in ACCO. The

BOD/COD ratio in ACCO obtained 0.4 after 120 min of reaction time, which confirms the conversion of recalcitrant organic compounds to the biodegradable compounds. Therefore, ACCO makes the organic compounds bioavailable for microorganism, which are playing the main role in biological wastewater treatment. Finally, it can be concluded that ACCO could be used as pre-treatment level in the hospital wastewater treatment to increase bioavailability of organic compounds for the following biological treatment processes.

Kinetics of degradation

As shown, degradation of vancomycin and ciprofloxacin in SOZ and ACCO is following pseudo-first order kinetic models. By increasing the antibiotics concentration of SOZ and ACCO, the reaction rate constants are decreasing, which is in accordance with similar studies (29). This is due to the increase in pollutants to the oxidizing agent ratio in SOZ and ACCO, which leads to the reduction in removal efficiency and reaction rate constant. As it is shown in tables, the reaction rate constants in ACCO is more than SOZ, which is confirming the synergistic effect of ozonation and adsorption process. It was found that, reaction rate constants in ACCO is 5.5 times more than SOZ. Therefore, it can be concluded that ACCO could be an efficient process for degradation of antibiotics in the real hospital wastewater.

Conclusion

The ACCO is an efficient process for the oxidation of vancomycin and ciprofloxacin antibiotics. Therefore, the process can be used to remove antibiotic residuals from hospital wastewater as a pre-treatment process and before discharge into the municipal wastewater sewer. On the other hand, SOZ and ACCO processes showed siggnificant reduction in BOD and COD of hospital wastewater, which could be a promising technology for lessening environmental risk of toxic pollutants.

Journalism Ethics considerations

Ethical issues (Including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc.) have been completely observed by the authors.

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Conflicts of interest

There is no conflict of interest for the authors.

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