BIOLOGICAL, PHOTOCATALYTIC AND ULTRASOUND TREATMENT 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.

Keywords: aerobic, anaerobic, CeO_2 nanoparticle, ciprofloxacin, fluoroquinolone, photocatalytic, sonication.

1. 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 (Frédéric and Yves, 2014). 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.

2. Materials and methods

2.1. 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. 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

2.2. Analytical procedure

Ciprofloxacin antibiotic was extracted from hospital wastewater by solid-phase extraction method using OASIS HLB Cartridges. CIP concentrations were tested in HPLC (Agilent 1100 Series HPLC). 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 (Anderson and Yang, 1992). 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.

3. Results and discussion

3.1. 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. After the system reached the steady-state conditions the biological reactor systems started to fed with raw hospital wastewater at an OLR of 0.19 gr COD/L.day then the OLRs were increased to 0.22 gr COD/L.day and 0.44 gr COD/L.day. The operation intervals, COD and CIP removal efficiencies and oxidation reduction potentials were not shown for the start-up period.

3.2. Effects of OLR on the removal of Chemical oxygen demand (COD) in biological reactors

COD analyses were summerized in Figure 2. 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).

3.3. Effects of OLR on Ciprofloxacin (CIP) removal efficiency in biological reactors

CIP analyses were summerized in Figure 3. 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.

3.4. Variation of pH in biological reactors and effects of OLR on the variation of VFA and methane gas in anaerobic reactors

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 (Data not shown). Total VFA concentrations of single anaerobic reactor effluent and the anaerobic reactor of the anaerobic/aerobic sequential reactor system effluent were monitored regularly (Data not shown). 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). 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 (Data not shown). A linear regression beetwen OLR and methane production (R=0.69) was observed and this correlation was found to be significant (F=0.51).

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

3.5.1. 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 (Data not shown).

3.5.2. 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 (Data not shown). 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).

3.5.3. 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 (Data not shown). Maximum CIP yield at 35°C was obtained as 82.0% for the same operating conditions (Data not shown). Maximum CIP yield at 45°C was obtained as 85.1% under the same operating conditions (Data not shown). 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).

3.6. 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.

3.7. 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)

3.7.1. 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.

3.7.2. 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 (Data not shown). 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).

3.7.3. 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 (Data not shown). Maximum CIP yield at 210 W for the same operating conditions was obtained as 86.0% (Data not shown). Finally, maximum CIP yield at 300 W was obtained as 93.4% under the same operating conditions (Data not shown). 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).

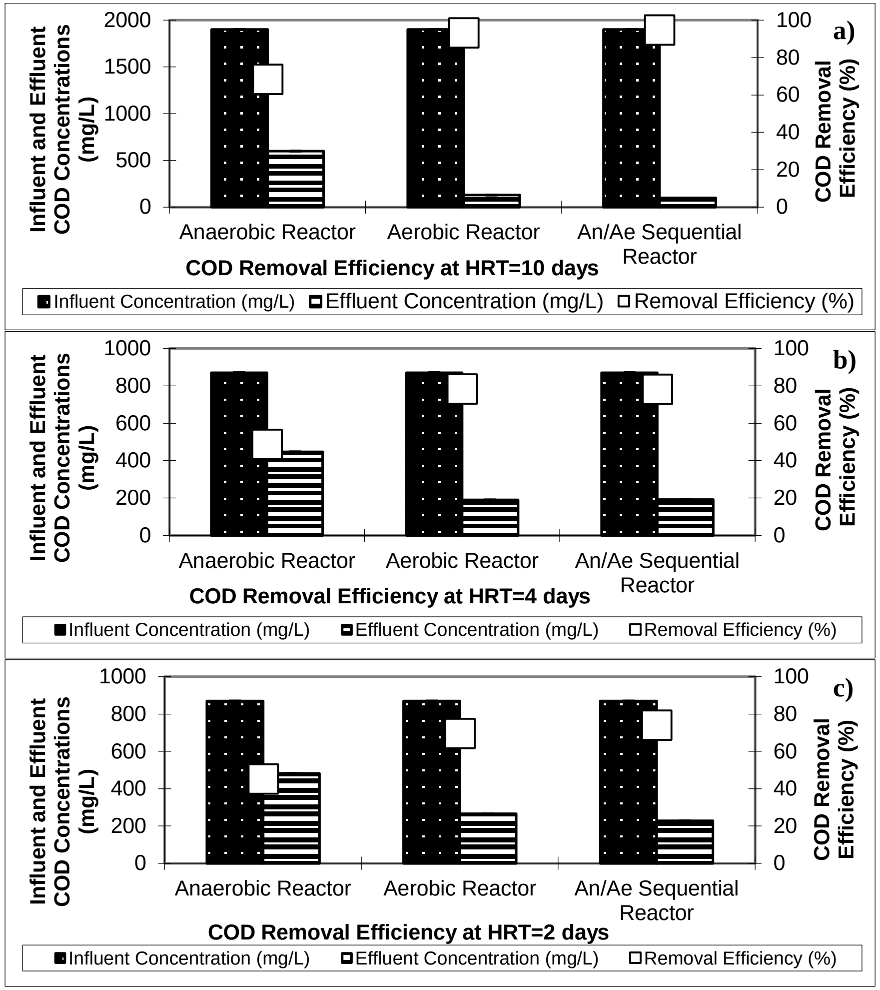

Figure 2: a) COD concentrations and yields during the 10 days of HRT operation at 0.19 gr COD/L.day OLR, b) COD concentrations and yields during the 4 days of HRT operation at 0.22 gr COD/L.day OLR, c) COD concentrations and yields during the 2 days of HRT operation at 0.44 gr COD/L.day OLR

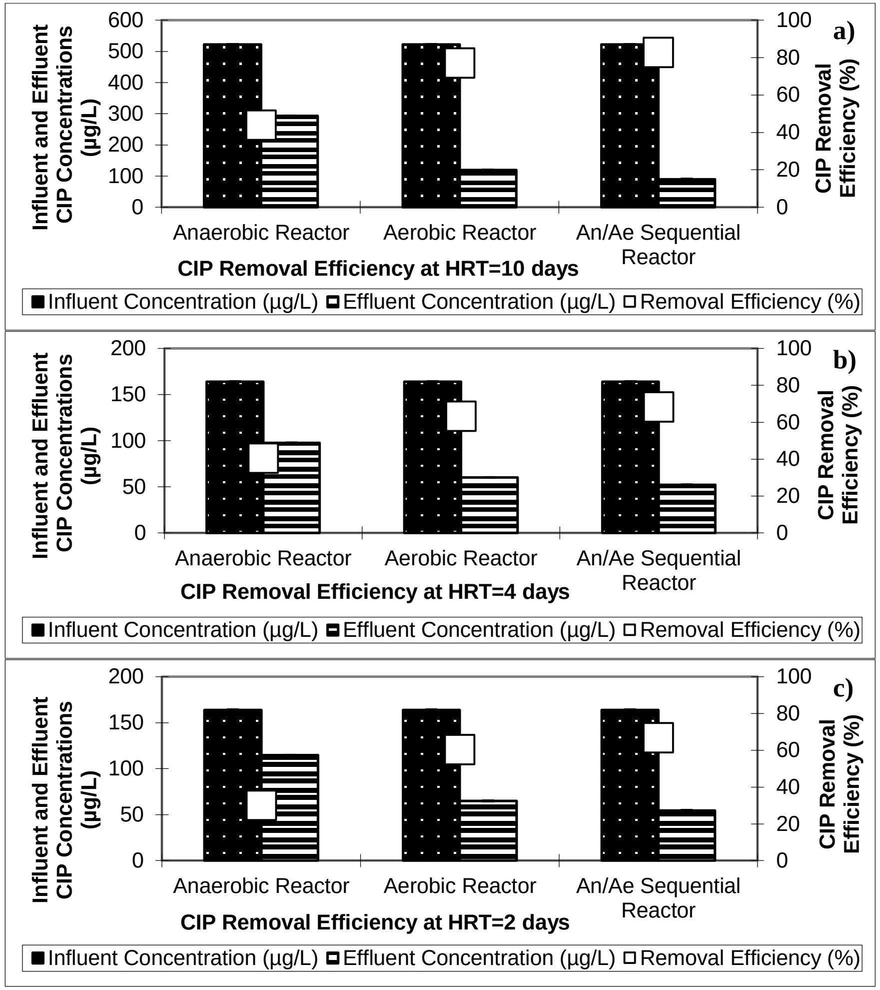

Figure 3. a) CIP concentrations and yields during the 10 days of HRT operation at 0.19 gr COD/L.day OLR, b) CIP concentrations and yields during the 4 days of HRT operation at 0.22 gr COD/L.day OLR, c) CIP concentrations and yields during the 2 days of HRT operation at 0.44 gr COD/L.day O

4. 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 wastewater effluents.

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