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Removal of a Fluoroquinolone Antibiotic Ciprofloxacin

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Abstract

This study presents the comparision of biological and advanced treatment processes for the treatment of Ciprofloxacin (CIP) antibiotic which is an important micropollutant from hospital effluents. The treatability of this antibiotic was investigated using a single aerobic, a single anaerobic, an anaerobic/aerobic sequential reactor system, a sonicator, and a photocatalytic reactor with Cerium (IV) Oxide (CeO_2) nanoparticle in a raw hospital wastewater. Effect of temperature, sonication time and nanoparticle concentration were chosen for operating parameters of the sonicator. The effects of irradiation time, UV light power and CeO_2 nanoparticle concentration on the micropollutant yields were determined as the operating parameters of photocatalytic process. COD and Ciprofloxacin (CIP) yields were determined. Methane gas productions and total VFA concentrations were also monitored in anaerobic reactor. pH changes, dissolved oxygen variations and redox potentials were monitored in anaerobic and aerobic reactors. Furthermore, the effects of HRT and OLR on the pollutant yields was researched in both reactors. Among the aforementioned treatment processes, it was found that the high treatment yields for ciprofloxacin pollutant were obtained with photocatalytic process for 0.50 gr/L nano CeO_2 concentration at 300 W UV light power for 45 min at 25 °C and a pH of 7.00 (93.4%) than anaerobic/aerobic sequential biological process at an OLR of 0.19 gr COD/L.day (82.7%) and sonication with nano CeO_2 for 0.50 gr/L nano CeO_2 concentration at 35 °C for 45 min and a pH of 7.00 (82.0%) to remove the CIP from hospital wastewater effluents.

Introduction

A great variety of toxic or persistent materials such as drugs, radionuclides, solvents and disinfectants are found in every compartment of the environment such as hydrosphere (surface waters, groundwaters, drinking waters), geosphere and biosphere. Hospitals are one of the main sources of these pollutant emissions because of medical activities performed inside and the large quantities of consumption. These materials occur in a low concentration range such as ng/L or µg/L in municipal wastewaters and are determined as micropollutants. Hospital wastewaters are almost untreated before being sent to municipal wastewater treatment plants [1]. There are no water treatment plants to treat both macro and micropollutants in wastewater for hospitals in Turkey. Macropollutants such as BOD_5, COD, nitrogen and phosphorus can be treated at municipal wastewater treatment plants, however micropollutants are discharged without any treatment to the receiving environment. If micropollutants in hospital wastewaters do not treat and discharge to the receiving environment, they cause ecotoxic effects in ecosystem and accumulates at the receiving environment because of low treatment efficiencies. For this reason it

is very important to treat the hospital wastewaters containing a great variety of micropollutants.

In this study, the Ciprofloxacin (CIP) antibiotic from the hospital wastewaters was isolated and it was treated by a single aerobic reactor, a single anaerobic reactor, an anaerobic/aerobic sequential reactor system, sonication and photocatalysis. The effects of HRT and OLR for biological process; the effects of temperatures, sonication times and nano CeO_2 concentrations for sonication; the effects of irradiation times, UV light powers and nano CeO_2 concentrations for photocatalytic process on the Ciprofloxacin (CIP) removals from the hospital wastewater were investigated.

Materials and methods

Laboratory scale treatment processes

Wastewater was taken from Dokuz Eylul University Hospital. The treatability of CIP antibiotic was investigated using a laboratory scale single aerobic reactor; single anaerobic reactor; anaerobic/aerobic sequential reactor system, a sonicator and a photocatalytic reactor with CeO_2 nanoparticle by using raw hospital wastewater.

Laboratory scale single aerobic reactor consist of a continuous flow stirred tank reactor without sludge return and has a total volume of 1600 mL. Laboratory scale single anaerobic reactor is an upflow anaerobic sludge reactor without sludge return and has a total volume of 1000 mL. Laboratory scale anaerobic/aerobic sequential reactor system consists of an upflow anaerobic sludge reactor without sludge return and an aerobic continuous flow stirred tank reactor without sludge return. Upflow anaerobic sludge reactor without sludge return has a total volume of 2000 mL. It was equipped with influent and effluent valves, sampling valves and gas outlet valves. Required temperature conditions for the both reactors were provided with an infrared heater at mesophilic conditions. Following the upflow anaerobic sludge reactor without sludge return, an aerobic continuous flow stirred tank reactor without sludge return which has a total volume of 1600 mL was used. MLSS values were 30000, 25000 and 5000 mg/L for the anaerobic/aerobic sequential reactor system, single upflow anaerobic sludge reactor without sludge return and single aerobic continuous flow stirred tank reactor without sludge return, respectively. The sonicator system has a volume of 10 liters and containing teflone coated quartz glass reactor with a volume of 500 mL while the UV photocatalysis system is made in steinless steel with steinlees steel covers.

System was fed with raw hospital wastewater containing an average COD concentration of 1200 mg/L. The effects of hydraulic retention time and organic loading rate on the pollutant yields was researched in both reactors. After the system was reached the steady state conditions, HRT was set to 10 days - 0.19 gr COD/L.day of OLR and then it was shortened to 4 days. After the 4 days of HRT – 0.22 gr COD/L.day of OLR operation, HRT was shortened to 2 days – 0.44 gr COD/L.day of OLR. COD and CIP yields were determined. Methane gas productions and total VFA concentrations were also monitored in anaerobic rectors. pH changes, dissolved oxygen variations and redox potentials were monitored in anaerobic and aerobic reactors.

Effect of temperature, sonication time and nanoparticle existance were chosen for operating parameters of the sonicator. Sonicator used in this study has 35 kHz frequency. In order to determine the sonicator performance on CIP yield, the sonicator was operated with and without CeO_2 nanoparticle. When the sonicator operated with nanoparticle, three different temperature conditions was studied as 25, 35 and 45 °C at pH=7.00. Nanoparticle concentration was changed in two different concentration such as 0.25 and 0.50 gr/L. Effect of sonication time was researched using three different time intervals such as 15, 30 and 45 minutes. When the sonicator operated without nanoparticle, three different temperature conditions was studied as 25, 35 and 45 °C at pH=7.00. Effect of sonication time was researched using three different time intervals such as 15, 30 and 45 minutes. The studies in sonicator were performed in a 500 mL teflone coated quartz glass reactor. The samples were taken in certain time intervals were above mentioned and the CIP yields were calculated according to the operational conditions.

The effects of irradiation time, UV light power and nanoparticle concentration on the CIP removals were determined according to the operating conditions of photocatalytic process. The effects of irradiation time was researched using three different time intervals such as 15, 30 and 45 minutes. In photocatalytic process, three different UV light powers was used such as 120, 210 and 300 watt at pH=7.00 and at a temperature of 25 °C (895.0 mm×26.0 mm, 30.0 Watt, 0.36 A, G13 Model, OSRAM). Effect of CeO_2 nanoparticle concentrations (0.25-0.50 gr/L) on the CIP yields were studied. The studies in the photoreactor were performed in 500 mL teflone coated quartz glass reactor. The samples were taken in certain time intervals as mentioned above. The operational conditions for all treatment processes used are summarized in Table 1.

Table 1: Operational conditions for biological and advanced treatment processes used in the treatment of CIP from hospital wastewater

	Biological Processes			Advanced Treatment Processes	
	Aerobic Reactor	Anaerobic Reactor	An/Ae Seq. Reactor	Sonication	Photocatalytic study with Nano CeO_2
HRT (day)	10; 4; 2	10; 4; 2	20; 8; 4	-	-
SRT (day)	10; 4; 2	10; 4; 2	20; 8; 4	-	-
OLR (gr COD/L.day)	0.19; 0.22; 0.44	0.19; 0.22; 0.44	0.19; 0.22; 0.44	-	-
MLSS (mg/L)	5000	25000	30000	-	-
Sonicator frequency (kHz)	-	-	-	35	-

Temperature (°C)	25±5	35±5	30±5	25; 35; 45	25
Nano CeO_2 concentration (gr/L)	-	-	-	0.25; 0.50	0.25; 0.50
Irradiation/sonication time (min)	-	-	-	15; 30; 45	15; 30; 45
Sonicator/UV power (Watt)	-	-	-	510	120; 210; 300

Analytical procedure

Aqueous ciprofloxacin stock solution was prepared from the ciprofloxacin standard (Fluka, ≥98.0%, HPLC). Ciprofloxacin is soluble in dilute aqueous acids, for this reason, stock solution was prepared by using 10% H_2SO_4 solution and was stirred for 24 hours on magnetic stirrer and was ensured an homogenous distribution. Calibration curve of ciprofloxacin was drawn for 5-10-25-50-75-100 µg/L (R^2=0,99996). Accuracy of the concentrations were tested in HPLC (Agilent 1100 Series HPLC). The mobile phase consisted of 0.02 M KH_2PO_4 in distilled water and pure acetonitrile. A Thermo C18 column (5 µm, 250 mm×4.6 mm, Thermo Scientific) was used and the injection volume of each sample was 20 µL. The flowrate was 1.5 mL/min and the column oven temperature was 30 °C. According to the spectrum determined in the HPLC the retention time for CIP was calculated as 8.1 minutes.

Ciprofloxacin antibiotic was extracted from hospital wastewater by solid-phase extraction method. Approximately 100 ml of accurately measured sample of the hospital water, filtered through 0.45-µ-filter membrane and acidified with sulphuric acid (pH=3) was loaded on an activated OASIS HLB Cartridge (activated with 5 ml methanol, 5 ml methanol/water (50:50) followed by 5 ml acidified water at pH 3). The cartridge was then washed with 5 ml acidified water and the adsorbed compounds were eluted with 5 ml eluant (5% solution of triethylamine in methanol). The eluant was evaporated using Nitrogen evaporator. The dried extract was then dissolved in acetonitrile and the final volume made to 1 ml.

Conventional pollutants in hospital wastewater such as Chemical Oxygen Demand (COD) and MLSS were measured according to Standard Methods. Total nitrogen and total phosphorus were measured with reagent kits in a Photometer Nova 60/ Spectroquant. pH, Dissolved Oxygen (DO), Oxidation Reduction Potential (ORP) were measured with WTW probes. Bicarbonate alkalinity and Total Volatile Fatty Acids (TVFA) were measured with Anderson and Yang method [2]. Methane gas (CH_4) productions were measured with liquid replacement methods by using 3% NaOH solution.

ANOVA test statistics were performed with dependent and independent variables to determine the regressions, correlations and significance between parameters and yields using Microsoft Excell 2010.

Results and discussion

Start-up of biological treatment processes

Single aerobic, single anaerobic and anaerobic/aerobic sequential reactor systems were operated through 50 days with synthetic wastewater under steady-state conditions to provide the acclimation of biomass in the reactors. Steady-state condition was defined with COD yields around 90% for consecutive five days for all biological reactors. After the system reached the steady-state conditions at an OLR of 0.19 gr COD/L.day (HRT=10 days) the biological reactor systems started to fed with raw hospital wastewater throught 34 days at an OLR of 0.19 gr COD/L.day. The steady state conditions were defined with 90% and 80% COD yields and with 82% and 72% CIP yields in aerobic and anaerobic reactors, respectively (Data not shown) at the aforementioned OLR. Then the OLRs were increased to 0.22 gr COD/L.day and 0.44 gr COD/L.day. The operation intervals were choosen as 38 and 40 days for aerobic and anaerobic reactors to reach the same yield and effluent concentrations for 4 consecutive 4 days. During the aerobic phase, the oxidation reduction potential increased from +15 to +315 mV and remained between +315 and +330 mV (Data not shown). During the anaerobic phase, zero dissolved oxygen was observed and the redox potential was around -700 mV (Data not shown). During the sequential anaerobic/aerobic phase, the redox potential increased from -700 mV to +325 mV and remained between +325 and +350 mV (Data not shown).

Effects of OLR on the removal of chemical oxygen demand (COD) in biological reactors

COD analyses were performed regularly for monitoring the organic material degradation based on COD concentrations in the influent of hospital wastewater, in single aerobic reactor effluent, in single anaerobic reactor effluent and in the anaerobic/ aerobic sequential reactor system effluent.

During the 10 days of HRT operation, the maximum COD removal efficiency of single aerobic reactor was obtained as 93.1% with a COD effluent of 130.6 mg/L at an Organic Loading Rate (OLR) of 0.19 gr COD/L.day. For the single anaerobic reactor, maximum COD removal efficiency was measured as 68.4% with an effluent of 600 mg/L. For the anaerobic/aerobic sequential reactor system, COD removal efficiency reached 94.7% with an effluent of 100 mg/L at an OLR of 0.19 gr COD/L.day (**Figure 1a**). Thereafter, OLR was increased to 0.22 gr COD/L.day corresponding to a HRT of 4 days. In single aerobic reactor, the maximum COD removal efficiency was obtained as 78.2% with a COD effluent of 189.7 mg/L. For the single anaerobic reactor, maximum COD removal efficiency was measured as 48.6% with an effluent of 447.4 mg/L. For the anaerobic/aerobic sequential reactor system, COD removal efficiency reached 78.1% with an effluent COD concentration of 191.0 mg/L at an OLR of 0.22 gr COD/L. day (**Figure 1b**). Later, OLR was increased to 0.44 gr COD/L.day corresponding to a HRT of 2 days. In single aerobic reactor, the maximum COD removal efficiency was obtained as 69.5% with a COD effluent of 265.2 mg/L. For the single anaerobic reactor, maximum COD removal efficiency was measured as 44.7% with an effluent of 481.1 mg/L. For the anaerobic/aerobic sequential reactor system, COD removal efficiency reached 73.8% with an effluent COD concentration of 227.6 mg/L (**Figure 1c**).

The results obtained showed that increasing the OLR from 0.19 to 0.44 gr COD/L.day decreased significantly the reactor performances. ANOVA test statistic showed that a linear regression between OLR and COD yields was found in aerobic (R=0.83) and anaerobic (R=0.71) reactors and the relationship was significant (ANOVA, F=0.37 and F=0.49).

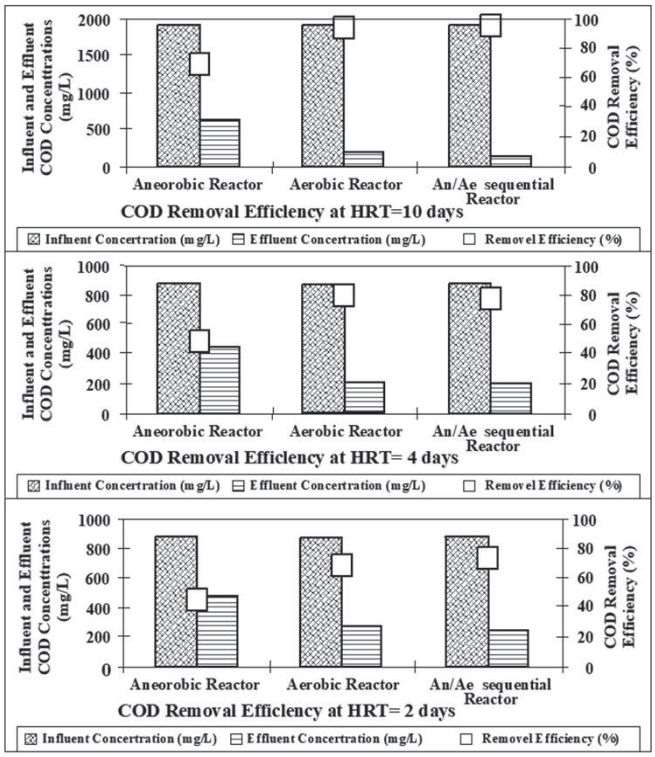
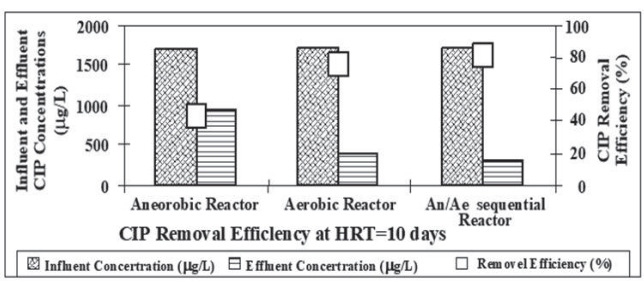


Figure 1: **(a)** COD concentrations and yields during the 10 days of HRT operation at 0.19 gr COD/L.day OLR. **(b)** COD concentrations and yields during the 4 days of HRT operation at 0.22 gr COD/L.day OLR. **(c)** COD concentrations and yields during the 2 days of HRT operation at 0.44 gr COD/L.day OLR.

Effects of OLR on ciprofloxacin (CIP) removal efficiency in biological reactors

In this study, CIP removal efficiency of the single aerobic reactor, single anaerobic reactor and anaerobic/aerobic sequential reactor system was investigated at three different HRT - OLR conditions. The experimental studies were carried out to determine the effect of HRT and OLR variations on CIP yields.

During the 10 days of HRT operation, the maximum CIP yield of single aerobic reactor was obtained as 77.1% with a CIP effluent of 119.8 µg/L at an OLR of 0.19 gr COD/L.day (**Figure 2a**). For the single anaerobic reactor, maximum CIP yield was measured as 43.9% with a CIP effluent of 292.9 µg/L (**Figure 2a**). For the anaerobic/aerobic sequential reactor system, CIP yield reached 82.7% with a CIP effluent of 90.1 µg/L (**Figure 2a**). Thereafter, OLR was increased to 0.22 gr COD/L.day corresponding to a HRT of 4 days. In single aerobic reactor, the maximum CIP yield was obtained as 63.3% with a CIP effluent of 60.2 µg/L (**Figure 2b**). For the single anaerobic reactor, maximum CIP yield was measured as 40.4% with an effluent of 97.6 µg/L (**Figure 2b**).



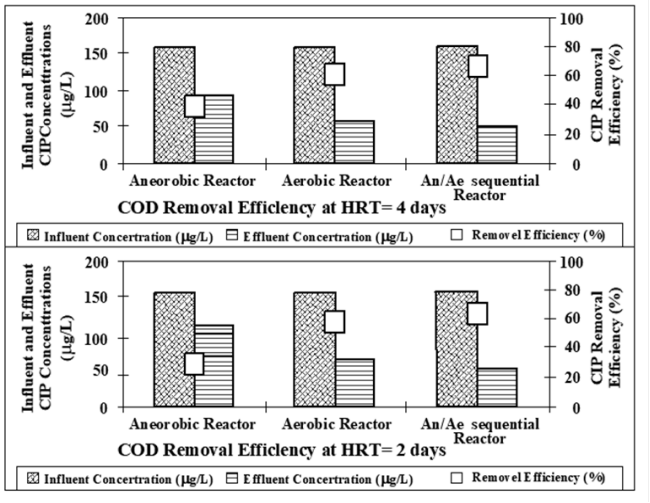


Figure 2: **(a)** CIP concentrations and yields during the 10 days of HRT operation at 0.19 gr COD/L.day OLR. **(b)** CIP concentrations and yields during the 4 days of HRT operation at 0.22 gr COD/L. day OLR. **(c)** CIP concentrations and yields during the 2 days of HRT operation at 0.44 gr COD/L.day OLR.

For the anaerobic/aerobic sequential reactor system, CIP yield reached 68.2% with an effluent CIP concentration of 52.1 µg/L (**Figure 2b**). Later than 4 days of HRT operation, OLR was increased to 0.44 gr COD/L.day corresponding to a HRT of 2 days. In single aerobic reactor, the maximum CIP yield was obtained as 60.4% with a CIP effluent of 65.0 µg/L (**Figure 2c**). For the single anaerobic reactor, maximum CIP yield was measured as 30.1% with an effluent of 114.6 µg/L (**Figure 2c**). For the anaerobic/aerobic sequential reactor system, CIP yield reached 66.7% with an effluent CIP concentration of 54.6 µg/L (**Figure 2c**). Increasing the organic load from 0.19 to 0.44 gr COD/L.day decreased slightly the reactor performances. No significant effects of HRT on the CIP yields were obtained at all biological reactors. Linear regressions between OLR and CIP yields were obtained for aerobic (R=0.71) and anaerobic (R=0.98) reactors while this regression was found to be significant for aerobic (F=0.49) and anaerobic (F=0.10) reactors, respectively.

Effects of OLR on the variation of VFA in biological reactors

Since determination of volatile fatty acids concentration is very important for an anaerobic system control, total VFA concentrations of single anaerobic reactor effluent and the anaerobic reactor of the anaerobic/aerobic sequential reactor system effluent were monitored regularly. The TVFA concentrations of single anaerobic reactor and the anaerobic reactor of the sequential reactor system reached 156 and 126 mg acetic acid/L at the end of the 10 days of HRT - 0.19 gr COD/L.day of OLR operation, respectively (**Table 2**). At the end of the 4 days of HRT - 0.22 gr COD/L.day of OLR operation, the TVFA concentrations of single anaerobic reactor and the anaerobic reactor of the sequential reactor system reached to 153 and 138 mg acetic acid/L, respectively (**Table 2**). Moreover, at the end of the 2 days of HRT - 0.44 gr COD/L.day of OLR operation, the TVFA concentrations of single anaerobic reactor and the anaerobic reactor of the sequential reactor system reached to 31 and 16 mg acetic acid/L, respectively (**Table 2**). Although it was expected to decrease in TVFA concentrations at low OLRs, in this study slightly high TVFA concentrations were obtained at low OLRs. It is important to note that the TVFA concentrations were measured as 156 and 31 mg acetic acid/L at 0.19 gr COD/L.day and 0.44 gr COD/L.day, respectively. These results can be explained as

follows: The high TVFA concentrations at low OLRs was not so high compared to initial COD concentration. This means that a significant TVFA accumulation was not detected since the COD yields not decrease significantly as the OLRs were increased from 0.19 to 0.22 and 0.44 gr COD/L.day in anaerobic reactors. However, the CIP yields decreased significantly as the OLRs were increased from 19 to 0.22 and 0.44 gr COD/L.day in anaerobic reactors. ANOVA test statistics showed that a linear regression between OLR and TVFA was found (R=0.99) while this correlation was significant (F=0.06).

TVFA and alkalinity parameters alone may not be a good indicator to assess the stability of anaerobic reactors. Instead, TVFA/Alkalinity ratio is a better alternative to detect the performance of the anaerobic treatment. Sánchez et al. (2005) and Malpei et al. (1998) [3,4] suggested that values lower than 0.3-0.4 are optimum. In this study, TVFA to alkalinity ratios during the experimental studies were 0.06 and 0.05 for the single anaerobic reactor and anaerobic reactor of the sequential reactor system at 10 days of HRT operation, respectively (**Table 2**). TVFA to alkalinity ratios were 0.13 and 0.11 for the single anaerobic reactor and the anaerobic reactor of the sequential reactor system at 4 days of HRT operation, respectively (**Table 2**). TVFA to alkalinity ratios during the experimental studies were 0.04 and 0.02 for the single anaerobic reactor and anaerobic reactor of the sequential reactor system at 2 days of HRT operation, respectively (**Table 2**). These TVFA/Alkalinity levels are below of the limits given by Sánchez et al. (2005) and Malpei et al. (1998) [3,4].

Table 2: TVFA and alkalinity concentrations with TVFA/Alkalinity ratios

Single Anaerobic Reactor					Anaerobic Reactor of the Anaerobic/Aerobic Sequential Reactor System				
HRT (day)	OLR (gr COD/L.day)	TVFA (mg Acetic Acid/L)	Alkalinity (mg $CaCO_3$/L)	TVFA/ Alkalinity Ratio	HRT (day)	OLR (gr COD/L.day)	TVFA (mg Acetic Acid/L)	Alkalinity (mg $CaCO_3$/L)	TVFA/ Alkalinity Ratio
10	0.19	156	2459	0.06	10	0.19	126	2682	0.05
4	0.22	153	1158	0.13	4	0.22	138	1270	0.11
2	0.44	31	751	0.04	2	0.44	16	764	0.02

Variation of pH and dissolved oxygen (DO) in biological reactors

pH is the one of the most important operating parameters to control biological system stability. Therefore, during the experimental studies, pH values of influent hospital wastewater, single aerobic reactor effluent, single anaerobic reactor effluent and anaerobic/aerobic sequential reactor system effluent were monitored regularly. There were no significant pH fluctuations for the period of the experiments carried out with both 10 days, 4 days and 2 days of HRTs. Influent hospital wastewater pH was almost stable and changed between 8.00 and 8.30 (Data not shown). The single aerobic reactor effluent pH was changed between 6.32 and 8.20 for both 10 days, 4 days and 2 days of HRTs, which is the optimum value for the growth of the aerobic bacteria (Data not shown). The single anaerobic reactor effluent pH did not fall to below 7.00 both 10 days, 4 days and 2 days of HRTs, which is slightly lower the adequate value for the growth of methanogenic bacteria (Data not shown). The pH of the single anaerobic reactor had an average of 8.20 at three different HRTs. Anaerobic/aerobic sequential reactor system effluent pH had an average of 8.59, 9.15 and 8.75 for the 10 days, 4 days and 2 days of HRTs, respectively (Data not shown).

Optimum dissolved oxygen concentration in aerobic reactors is considered as 2.0 mg/L. Sufficient DO concentration is necessary to keep aerobic microorganisms alive for the biodegradation of the organic compounds. In this study, DO concentrations of aerobic reactors were changed between 2.0 and 3.0 mg/L for both 10 days, 4 days and 2 days of HRTs conditions (Data not shown). Zero dissolved oxygen concentrations were determined for anaerobic reactors (Data not shown).

Effects of OLR on methane gas variation in anaerobic reactors

Methane content of the biogas is accepted as one of the most important indicator of anaerobic degradation. In this study, average methane volume of single anaerobic reactor and the anaerobic reactor of the sequential reactor system were determined as 360 and 350 mL CH_4/day for 10 days HRT - 0.19 gr COD/L.day of OLR operation, respectively (Data not shown). After 10 days of HRT operation, average methane volume of single anaerobic reactor and the anaerobic reactor of the sequential reactor system were measured as 110 and 210 mL CH_4/day for 4 days of HRT - 0.22 gr COD/L.day of OLR operation (Data not shown). After 4 days of HRT operation, average methane volume of single anaerobic reactor and the anaerobic reactor of the sequential reactor system were measured as 70 and 200 mL CH_4/day for 2 days of HRT - 0.44 gr COD/L.day of OLR operation (Data not shown).

As a consequence, decreasing the HRT from 10 to 2 corresponding to increase in OLR from 0.19 to 0.44 gr COD/L.day affected negatively the methane gas production. Methane gas production at 10 days of HRT is better than that 4 days and 2 days of HRT conditions. Increasing the HRT caused accumulation of VFA based on fatty acids. Low HRTs (high OLRs) was not enough to growth and activity of *Archae* bacteria. Under these conditions the VFA produced remained in the anaerobic reactor and the *Archae* bacteria can not convert the fatty acids to methane gas satisfactory. A linear regression beetwen OLR and methane production (R=0.69) was observed and this correlation was found to be significant (F=0.51).

Effects of nano CeO_2 concentrations, sonication times and sonication temperatures on CIP yields throughout sonication at constant pH=7.00

Effect of nano CeO_2 concentration on the yield of CIP at constant sonication time (15 min) and constant temperature (25 °C)

In order to determine the optimum nano CeO_2 concentration, sonicator operated with 0.25 gr/L nano CeO_2 at 25°C for 15 min at pH=7.00. Maximum CIP yield for the 0.25 gr/L nano CeO_2 concentration was determined as 63.3% after 15 min sonication at 25 °C, at a frequency of 35 kHz and a power of 510 W

and at a pH of 7.00 (Data not shown). After than, nano CeO_2 concentration was increased to 0.50 gr/L under same operation conditions and the maximum CIP yield reached to 72.4%. Optimum nano CeO_2 concentration was found as 0.50 gr/L at 15 min sonication time, 25 °C temperature and pH=7.00.

Effect of sonication time on the yield of CIP at constant nano CeO_2 concentration (0.50 gr/L) and constant temperature (25 °C)

In order to determine the sonication time effect on CIP yield, the sonicator was operated using three different time intervals such as 15, 30 and 45 minutes at pH=7.00. Maximum CIP yields for 0.50 gr/L nano CeO_2 concentration were determined as 72.4% for 15 min, 75.9% for 30 min and 78.0% for 45 min sonication at 25 °C at a pH of 7.00 at a frequency of 35 kHz and a power of 510 W (**Figure 3a**). Optimum sonication time was found as 45 min for 0.50 gr/L nano CeO_2 concentration and 25 °C temperature at a pH of 7.00. A linear regression between sonication time and CIP yields were obtained (R=0.96); and this correlation was significant (F=0.18).

Effect of sonicator temperature on the yield of CIP at constant nano CeO_2 concentration (0.50 gr/L) and constant sonication time (45 min)

Three different temperature conditions were studied as 25, 35 and 45 °C at pH=7.00 in order to determine the sonicator temperature effect on the yield of CIP at 0.50 gr/L nano CeO_2 concentration for 45 min at a pH of 7.00. Maximum CIP yield at 25°C was obtained as 78.0% for the mentioned operating conditions (**Figure 3b**). Maximum CIP yield at 35°C was obtained as 82.0% for the same operating conditions (**Figure 3b**). Maximum CIP yield at 45°C was obtained as 85.1% under the same operating conditions (**Figure 3b**). As a result of this, optimum sonication temperature was accepted as 35°C for 0.50 gr/L nano CeO_2 concentration after 45 min sonication time and at a pH of 7.00 since high temperatures requires high energy costs. ANOVA test statistics showed that a linear regression between sonication temperature and CIP yields was obtained (R=0.99) and this correlation was significant (F=0.05).

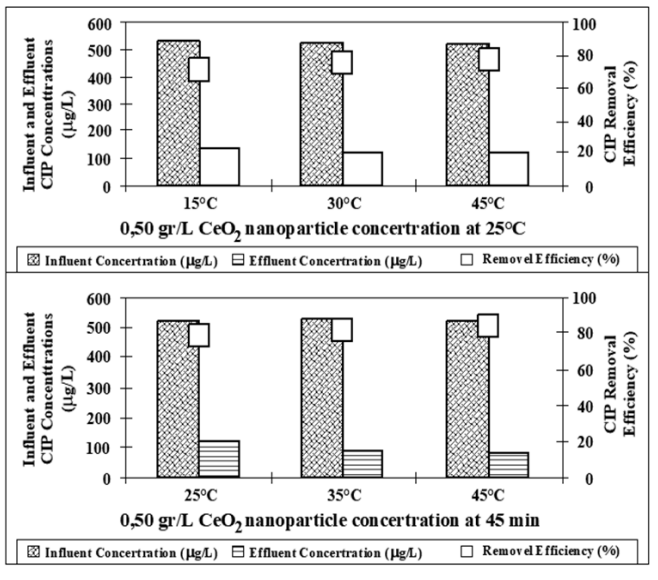


Figure 3: (a) CIP yields at different sonication times at 25 °C for 0. 50 gr/L nano CeO2 concentration at pH=7.00 at a frequency of 35 kHz and a power of 510 W. **(b)** CIP yields at different sonication temperatures at 45 min for 0.50 gr/L nano CeO2 concentration at pH=7.00 at a frequency of 35 kHz and a power of 510 W

Effect of sonication on CIP yields without nanoparticle

Sonicator was operated without nanoparticle in order to determine the sonication effect alone on CIP yields at three different temperature conditions (25, 35 and 45 °C) at pH=7.00 and for three different sonication time intervals (15, 30 and 45 minutes). Maximum CIP yields were determined as 41.3%, 53.3% and 69.1% at 25°C, 35 °C and at 45 °C, respectively, after 45 minutes sonication time (Data not shown). Maximum CIP yield reached at higher temperature compared to low temperatures without nanoparticle.

Effects of nano CeO_2 concentrations, irradiation times and UV light powers on CIP yields throughout photocatalysis at constant pH (7.00) and constant temperature (25 °C)

Effect of nano CeO_2 concentration on the yield of CIP at constant irradiation time (15 min) and constant UV light power (120 W)

In order to determine the optimum nano CeO_2 concentration, photocatalytic reactor operated with 0.25 gr/L nano CeO_2 at 120 W for 15 min at 25 °C and at a pH of 7.00. Maximum CIP yield for the 0.25 gr/L nano CeO_2 concentration was determined as 48.4% after 15 min irradiation time (Data not shown). After than, nano CeO_2 concentration was increased to 0.50 gr/L under same operation conditions and the maximum CIP yield reached to 64.0%. Optimum nano CeO_2 concentration was found as 0.50 gr/L at 15 min irradiation time for 120 W at 25 °C and pH=7.00.

Effect of irradiation time on the yield of CIP at constant nano CeO_2 concentration (0.50 gr/L) and constant UV light power (120 W)

In order to determine the irradiation time effect on CIP yield, the photocatalytic reactor was operated using three different time intervals such as 15, 30 and 45 minutes at 25 °C and pH=7.00. Maximum CIP yields for 0.50 gr/L nano CeO_2 concentration were determined as 64.0% for 15 min, 66.7% for 30 min and 76.6% for 45 min irradiation time at 120 W at 25°C and at a pH of 7.00 (**Figure 4a**). Adsorption studies showed that CIP removal was only 5.4% at 0.50 gr/L nano CeO_2 concentration after 45 min stirring time under dark experimental conditions at a pH of 7.00 and a temperature of 25 °C. In the light of these results, having the lower adsorption rates of CIP with nano CeO_2 indicates that degradation of CIP occurred mainly with photocatalytic processes. Optimum irradiation time was found as 45 min for 0.50 gr/L nano CeO_2 concentration at 120 W UV light power at 25°C and at a pH of 7.00. A significant regression between UV irradiation time and CIP yields (R=0.95) and this regression was found to be significant (F=0.19).

Effect of UV light power on the yield of CIP at constant nano CeO_2 concentration (0.50 gr/L) and constant irradiation time (45 min)

Three different UV light powers were studied as 120, 210 and 300 W at 25°C in order to determine the UV light power effect on the yield of CIP for 0.50 gr/L nano CeO_2 concentration at 45 min and at a pH of 7.00. Maximum CIP yield at 120 W was obtained as 76.6% under the aforementioned operating conditions (**Figure 4b**). Maximum CIP yield at 210 W for the same operating conditions was obtained as 86.0% (**Figure 4b**). Finally, maximum CIP yield at 300 W was obtained as 93.4% under the same operating conditions (**Figure 4b**). As a result of this, optimum UV light power was determined as 300 W for 0.50 gr/L nano CeO_2 concentration at 45 min irradiation time at 25°C and at a pH

of 7.00. ANOVA test statistics showed that a significant lineaer regression between UV light power and CIP yields (R=0.99) and this correlation was significant (F=0.05).

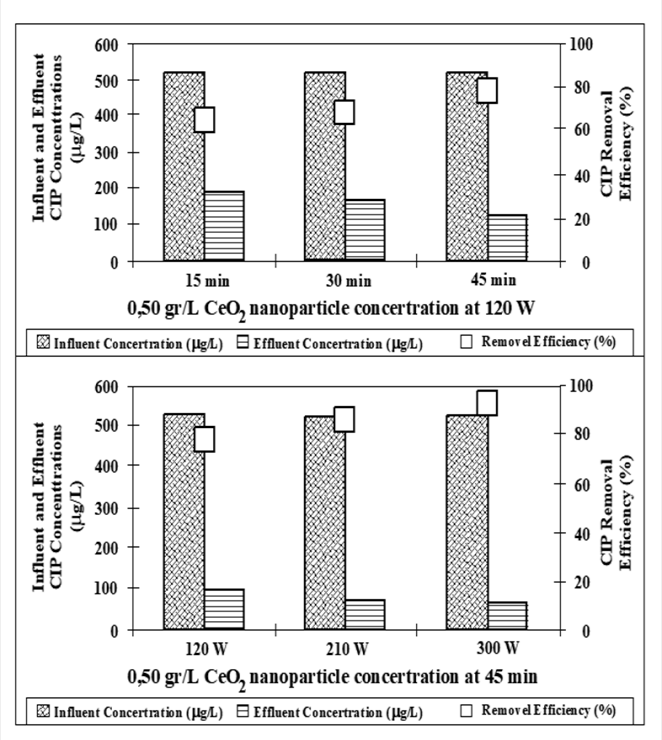


Figure 4: (a) CIP yields at different irradiation times at 120 W for 0.50 gr/L nano CeO2 concentration at 25 °C and at a pH of 7.00. **(b)** CIP yields at different UV powers at 45 min for 0.50 gr/L nano CeO2 concentration at 25 °C and at a pH of 7.00

Conclusions

In this study, treatability of (CIP) antibiotic was investigated using a single aerobic reactor, a single anaerobic reactor, an anaerobic/aerobic sequential reactor system, a sonicator, and a photocatalytic reactor with (CeO_2) nanoparticle in a raw hospital wastewater. Higher COD yields were obtained at 10 days of HRT - 0.19 gr COD/L.day of OLR (94.7%) than 4 days of HRT - 0.22 gr COD/L.day of OLR (78.1%) and 2 days of HRT - 0.44 gr COD/L.day of OLR (73.8%) in anaerobic/aerobic sequential reactor system. The maximum yield of anaerobic/aerobic sequential reactor system was recorded as 94.7% at this loading rate. The yield of total biological system decreased to 78.1% at an OLR of 0.22 gr COD/L.day.

Increasing of OLR had a negative effect on CIP yields of all biological reactor systems. For the 10 days HRT operation - 0.19 gr COD/L.day of OLR, single aerobic reactor (77.1%) found to be more efficient for CIP removal than that single anaerobic reactor (43.9%) and anaerobic/aerobic sequential reactor system (82.7%) at an OLR of 0.19 gr COD/L.day. The CIP yields decreased at other OLRs in sequential reactor systems

Throughout sonication, utilization of 0.50 gr/L nano CeO_2 increased the removal of CIP to 82.0% at a sonication time of 45 min and at a temperature of 35 °C at a frequency of 35 kHz at a power of 510 W and at a pH of 7.00. Increasing of nano CeO_2 concentration, increasing temperature and increasing time had a positive effect on CIP yields throughout sonication.

In photocatalytic studies, throughout photocatalysis with 0.50 gr/L nano CeO_2 increased the removal of CIP to 93.4% at an irradiation time of 45 min, at a UV power of 300 W, at a temperature of 25 °C and at a pH of 7.00. Increasing both UV light powers and irradiation times increased the CIP yields.

As a result of the study, among the used removal processes it was found that photocatalytic process with nano CeO_2 (93.4%) is more efficient than anaerobic/aerobic sequential biological process at an OLR of 0.19 gr COD/L.day (82.7%) and sonication with nano CeO_2 (82.0%) to remove the CIP from hospital waste water effluents [5].

References

1. Frederic O, Yves P. Pharmaceuticals in hospital wastewater: Their ecotoxicity and contribution to the environmental hazard of the effluent, Chemosphere. 2014; 115: 31-39.

2. Anderson GK, Yang G. Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration, Water Environment Research. 1992; 64: 53-59.

3. Sánchez E, Borja R, Travieso L, Martin A, Colmenarejo MF. Effect of organic loading rate on the stability, operational parameters and performance of a secondary upflow anaerobic sludge bed reactor treating piggery waste, Bioresource Technology. 2005; 96: 335-344.

4. Malpei F, Andreoni V, Daffonchio D, Rozzi A. Anaerobic digestion of print pastes: A preliminary screening of inhibition by dyes and biodegradability of thickeners, Bioresource Technology.1998; 63: 49-56.

5. Standard Methods for the Examination of Water and Waste water. 20th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA. 1998.