REMOVAL OF CIPROFLOXACIN ANTIBIOTIC WITH NANO GRAPHEN OXIDE MAGNETITE: COMPARISON OF ADSORPTION AND PHOTOOXIDATION PROCESSES

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ABSTRACT

1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinolinecarboxylic acid ($C_{17}H_{18}FN_3O_3$)-Ciprofloxacin (CIP) is a widely used fluoroquinolone antibiotic both in aquatic life and agriculture. Graphene has been extensively utilized in various fields due to its favorable physical and chemical properties with large surface area and high chemical and termal stabilities. The aim of the study was to investigate the removal of CIP at increasing concentrations (1 mg/L, 3 mg/L , 5 mg/L , 25 mg/L , 100 mg/L , 500 mg/L , 1000 mg/L) at increasing nano graphene oxide-magnetite concentrations (nano-GO/M) (0,5 g/L, 2 g/L, 10 g/L), contact times (15 min, 30 min and 60 min) and pH values by two different removal processes namely adsoption and photooxidation. For maximum 1 mg/L CIP removal (6%), the optimum nano-GO/M concentration, contacting time and, pH were found as 0.5 g/L, 30 min, and 6.5, respectively by adsorption. For maximum 1 mg/L CIP removal (93%), the optimum nano-GO/M concentration, contacting time and, pH were found as 0.5 g/L 30 min, and 6.5, respectively, by photooxidation. Among the Langmuir and Freundlich adsorption models it was found that CIP adsorption on nano-GO/M was suitable for Freundlich isotherm and the K_F and n kinetic constants were calculated as 0.55 unitless and 1.39 unitless, respectively.

Keywords: Ciprofloxacin, Photooxidation, Adsorption, Retention time, Nano composite

1. Introduction

Excessive amount use of pharmaceuticals have resulted in their detection in effluents of wastewater treatment plants. Many of these pharmaceuticals have low biodegradability in the environment and those taken by living beings are disposed of from living metabolism as unchanged or little transformed. Among widespread used antibiotics, fluoroquinolone antibiotics are an important type with undetectable biodegradability (Kagle *et al*., 2009). CIP is a synthetic antibiotic used worldwide for the treatment of several bacterial infections in both humans and animals. In receiving environments, low concentrations of antibiotic traces can cause resistance to microorganisms (Bhandari *et al*., 2008). Concentrations of CIP in wastewaters have been obtained to range from ng to mg L^{-1}, (i.e. 50 mg L^{-1} near drug manufacturing plants) (Larsson *et al*., 2007), therefore CIP removal from wastewater has become important. In the last literature surveys, a few studies have been reported for the removal of CIP from water which includes photooxidation (Belden *et al*., 2007), photo-Fenton oxidation (Sun *et al*., 2009), , dissolved organic carbon (Carmosini and Lee, 2009) ozonation (De Witte *et al*., 2010), montmorillonite (Wang *et al*., 2011), surface modified carbon materials (Carabineiro *et al*., 2011), adsorption onto biocomposite fibers of graphene oxide/calcium alginate (Shaoling *et al*., 2013), adsorption on activated carbon (Yuanyuan *et al*., 2014).

Graphene has the perfect sp^2 hybrid carbon nanostructure wıth two-dimensional carbon structure havıng excellent conductivity and the high specific surface area. Graphene oxide (GO) is a kind of novel two-dimensional graphene-based material, was developed for the removal of pollutants in the aquatic environment which have dispersibility and beneficial to remove

pollutants in wastewater because of different functional groups, such as hydroxyl, carboxyl and epoxy groups (Zhen *et al*,. 2013). These functional groups make GO suitable to remove the pharmaceutıcals wıth low cost. Thus, the combination of GO with magnetic NPs to produce a magnetic graphene-based composite and it will be separated from the matrix rapidly and easily by an external magnetic field.

In this study, photo-catalytic treatment and adsorption of CIP was studied with nano-GO/M composite, which is developed under laboratory circumstances. The effects of concentration developed nano-GO/M, the doses of CIP, the light intensity of UV and the retention time were studied. In addition to those effect of pH on adsorption capacity of nano-GO/M composite was also probed. Removal efficiencies of CIP by adsorpsiton and photo-oxidation were compared.

2. Metarial and methods

2.1. The synthesis of Nano-GO/M Composite

GO was synthesized from natural graphite powder by a modified Hummers method (Chen *et al*., 2009). 120 mL of H_2SO_4 was added into 5 g of graphene and 2.5 g of $NaNO_3$ containing flask and followed by stirring the mixture for 30 min inside an water bath. Next, 15 g of $KMnO_4$ was added gradually to the mixture. The reaction temperature was kept below 20 °C during this step. The mixture was stirred at room temperature overnight, continuously. After this period, 150 mL of H_2O was slowly added under stirring. The mixture was stirred for one day at 98 °C. Following, 50 mL of 30% H_2O_2 was added to the final mixture. For purification, the mixture was washed with 5% HCl and deionized (DI) water for many times and then, centrifugated and dried under vacuum. The final product GO was obtained as a solid phase (Lunhong *et al*., 2011). The Fe_3O_4 Nano particules were dispersed in 25 mL of water and added to 50 mL of GO aqueous solution, drop by drop (1 mg/mL). The mixture was stirred at 60 °C through 1 h. The product was collected by using a magnet and washed with water three times. Finally, the Fe_3O_4/GO composite was obtained (Nengsheng *et al*,. 2014).

2.2. Adsorption experiments

Adsorption experiments were conducted to investigate the removal of CIP using nano-GO/M. For this purpose, different CIP concentrations (1 mg/L, 3 mg/L , 5 mg/L , 25 mg/L , 100 mg/L , 500 mg/L , 1000 mg/L) and nano-GO/M dosages (0,5 g/L, 2 g/L, 10 g/L) were used. Selected dosages of nano-GO/M were added into CIP solution and was shaken in an incubator using teflon coated glass reactors with a volume of 250 mL for 15 min, 30 min, 60 min. At the end of the adsorption experiments, nano-GO/M were separated magnetically from the solution, and then, samples were analyzed in HPLC. Langmuir and Freundlich isotherms were used to fit the equilibrium data on nano-GO/M composite. Equation 1 shows the maximum adsorption capacity;

$$q_e = \frac{(C_0 - C_e).V}{m} \quad (1)$$

where V is the volume of solution (L), q_e is the maximum adsorption capacity, C_i and C_e are the initial and equilibrium concentrations of the CIP (mg/L), and m is the amount of adsorbent.

2.3. Photocatalytic experiments

Photocatalytic experiments were conducted in a system which is well-sealed and constructed with stainless steel material, at room temperature of 21 °C. Quartz glass reactors and 10 UV lambs (each one has a power of 30 watt) were used for photocatalytic experiments. The effects of retention times (15 min, 30 min, 60 min) and pH levels (4, 6.5, 10) on the treatment of CIP was investigated. After experiments, magnetically separated CIP solution were analyzed in HPLC. All the experiments data were found from the duplicates analysis and the results presented as the mean values of the duplicates samples.

2.4. Analytical procedures

HPLC Analysis: A HPLC Degasser (Agilent 1100), a HPLC Pump (Agilent 1100), a HPLC Auto-Sampler (Agilent 1100), a HPLC Column Oven (Agilent 1100) and a HPLC Diode-Array-Detector (DAD) (Agilent 1100) and C-18 (5 µm, 4.6 mm 250 mm, Thermo Scientific) column were used. The analyte was separated at ambient temperature. The mobile phase consisted of KH_2PO_4 in aqueous solution and Acetonitrile (95:5, v/v). The flow rate was set at 1.5 mL/min and injection volume at 20 µL. The detection wavelengths of DAD was set at: 210 nm.

2.5. Adsorption Isotherms Used in This Study

In this study Freundlich (Equation 2) and Langmuir (Equation 3) isotherms were used to detect the adsorptıon kinetics in CIP solution on nano-GO/M composite.

$$q_e = K_F . C_e^{\frac{1}{n}} \qquad (2)$$

$$q_e = \frac{q_m . K_L . C_e}{1 + K_L . C_e} \qquad (3)$$

q_e and C_e are the equilibrium concentrations of the pollutants compound on the sorbent (mg/g) and in the solution (mg/L), respectively. Langmuir adsorption constant (K_L ,unitless) are the fitted Langmuir parameters and Freundlich constant (K_F, unitless) are the fitted Freundlich constant and n (unitless) represents the maximum adsorption capacity.

3. Results and discussion

3.1. Batch Adsorption Studies

3.1.1. Effects of Nano-GO/M Composite Concentrations on the Treatment of CIP

In order to determine the maximum adsorption removal efficiencies, 0.5 g/L, 2g/L, 10g/L nano-GO/M composite concentrations were researched. The maximum removal yield of CIP (for initial CIP, 1 mg/L) was found as 6 % at 0.5 g/L nano composite after 30 min contact time at pH 6.5 and 21°C (Figure 1a). Similarly, the same yield was obtained for 2 g/L nano-GO/M at same operation (30 min contact time, at pH 6.5 and 21°C) for initial CIP concentration of 1 mg/L (Figure 1b). However, with 10 g/L nano-GO/M composite concentration lower removal efficiency (4%) was obtained at the same operation time (30 min) (Figure 1c). Thus, for maximum CIP removal yields (6%) the optimum nano-GO/M concentration was obtained as 0,5 g/l. Figure 1d summarizes the effects of increasing nano GO/M concentrations (0,5, 2 and 10g/L) on CIP yields at a CIP concentration of 5 mg/L after 30 min adsorption time at pH=6.5 and at 21°C .

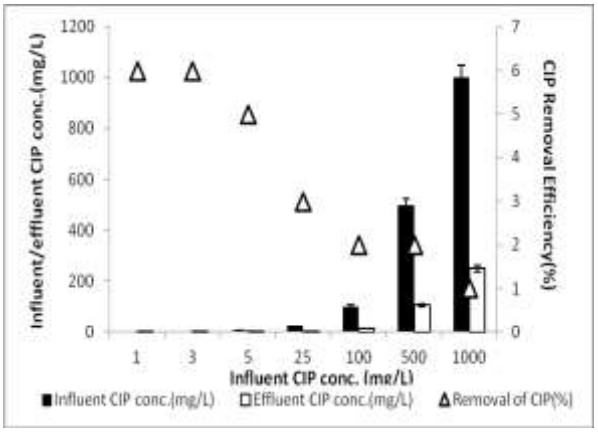

Figure 1a: Effect of increasing CIP concentration on the yields of CIP removal at a nano-GO/M concentration of 0.5 g/L at pH=6.5, at 21°C and 30 mİn contacting tıme

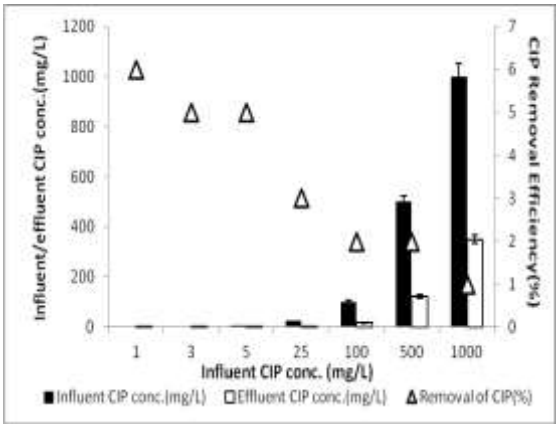

Figure 1b: Effect of increasing CIP concentration on the yields of CIP removal at a nano-GO/M concentration of 2 g/L at pH=6.5, at 21°C and 30 min contacting time

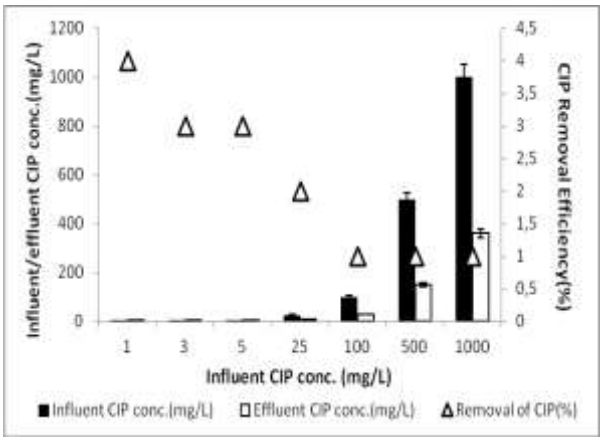

Figure 1c: Effect of increasing CIP concentration on the yields of CıP removal at a nano-GO/M concentration of 10 g/L at pH=6.5, at 21°C and 30 mın contactıng tıme

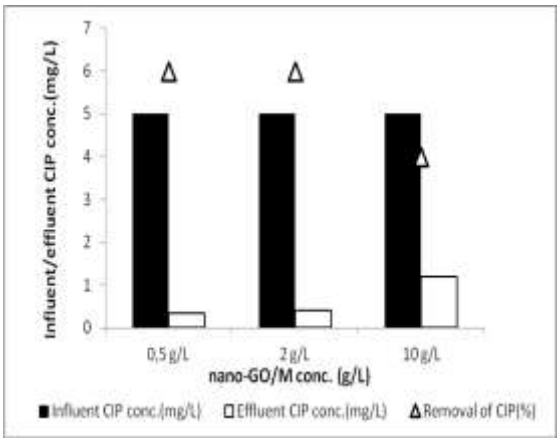

Figure 1d: Comparison of increasing concentration of nano-GO/M (0.5, 2 and 10 g/L) on the yields of CıP removal for constant CIP concentration (5 mg/L) at pH=6.5, at 21°C and 30 mın contactıng tıme

3.1.2. Effect of Contacting Time On The Removal of CIP

After determining the optimum concentration of nano-GO/M (0,5 g/l), it was decided to investigate the effect of contact time on the removal of CIP at increasing retention times (15 min, 30 min, 60 min) at pH = 6.5 at a temperature of 21°C. As the contacting time was increased from 15 min to 30 and 60 min the CIP removals increased from 3% to 6% and to 7% for initial CIP concentration of 5 mg/l (Figure 2). Further increase in contact time from 60 min to 900 min decreased the CIP yield from 6% to 2%. As a result, the optimum contact time for maximum CIP removal (6%) was found to be 30 min. It was not found a significant difference on removal efficiency of CIP between 30 and 60 min.

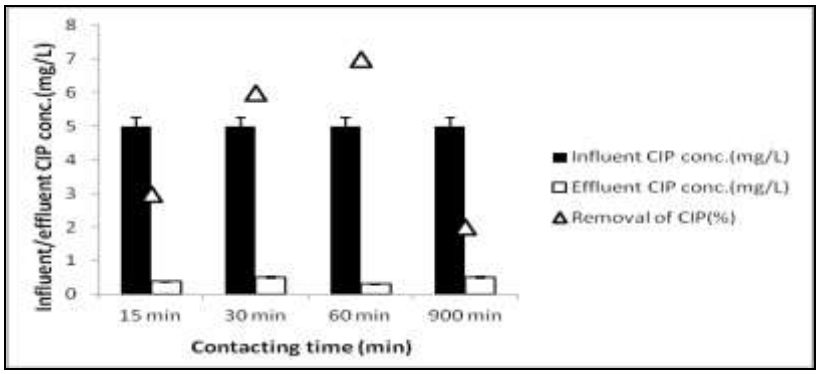

Figure 2: Effect of contacting time on the yields of constant CIP concentration (5 mg/L), at a constant nano GO/M concentration (0,5 g/L), at a pH of 6.5 and at 21°C

3.1.3. Effect of Increasıng CIP concentrations on the CIP removal

In this step of this study, the effects of increasing CIP concentrations (1 mg/L, 3 mg/L , 5 mg/L , 25 mg/L , 100 mg/L , 500 mg/L , 1000 mg/L) on the CIP removals were studied (Figure 3) at a nano-GO/M concentration of 0.5 g/L, after 30 min contacting time, at pH= 6.5 and at a temperature of 21°C. Results showed that increasing in the CIP concentration reduced the removal efficiency of CIP at a nano-GO/M concentration of 0.5 g/L. For 1 mg/L initial CIP concentration the maximum CIP removal efficiency was found as 6% while the removal efficiency of 1000 mg/L CIP was found almost 1%. For the maximum adsorption yield of CIP (6%) the optimum CIP concentration was found to be 1 mg/L.

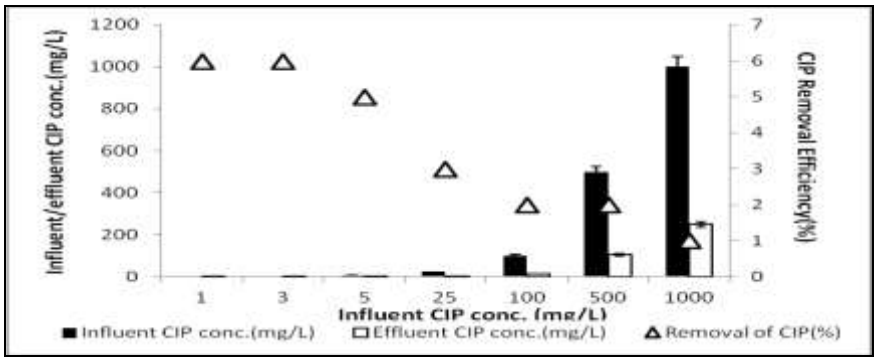

Figure 3: Effect of increasing CIP concentration on the yields of CıP removal at a nano-GO/M concentration of 0.5 g/L at pH=6.5, at 21°C and 30 mın contactıng tıme

3.1.4. Effect of pH on the treatment of CIP with nano-GO/M composite

The effects of pH on the removals of CIP were studied under acidic, neutral and alkaline pHs(4, 6.5 and 10) at an adsorption time of 30 min at a nano-GO/M concentration of 0.5 g/L and at 21°C (Figure 4). It was not found a significant difference between pH and CIP yields for CIP concentrations varying betwen 1 and 5 mg/l. For > 25 mg/L CIP concentrations the CIP yields decreased to 1 % from 3-4%.

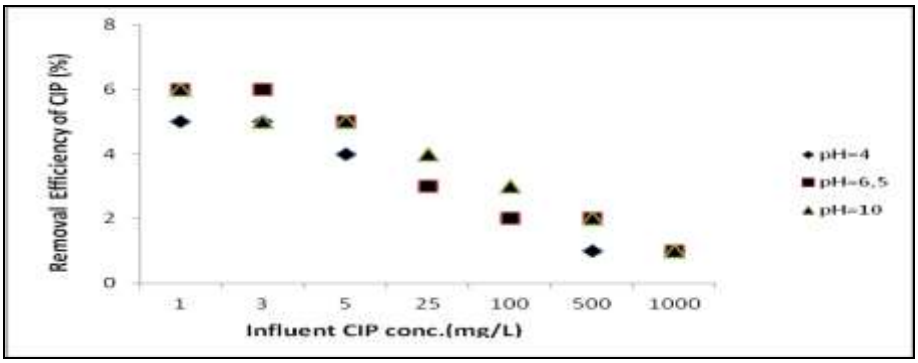

Figure 4: Effect of different pHs (4, 6.5 and 10) on the yield of CIP removal at a nano-GO/M concentration of 0.5 g/L at pH=6.5, at 21°C and 30 mİn contactİng tİme

3.2. Adsorption Kinetics

Langmuir and Freundlich adsorption isotherms were applied to the yields values obtained from the adsorption process. In Langmuir isotherm the R^2 value of the linear line was 0.81, K_L (Langmuir adsorption constant, L/mg) and q_m (maximum adsorption capacity of adsorbent, mg/g) were calculated as 0.068 L/mg and 1.36 mg/g, respectively (Figure 5a).

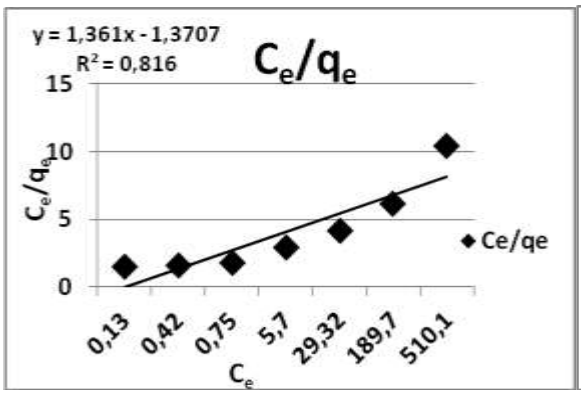

Figure 5a: Langmuir Isotherm for CIP

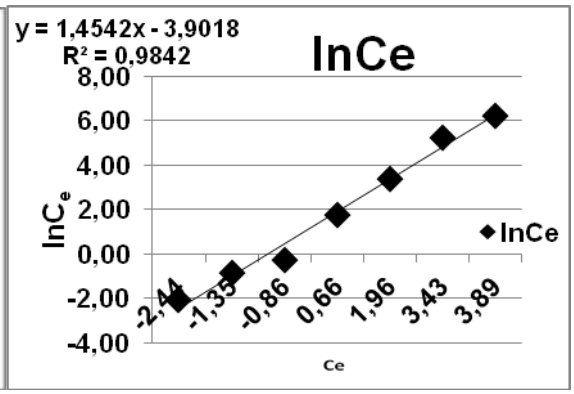

Figure 5b: Freundlich Isotherm for CIP

The linear lines between C_e and lnC_e in Freundlich isotherm showed that the K_F (indicator of adsorption capacity) and n (measure of intensity of adsorption) kinetic constants were calculated as 0.55 unitless and 1.39 unitless, respectively. The R^2 value between C_e and lnC_e were 0.98 for CIP removal by adsorption in the Freundliich isotherm (Figure 5b). It was found that the R^2 value in Freundlich isotherm were higher than that in Langmuir isotherm (R^2= 0.81) for CIP adsorption with high adsorption capacity of 0.55 unitless. Therefore, The CIP was adsorbed according to Freundlich isoterm.

3.3. Photocatalytic Studies

3.3.1. Effects of Nano-GO/M Composite Concentrations on the Treatment of CIP by Photooxidation

The photocatalytic experiments were carried out at increasing nano-GO/M composite concentrations, different pH values (4, 6.5 and 10) and irradiation times (15, 30, 60 min).

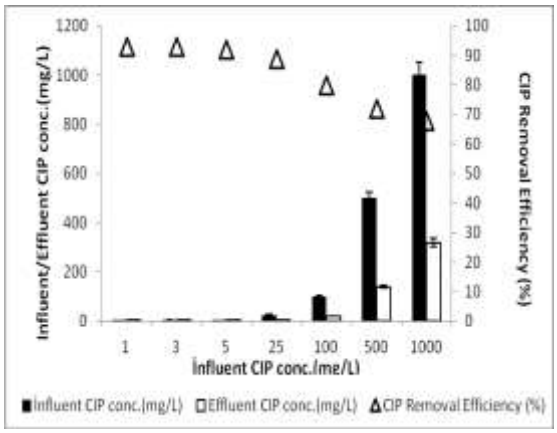

Figure 6a: Effect of increasing CIP concentration on the yields of CIP removal at a nano-GO/M concentration of 0.5 g/L at pH=6.5, at 21°C and 30 min contacting tıme by photooxidation

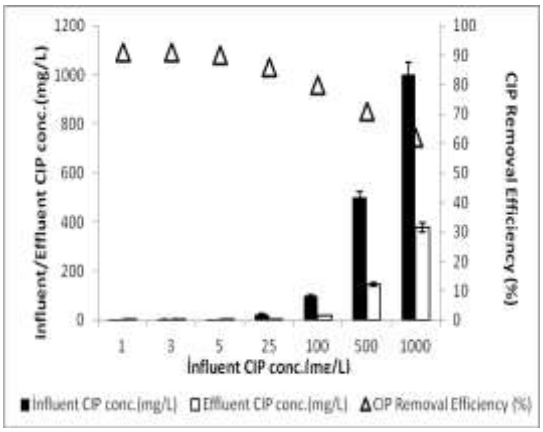

Figure 6b: Effect of increasing CIP concentration on the yields of CıP removal at a nano-GO/M concentration of 2 g/L at pH=6.5, at 21°C and 30 min contacting time by photooxidation.

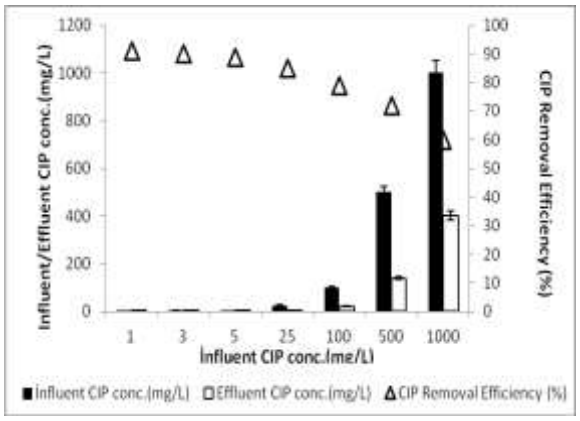

Figure 6c: Effect of increasing CIP concentration on the yields of CIP removal at a nano-GO/M concentration of 10 g/L at pH=6.5, at 21°C and 30 min contacting time by photooxidation.

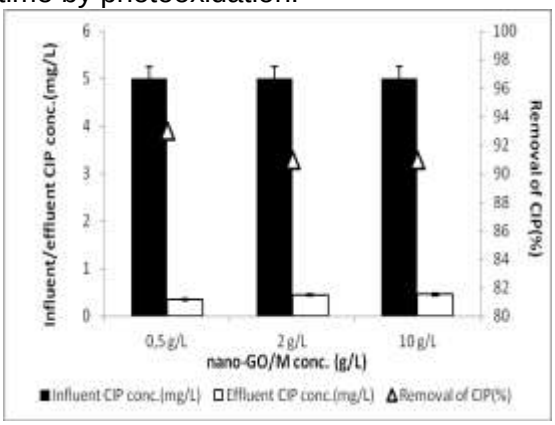

Figure 6d: Comparison of increasing concentration of nano-GO/M (0.5, 2 and 10 g/L) on the yield of CIP removal for constant CIP concentration (5 mg/L) at pH=6.5, at 21°C and 30 min contacting time by photooxidation.

Among the nano composite concentrations (0.5, 2, 10 g/L), the maximum removal efficiency of CIP (initial conc. 1mg/L) was found at 0.5 g/l nano-GO/M composite at pH 6.5 after 30 min retention time. The maximum removal efficiency of CIP was 93% (Figure 6a.). Similarly, 91 %

removal yield was obtained for 2 g/L nano-GO/M at the same operational conditions (30 min contact time, pH 6.5 and 21°C) for initial CIP concentration of 1 mg/L (Figure 6b). With 10 g/L nano-GO/M composite concentration the same removal efficiency (91%) was obtained at the same operation time (30 min) (Figure 6c). Thus, for maximum CIP yields (93%) the optimum nano-GO/M concentration was obtained as 0,5 g/l. Figure 6d. summarizes the influent/effluent CIP concentrations and removal yields with increasing nano GO/M concentration (0,5, 2 and 10g/L) for 30 min irradiation time.

Adsorption of UV light with sufficient energy, leads to nano-GO/M particles produce electrons (e−) and valence band holes (h+). The hole in the valence band can react with H_2O or hydroxide ions adsorbed at the particle surface to produce OH•, while the electron in the conduction band can reduce O_2 to produce O_2•. Both, holes and OH• are very reactive toward pollutants in the wastewater (Adel *et al*., 2013). The oxidizing power of the •OH radicals can break C-C and C-H bonds of CIP adsorbed on the surface of nano-GO/M composite.

3.3.2. Effect of Irradiation Time On The Removal of CIP

CIP treatment with nano-GO/M was investigated at different irradiation times. Irradiation times were chosen as 15, 30 and 60 min. The concentration of nano-GO/M was selected as 0.5 g/L to determine the optimum irradiation time since the maximum CIP removal was found in this nano-composite concentration. The irradiation time experiments were realized in the original pH of CIP (6.5) at 21°C. The maximum removal efficiency of CIP was obtained at 30 min among the irradiation times used for the experiments. As the contacting time was increased from 15 min to 30 and 60 min the CIP removals increased from 82% to 93% and to 98% for initial CIP concentration of 5 mg/L (Figure 7). Further increase in contact time from 60 min to 900 min decreased the CIP removals from 98% to 95%. Thus optimum irradiation time was selected as 30 min.

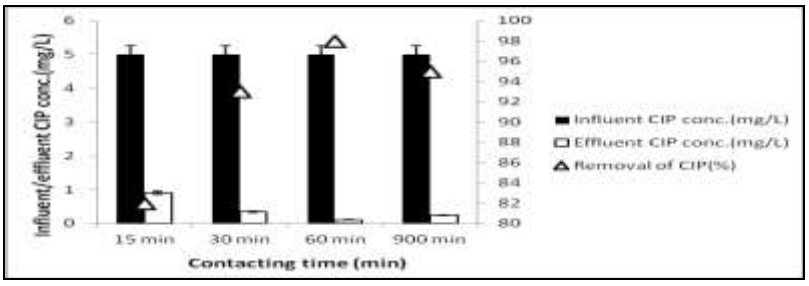

Figure 7: Effect of irradiation time on the yields of constant CIP concentration(5 mg/L), at a constant nano GO/M concentration (0.5 g/L), at a pH of 6.5 and at 21°C

3.3.3. Effect of pH on the UV treatment of CIP with nano-GO/M composite

In this step, the effect of acidic, neutral and alkaline pHs were investigated on the treatment efficiency of CIP with nano-GO/M. (Figure. 8).

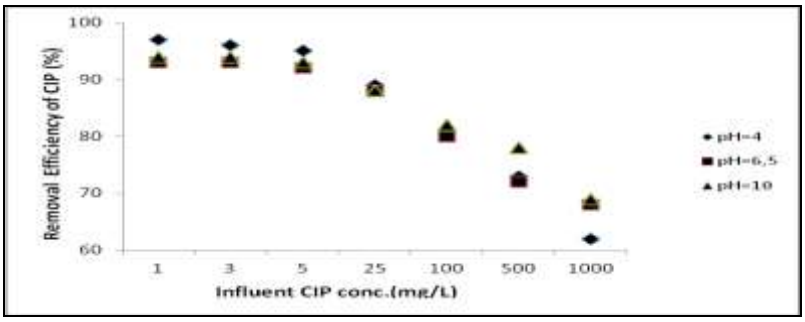

Figure 8: Effect of different pHs (4, 6.5 and 10) on the yield of CIP removal at a nano-GO/M concentration of 0.5 g/L at pH=6.5, at 21°C and 30 mın irradiation tıme

3.3.4. Effect of Increasıng CIP concentrations on the CIP removal by Photooxidation

The effects of increasing CIP concentrations (1 mg/L, 3 mg/L , 5 mg/L , 25 mg/L , 100 mg/L , 500 mg/L , 1000 mg/L) on the CIP removals were studied (Figure 9) at a nano-GO/M concentration of 0.5 g/L, 30 min contacting time, at pH= 6.5 and at a temperature of 21°C. Results showed that increasing in the CIP concentration yielded a decrease on removal efficiency of CIP at a nano-GO/M concentration of 0.5 g/L. For 1- 5 g/L CIP concentration, the maximum removal efficiency of CIP antibiotic was found as 93%. For CIP concentration varying between 100 and 500 mg/L the CIP yields were 79% and 72% while the CIP removal was 68% at a CIP concentration of 1000 mg/L.

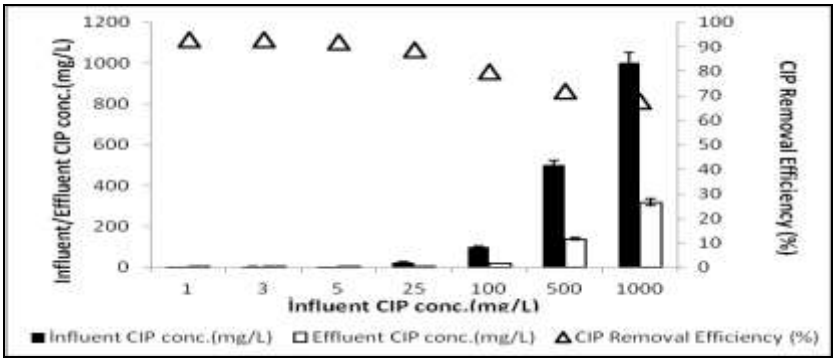

Figure 9: Effect of increasing CIP concentrations (1 mg/L, 3 mg/L, 5 mg/L, 25 mg/L, 100 mg/L, 500 mg/L, 1000 mg/L) on the yield of CIP removal at a nano-GO/M concentration of 0.5 g/L at pH=6.5, at 21°C and 30 min irradiation time

3.4. FTIR analysis of nano-GO/M composite

The produced nano particles (raw nano-GO/M composite) and treated samples (100 mg/L of CIP) with UV were characterized using Fourier transform infrared spectroscopy (FTIR) (**Figures 10a, 10b**). **Figure 10a** shows the peaks of GO plotted between wave number $(cm)^{-1}$ and percent transmittance (%). In the spectrum of nano-GO/M, the peaks at 2359, 1568 cm^{-1} are the characteristics spectrum of benzene ring while the peak at 1073 cm^{-1} is the characteristic spectrum of the C–OH rings. This, confirms the presence of graphene oxide peak at 600 cm^{-1} is the characteristics of Fe_3O_4 which gives evidence of the successful preparation of the nano-GO/M as reported by Huamin *et al*., (2012). **Figure 10b**. shows the FTIR analysis of nano-GO/M composite after CIP treatment with UV. The maximum peaks obtained in this figure are similar to the nano composite before UV treatment. Condensation of nano-GO/M composite remained almost the same after UV treatment. This shows that nano-GO/M composite can be recovered and can be used again for the treatment CIP with UV.

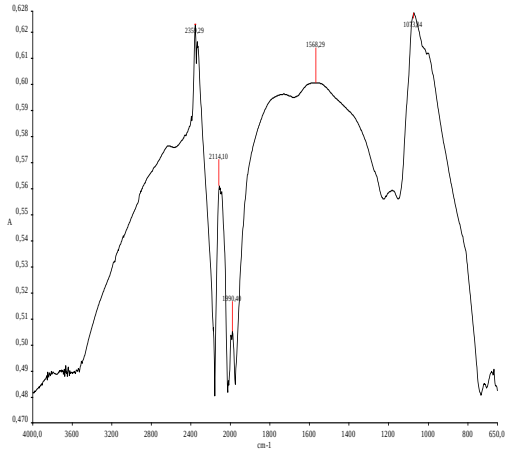

Figure 10a. FTIR analysis of nano GO/M

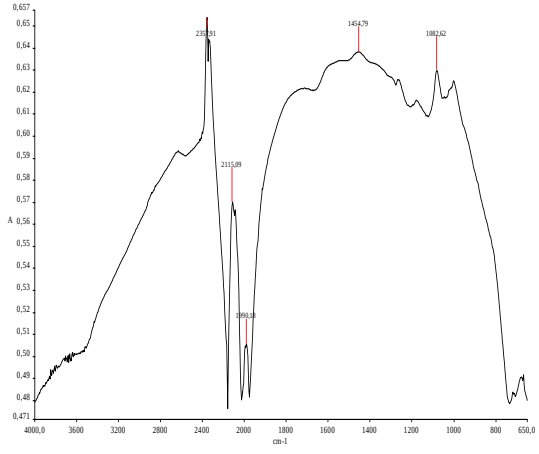

Figure 10b. FTIR analysis of nano GO/M after UV

4. Conclusion

For maximum CIP removal (93%) the optimum nano-GO/M concentration was found to be 0.5 g/L at 1- 25 mg/L initial CIP concentration, at pH of 6.5, at a UV power of 300 W and at a temperature of 21°C after 30 minutes irradiation time throughout photocatalytic degradation. The minimum CIP removal was found to be 68% at 1000 mg/L CIP at the optimum nano-GO/M concentration (0.5 g/L) at a pH of 6.5, at a UV power of 300 W and at a temperature of 21°C after 30 minutes irradiation time by photooxidation. The maximum adsorption yield was found to be 6% for 1-25 mg/L CIP at a GO/M concentration of 0,5 g/L at a pH of 6.5 and at a temperature of 21°C after 30 minutes retention time. The minimum CIP removal was 1% at a nano-GO/M concentration of 0.5 g/L for 1000 mg/L CIP concentration, at a pH of 6.5 and at a temperature of 21°C after 30 minutes retention time by adsorption. 1-25 mg/L CIP was adsorbed according to the Freundlich isotherm compared to Langmuir isotherm with high R^2 values. It was found that the CIP was mainly removed by 300 W UV (93%) by 0.5 g/l nano-GO/M concentration at pH = 6.5 at 21°C while the CIP removal by adsorption was found to be minor (6%) at 0.5 g/l nano-GO/M concentration at pH = 6.5 at 21°C for 1 mg/L CIP.

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