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Research article

Characterization and removal of antibiotic residues by *NFC*-doped photocatalytic oxidation from domestic and industrial secondary treated wastewaters in Meric-Ergene Basin and reuse assessment for irrigation

Reyhan Ata, Günay Yıldız Töre*

Environmental Engineering Department of Çorlu Engineering Faculty, Namik Kemal University, 59860 Tekirdag, Turkey

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ABSTRACT

Antibiotics are important contaminants that have become an increasingly big problem due to the discharge of the receiving environment. The presence of these organic based pollutants in influent wastewater can inhibit the biological processes and resist to degradation in wastewater treatment plants. Moreover, the consumption of agricultural products, irrigated with water containing antibiotic residues, leads to major harmful effects to the human body through the food chain. In this study; firstly, a conventional characterization was made in terms of COD, TOC, SS, color and of antibiotic residue characterization of untreated raw (influent) and biologically treated (effluent) water from domestic and industrial wastewater treatment plants located in the Meriç-Ergene Basin. After that, photocatalytic activity test was run under visible light for selected antibiotics (Erythromycin, Ciprofloxacin, Sulphametoxasol) which were detected by HPLC MS/MS in excess amount. Finally, for the photocatalytic oxidation, a new generation *NFC (Nitrogen-Floride-Carbon)*-doped titanium dioxide photocatalyst, which has never been studied in the literature before, was prepared according to the sol-gel method without using thermal processing. Photocatalysts were characterized by UV–vis DRS reflectance and Laser Raman Spectra measurements. All other analyzes were made according to the standard methods. Considering the conventional characterization results; investigated domestic wastewaters exhibited moderate characteristics while industrial wastewater samples had strong characteristics in terms of COD, TOC and SS pollution in accordance with the literature. By the way, contrary to expectations, antibiotic residue results have proved that the effluent wastewater contains more antibiotics than the influent. This can be explained by the fact that, some antibiotics in domestic wastewaters are probably already trapped in feces and cannot be purified by conventional systems since they are released after biological treatment, as mentioned similar studies in the literature. Moreover, by means of 7 h *NFC*-doped photocatalytic oxidation under visible light, beside approximately % 62 to %79 COD and 62%–86% TOC removal, %99 to %100 removal of antibiotic residue was provided. According to these results, domestic and industrial secondary treated wastewaters in Meric-Ergene Basin can be advance treated, succesfully, with *NFC*-doped photocatalyst to remove antibiotic residues besides conventional pollutants. This result show that Meriç-Ergene discharge criteria determined by Forest and Water Ministry of Turkey can be provided with this new type photocatalytic process and healthy reuse of this river for irrigation will be possible.

1. Introduction

The Meriç Ergene River Basin, which starts with the Istanbul provincial border and covers the border area with Bulgaria and Greece, is one of the most important agricultural lands of our country containing a considerable amount of irrigation and drinking water for the Thrace region. The rapidly developing industry, population, settlements and agriculture in the 1980s resulted in increasing water require problem and led to increase in both the amount of pollution and pollution load in the Ergene Basin. Ergene and Meriç River waters, which are much lower-quality water source carrying the pollution loads of domestic and industrial treated/untreated. Until last years, although it is known that this pollution loads contain conventionally treatable pollutants, unfortunately new scientific researches showed that most dangerous refractory pollutants, such as antibiotics which can be found in both domestic and industrial wastewaters can not be treated in conventional

* Corresponding author.
E-mail address: gyildiztore@nku.edu.tr (G. Yıldız Töre).

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treatment systems. Moreover, because both Meriç-Ergene River discharge criteria do not determined that provide the irrigation water quality standards and also these discharges include most dangerous refractory pollutants such as antibiotics residues. So, antibiotics residue discharges are the most important and most worrisome part of the water pollution in the basin.

Sources of antibiotics, consumed by prescription/non-prescription by people and animals in hospitals, are houses, hospitals, health centers (medical treatment, disposal of unused drugs), poultry, livestock feeding operations (growth promoters), drug manufacturers (Cabello, 2006; Sarmah et al., 2006; Gao et al., 2012; Kemper, 2008). According to the investigations, approximately 60%–75% of the antibiotics, that can be metabolized partly after being used by humans and animals, are expelled without being absorbed and so that it is mixed into the wastewater, in unchanged form by urine and feces, or excreted in the form of its metabolites (Gao et al., 2012; Kümmerer and Henninger, 2003; Chee-Sanford et al., 2009; Halling-Sorensen et al., 1998; Perez et al., 2008; Pruden, 2009). As a result, antibiotics have been repeatedly detected in surface water and sediment (Cheng et al., 2018b; Guo et al., 2017; Huang et al., 2016; Liu et al., 2017; Zhang et al., 2016). Therefore, antibiotics have become a growing problem in wastewater treatment plants and at the same time they have been corrupting the ecological balance due to the toxicity on organisms in the ecosystem and biological treatment systems. They also inhibit biological treatment systems since they are persistent but not easily degradable species pollutants (Kasprzyk-Hordern et al., 2009; Karthikeyan and Meyer, 2006; Homem and Santos, 2011; Lai et al., 2016; Li et al., 2017; Yang et al., 2010) in Meriç-Ergene Basin.

Moreover, the consumption of agricultural products, irrigated with water containing antibiotic residues, leads to major harmful effects on to the endocrine and reproductive systems when taken back to the human body through the food chain. Antibiotics and Endocrine Disrupting Chemicals are essential substances to be treated with water and which are difficult to measure due to their extremely low levels in the effluent in the secondary treatment plant (Schafer and Waite, 2002; Rickman and Mezyk, 2010; Snyder et al., 2003a) and they need to be degraded by advanced oxidation processes for complete removal. Advanced oxidation processes (AOPs) are promising techniques for the disposal of toxic and persistent organic pollutants, like antibiotics, in wastewaters (Cheng et al., 2017b; Huang et al., 2017a; Yang et al., 2016, 2017). Among these techniques, Fenton process, based on the generation of highly reactive hydroxyl radicals ($HO^{\cdot}$), has received particular attention (Cheng et al., 2016b).

Particularly titanium dioxide (TiO_2), as a heterogeneous photocatalyst, is an effective water and wastewater treatment process for the removal of recalcitrant and photo-stable organic contaminants such as pharmaceuticals and antibiotics in wastewater treatment (Singh et al., 2015). Although having an excellent photocatalytic activity, non-toxicity, long-term stability and low cost, TiO_2 has limited applications with a 3.2 eV band gap energy in anatase form absorbing only ultraviolet (UV) light in an effective way. In order to extend the photo absorbtion capability from the UV to the visible light region, recently doping methods with N, C, F, B, P, S elements have been widely used. (Asahi et al., 2001; El-Sheikh et al., 2014; Sacco et al., 2012; Devi and Kavitha, 2013). Studies revealed that N doped TiO_2 seems to be the most promising photocatalyst which is active under visible light irradiation (Asahi et al., 2001; Saien and Mesgari, 2016; Nosaka et al., 2005; Rizzo et al., 2014). Asahi et al. reported that N doping can achieve band gap narrowing through substitution lattice sites by mixing of N 2p with O 2p states in the valence band. Another point of view (Irie et al., 2003) proved that interstitial type of N-atoms are achieved by generation of inter-gap states induced by formation of NO bond with the π character at interstitial lattice sites (Valentin et al., 2007). Beside N-doping, the advantages of double and triple doping have been disclosured in the literature (Li et al., 2005a,b). On the other hand, as for the examination of TiO_2 doping with carbon, similar to N-doping, there has also been a dispute if the doped type of carbon is substitutional (Choi et al., 2004) or interstitial (Tachikawa et al., 2004; Li et al., 2005a,b). In this sense, Cong et al. (Cong et al., 2006) synthesized C-N-doped TiO_2 nanoparticles by microemulsion-hydrothermal process and then examined the structures and photocatalytic activities of these particles. However, they did not discuss the increase in photocatalytic activity in a profound way. Moreover, there are some disadvantages, such as the low yield, the use of organic solvents and high cost requirement, while the method they use when preparing C-N doped TiO_2 nanoparticles may be inconvenient for practical applications. Among non-metal doped TiO_2 materials, co-doped TiO_2 with three kinds of non-metals such as N, S and C (Dong et al., 2008; Wang et al., 2009; Wang et al., 2011 Zhang et al., 2014; Cheng et al., 2012; Cheng et al., 2013; Lin et al., 2013) shows higher photocatalytic activity in the visible range compared with single element doping to TiO_2 because of the beneficial merits from each dopant. Anatase is the most popular phase of TiO_2 to be employed as a photocatalyst because of its high photocatalytic activity (Rengifo-Herrera et al., 2008). On the other hand, the heterojunction of anatase/brookite biphase TiO_2 can achieve higher photocatalytic activity than single phase TiO_2, due to the synergistic effect between the two phases. In addition, the doping of the anatase/brookite biphase TiO_2 with one non-metal element has attracted much attention due to the improvement of the photocatalytic activity under visible light (Li and Liu, 2009; Etacheri et al., 2013).

Therefore, it is also very important to find an easier method for preparing C-N-F three-doped TiO_2 nanomaterials generated by the C, N and F doping. This study will make an important contribute to the literature, since, there is no study on doping TiO_2 with NFC (Nitrogen, Fluorine and Carbon) elements by using solvent-cast method at ambient temperature and at the same time in order to extend photo absorption capability and on photocatalytic activity study with the real wastewater under visible light. Another contribution of this study is to understand the synergistic antibiotic removal efficiency of *NFC*-doped photocatalyst in Meriç-Ergene Basin wastewater with a more effective and previously untested method.

So; the main objectives of this study can be summarized as followings;

- A characterization was made in terms of COD, TOC, color, temperature, pH, conductivity, dissolved oxygen and antibiotic residues of untreated (raw wastewater) from Kırklareli Malkara, Lüleburgaz and Karpuzlu Domestic Wastewater Treatment Plants and Çorlu and Çerkezköy OSB Industrial Wastewater Treatment Plants located in the Meriç-Ergene Basin, which contains a significant amount of irrigation and drinking water resources for Trakya region, and secondary treated effluent (biological treatment effluent) wastewater discharged to the surface waters of Meriç-Ergene Basin.
- Firstly, wastewater samples were taken, for three different seasons to follow seasonal changes, from influent and effluent of domestic and industrial waste water treatment plants (Malkara, Lüleburgaz, Kırklareli, Enez, Karpuzlu Domestic and Çerkezköy, Çorlu Industrial Conventional Wastewater Treatment Plants), located in Meriç Ergene Basin which contains a significant amount of irrigation and drinking water resources for Trakya region, and secondary treated effluent (biological treatment effluent) wastewater discharged to the surface waters,
- Then, these wastewater samples were characterized of in terms of both pollution parameters (such as pH, temperature, conductivity, color, DO-Dissolved Oxygen, COD- Chemical Oxygen Demand), SS-Suspended Solids) and 3 excess amount of antibiotic residues determined; Ciprofloxacine (CIP), Erythromicin (ERY), Sulphametoxasol (SMX).

Afterward, a cheap and effective *NFC*-doped (Nitrogen, Fluorine and Carbon doped) photocatalysts were prepared according to the sol-gel method (Sato, 1986) without using thermal processing which has never been studied in the literature before and then it was characterized.

- In order to follow decreasing and/or removal rate of antibiotics, HPLC MS-MS and UV–Vis Spectrophotometer measurements were used together with the measurements of COD and TOC removal rate at the end of the photocatalytic oxidation process.
- Finally, an assessment was made for the secondary treated and advanced treated domestic/industrial wastewater whether they are convenient for the usage in agricultural irrigation in the basin.

2. Material ve method

2.1. Sampling and characterization

Wastewater samples were collected from influent and effluent points of Malkara, Lüleburgaz, Kırklareli, Enez, Karpuzlu domestic and Çerkezköy, Çorlu industrial conventional wastewater treatment plants (WWTPs) in July, November and March according to the standard of “TS ISO 5667-10 Sampling from Domestic and Industrial Wastewaters”, kept in to the glass containers, labeled, and transported under +1 °C temperature. Conductivity, pH, DO (Dissolved Oxygen) measurements were performed simultaneously with sampling at the same time via a Hach HQ40D Multimeter device. All measurement were carried out according to the international standard methods carefully; COD (Chemical Oxygen Demand) measurements to ISO 6060 (ISO 6060, 1986), color measurments to ISO 7887 (ISO 7887, 2011), and all other analyzes to APHA, 1998 Standart Methods (APHA, 1998).

2.2. Photocatalysts preparation

Titanium tetraisopropoxide (TTIP by Sigma Aldrich) and ammonia aqueous solution (at 30 wt% supplied by Carlo Erba with a molar ratio N/Ti = 18.6 (Kasprzyk-Hordern et al., 2009)) was used to prepare *N*-doped TiO_2 photocatalyst by sol-gel method (Sato, 1986). 100 mL of ammonia aqueous was added to 25 mL of TTIP at 0 °C, while the solution was vigorously stirred to form a white precipitate. After that, ammonium floride NH_4F-HF (with a w(g)/V(mL) ratio 2,5 g/25 m/L) was put in to get *NF*-doped TiO_2. Finally Carbon nano particles (by Sigma Aldrich) were added and the precipitate was washed with water, centrifuged and calcined at 450 °C for 2 h to get *NFC*-doped TiO_2 in anatase phase. Thermal processing stage was not used here to obtain a cheap and effective photocatalyst.

2.3. Photocatalysts characterization

For the characterization of *NFC*-doped TiO_2 particles sample, several techniques were used. Laser Raman spectra were obtained by Dispersive Micro-Raman (Invia, Renishaw), equipped with a laser emitting at 514 nm in the range of 100–2000 cm^{-1} Raman shift. A Perkin Elmer spectrophotometer (Lambda 35) equipped with a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH) was used for the UV–Vis DRS reflectance measurements.

2.4. Experimental setup for photocatalytic activity test under visible light

A cylindrical, pyrex glass photo-reactor was designed and manufactured with a 35 cm total height, a 6 base diameter (R1) and a 14 cm diameter spherical section with 220 ml reaction volume (Fig. 1).

It was supported with an air distributor device ($Qair = 150\ cm^3/min$ (STP)), and a magnetic stirrer (Jeiotech Multi Channel Stirrer). It was irradiated by 4 cylindrical UV lamps (nominal power: 8W) positioned around in the range of 450–700 nm wavelength emission. Firstly, 3% w(g)/V(mL) *NFC*-doped photocatalyst was suspended for 1 h in dark condition to reach the adsorption equilibrium, and then photocatalytic activity test was started under visible lights up to 3 h firstly and then up to 7 h keeping their original pH to enhance the OH^* radical formation efficiency. At fixed time intervals, treated samples were centrifuged for sediment removal and then upper phase were taken and measured to determine the decreasing of antibiotic concentrations by a Perkin Elmer UV–Vis spectrophotometer at $\lambda = 663$ nm. Sediments were remove Total organic carbon (TOC) of the solution was measured by catalytic combustion at $T = 680\ ^\circ C$ with TOC LCPH/CPN SSM 5000 A.

2.5. Method validation

All water samples (influent, effluent and treated water samples by photocatalytic oxidation) were filtered by 0,45 μ filter before the solid phase extraction (SPE) in order to determine antibiotic contents. SPE were carried out by using 60 mg/3 ml Oasis HLB cartridges (Waters, Millford, MA, USA) under pH 4 to 6. This method was validated with the result of 70% Erythromicine (ERY), 100% Ciprofloxacine (CIP), 62% Sulphametoxasole (SMX) recovery yield. All water samples were injected to HPLC MS-MS (AB SCIEX 3200 QTRAP) equipped with C8 Supelco coloumn (100 mm, 3 × 2,7 μm) with acetonitrile and methanol mobile phase to measure antibiotic contents.

2.6. Photo-degradation mechanism of N-doped and NFC-doped titanium Dioksit

Photocatalytic activity of photocatalyst depends on band gap energy (Schneider et al., 2014). The band gap energy of TiO_2 is 3.2 eV (Christian et al., 2014) for anatase form. Band gap energy was reduced by doping TiO_2 with N, C and F elements so that it can absorb more visible light for the degradation of the antibiotic residues. The band gap energy was estimated from Kubelka-Munk function versus $h\nu$ as expressed in the following equation (Kubelka and Munk, 1931);

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S}$$

The important point is to find the treshold energy can be absorbed by the semiconductor material. Electron energy at absorbtion treshold is calculated by using following equation;

$$K = \frac{(hv - E_g)^\eta}{hv}$$

E_g = Optical absortion treshold energy,
η Variable due to optical transition by absorbing photon
K = Coefficient of light absorbtion

Band gap determinations were calculated from absorbtion treshold energy according to Kubelke-Munk theory by plotting $[F(R\infty) * h\nu]^2$ versus $h\nu$ (eV) with a line passing through $0.5 < F(R\infty) < 0.8$ regarding UV–Vis DRS measurement results.

The possible photocatalytic mechanism is that firstly, electrons and hole pairs were formed under the visible light when the energy was higher than band gap of TiO_2. The excited-state electrons in the lowest molecular orbital of Ti can easily migrate in to the lowest molecular orbital of N-F-C elements. The combination of these photogenerated electrons with O_2 could provided formation of the radical $*O_2^-$. At the same time the holes migrated to the surface and reacted with H_2O in order to produce OH* to decompose antibiotic pollutants. Consequently, more electrons and holes means more captured by oxygen or H_2O on the surface and generating more $*O_2^-$, *OH for the degradation of antibiotic pollutants.

3. Results and discussion

3.1. Wastewater characterization

Results of characterization regarding conventional pollutant paramaters and amount of antibiotic residues were reported in Table 1,

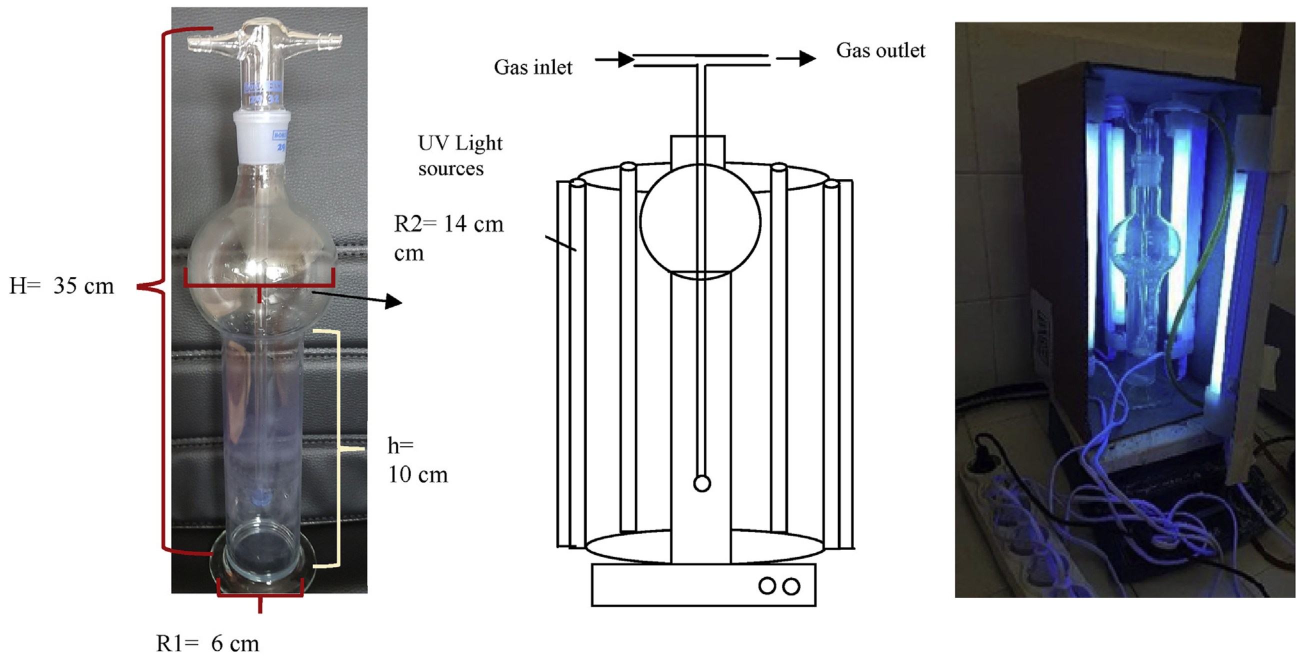


Fig. 1. Photocatalytic oxidation process experimental setup.

Table 3
Antibiotic characterization of waste water samples from domestic and industrial WWTP.

Sampling Point	CIP ng/L	ERY ng/L	SMX ng/L
Malkara Influent	7190	2220	6130
Malkara Effluent	26,400	< 0	5310
Kırklareli Influent	7280	4100	5350
Kırklareli Effluent	13,800	4680	10,100
Lüleburgaz Influent	24,900	< 0	19,700
Lüleburgaz Effluent	16,100	2950	5140
Karpuzlu Influent	9170	23,100	5610
Karpuzlu Effluent	14,000	5430	4970
Çerkezköy Industrial Influent	< 0	< 0	19,700
Çerkezköy Industrial Effluent	< 0	< 0	5100
Çorlu Leather Industrial Influent	< 0	< 0	2890
Çorlu Leather Industrial Effluent	< 0	< 0	2990

Table 2 and Table 3. According to characterization results; in terms of SS parameters, waste water samples, taken from Malkara WWTP, were at moderate-polluted characterization in July and November, and at high-polluted characterization in March. In terms of COD parameter waste water samples were at low-pollutant concentrations in July, at mid-polluted concentrations in November and March acording to Turkish Surface Water Quality Regulation Annex 5 (SWQR, 2004). Considering color parameters, IVth class quality influent water has been treated to III rd class quality water in July, to Ist class quality water in November, to IInd class quality water in March by biological conventional treatment process.

In terms of SS parameters, the raw influent wastewater samples, taken from Kırklareli, Lüleburgaz and Karpuzlu domestic WWTP, were characterized as high-polluted in July, November and March. In Lüleburgaz effluent water quality was also at high-polluted characterization in November, which means that biological treatment process was not capable to treat raw waste water at that time.

Table 1 (Please see Supplementary document).

Table 2 (Please see Supplementary document).

Due to the information given by the authorities of Enez domestic WWTP that the plant was not operated properly, waste water sampling has been carried out in Karpuzlu domestic WWTP instead of Enez in March which is the nearest plant in Edirne.

In terms of COD parameters in July, Kırklareli, Lüleburgaz ve Enez domestic WWTP's samples were characterized as low-polluted, on the other hand they were characterized as moderate-polluted in March and in November. Measurement results for TOC parameters revealed that influent wastewater samples were high-polluted taken from Kırklareli, Lüleburgaz ve Enez domestic WWTP. Color measurements presented that influent wastewater samples had IVth class water quality in Kırklareli, Lüleburgaz ve Enez domestic WWTP. After biologically conventional treatment process, water quality was increased to IInd or Ist in Lüleburgaz ve Enez domestic WWTP, but on the other hand Kırklareli domestic WWTP were still at IV th class water quality as it is reported at Table 1 in detailed.

According to the characterization results presented on Table 2, Çorlu Leather and Çerkezköy Industrial WWTP's water samples exhibited high-polluted characterization in terms of SS and COD parameters. In july, treatment process was failed so that, both influent and effluent of Çorlu Leather and Çerkezköy Organised Industrial WWTP samples were at IVth class water quality. In November and March conventional treatment process was succeeded to increase water quality to Ist or IInd class.

In addition to pollutant characterization, antibiotic characterization study was carried out for the domestic and industrial WWTP's water samples, collected from, in March, presented on Table 3 in detailed. Considering the SPE extraction method, which was validated through 70% Erythromicine (ERY) from the group of macrolides, 100% Ciprofloxacine (CIP) from the group of fluoroquinolones, 62% Sulphametoxasole (SMX) from group of the Sulfonamides recovery yield, gave an opportunity to investigate and to study for the photocatalytic oxidative removal of these three main antibiotic groups. Measurement results, from HPLC MS-MS, unexpectedly revealed that, antibiotic contents were higher in biologically treated effluent water rather than influent raw wastewater. As it is presented in Table 3, this interesting measurement results can be explained by the fact that some antibiotics in domestic wastewaters are probably already trapped in feces and can not be treated by conventional systems because they are released just after biological treatment.

Moreover, this may be due to the appearance of and/or some metabolites of antibiotics in influent water that are transformed back to the parent compounds in effluent water during the biological treatment process.

Antibiotic measurement results of wastewater samples, done by HPLC MS/MS, proved that; the highest amount of CIP antibiotic was measured as 26,400 ng/L, 16,100 ng/L, 14,000 ng/L and 13,800 ng/L respectively in the effluent wastewater sample of Malkara, Lüleburgaz, Karpuzlu and Kırklareli domestic WWTPs. Karpuzlu domestic effluent water has the highest measurement of ERY with 5430 ng/L. SMX was detected in the highest amount of 10,100 ng/L in the effluent water of Kırklareli domestic WWTP. In Çerkezköy industrial influent waste water only SMX was dedected at amount of 19,700 ng/L, 2990 ng/L in Çorlu leather industrial effluent waste water. These high amounts of antibiotics, even in industrial waste water, may be due to the pharmaceutical companies operating around of Çerkezköy and Çorlu Leather Industrial WWTPs.

3.2. Photocatalyst characterization results

UV-DRS reflectance data, for *N*-doped (*NT*), prepared special *NF*-doped and *NFC*-doped TiO_2, were reported as % reflectance versus the wavelength in Fig. 2. Comparing *undoped*, *N*-doped (*NT*), *NF*-doped and *NFC*-doped TiO_2, *NFC*-doped TiO_2 had the highest radiation absorbtion in UV range after the 500 nm interval. Therefore, TiO_2 photocatalysts (active at 380 nm UV) light have been acquired of more visible light absorbtion via *N*, *NF* and *NFC* doping method respectively.

Fig. 2. (Please see Supplementary document).

Band gap determinations of *NFC*-doped TiO_2 were calculated by plotting $[F(R\infty) * h\nu]^2$ versus $h\nu$ (eV) with a line passing through $0.5 < F(R\infty) < 0.8$ and graphed as the $F(R\infty)$ value from Kubelka-Munk theory (Kubelka and Munk, 1931) versus the wavelength in Fig. 3.

Fig. 3. (Please see Supplementary document).

As it is reported in Fig. 3, band gap energy of TiO_2 (which is 3.2 eV) has been decreased to 2,5 eV by means of *NFC* doping. This can be explained that, TiO_2 photocatalyst was obtained to absorbtion capability of visible light by having crystalline structure of nitrogen and more adsorbtion capability by carbon molecules.

By the way, comparison for the band gap determination of different photocatalysts, including *NFC*, were given in Fig. 4.

Fig. 4. (Please see Supplementary document).

As it is shown in Fig. 4, according to UV–Vis DRS measurements the band gap anergy of TiO_2 has been reduced to 2,5 eV firstly through doping with N-F-C elements so that UV visible light absorbtion has been increased. Thus, when irradiated with visible light, the electron was allowed to TiO_2. Electrons can be easily transferred due to the synergetic effect of N-F-C elements between TiO_2 and lower the probability of e-/h+ recombination due to a higher electron transfer rate (Yun et al., 2009).

In addition to all characterization studies, Raman shifts revealed the anatase form of *NFC*-doped TiO_2, as it is presented at Fig. 5.

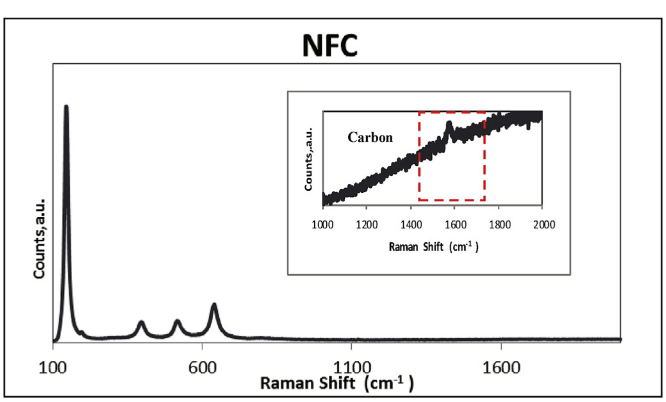


Fig. 5. Raman spectrum of *NFC*-doped TiO_2.

The only Raman signals were observed related to the anatase phase at 785 nm diodelaser Laser Raman spectrum in the range 100–2500 cm^{-1} Raman shift (Ohsaka et al., 1978).

3.3. *NFC*-doped TiO_2 photocatalytic activity test for the removal of antibiotics

NFC-doped TiO_2 photocatalytic activity test results are presented in Table 4.

Removal efficiency of CIP, ERY and SMX were 99.998% (0,96 ng/L could not be removed), 100%, 100% respectively by a 7 h photocatalytic oxidation in Malkara. In Kırklareli, removal efficiencies were 99,988% (0,27 ng/L could not be removed), 100%, 99,962% (3,79 ng/L could not be removed), respectively during 7 h. In Lüleburgaz, removal efficiencies were 100%, 100%, 94,377% (289 ng/L could not be removed), respectively during 3 h, SMX removal efficiency was enhanced to 99,955% (2,32 ng/L could not be removed) by a 7 h photocatalytic oxidation. In Karpuzlu, removal efficiencies were 99,994% (0,89 ng/L could not be removed), 100%, 99,935% (3,21 ng/L could not be removed), respectively during a 7 h photocatalytic oxidation. SMX removal of Çerkezköy was 99,881% during a 7 h photocatalytic oxidation process. As compared physico-chemical properties of these 3 antibiotics, although ERY has more complex structure than other antibiotics, CIP and SMX, it was possible to be removed completely from effluent water with a very comfortable degradation. This can be explained as having a branched and loose ring structure, high Log Kow value and pKa value close to its own pH value, with the presence of too many non-resistant carboxyl groups easily oxidizing and hydrophilic groups, easy degradable C bonds and higher solubility in water than CIP and SMX (Table 5).

SMX has been identified as the most difficult antibiotic to degrade than other antibiotics. The reason for this could be that the SMX has low water solubility, and too low Log K_{ow} value as it is presented in Table 5.

3.4. *NFC*-doped TiO_2 photocatalytic activity test for COD and TOC removal

The results of COD and TOC decreasing concentrations are presented in Table 6.

It is achieved respectively 78%, 79%, 73%, 77% COD and 86%, 78%, 79%, 73% TOC removal efficiencies by *NFC*-doped TiO_2 photocatalytic oxidation process carried out with Malkara, Kırklareli, Lüleburgaz and Karpuzlu domestic WWTP's effluent wastewater samples. COD and TOC removal rate was % 62 in Çerkezköy Industrial WWTP's effluent wastewater.

Table 5 (Please see Supplementary document).

3.5. UV–Vis Spectrophotometer measurements for NFC-Doped TiO_2 photocatalytic activity test

During the photocatalytic activity test with *NFC*-doped TiO_2, wastewater samples were taken at fixed time interval, after the first 1 h of darkness the lights were on during to 3 and to 7 h. These samples were measured by UV–Vis Spectrophotometer and the results are presented in Fig. 6.

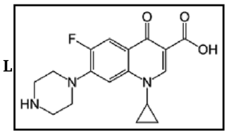
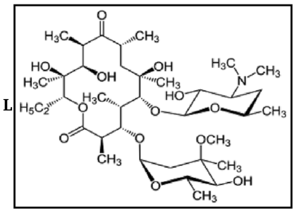
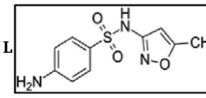
Fig. 6. (Please see Supplementary document).

UV–Vis spectrophotometer measurement results after *NFC*-doped TiO_2 photocatalytic advanced oxidation process of Lüleburgaz Domestic Wastewater Treatment Plant effluent waters.

According to the UV–Vis spectrophotometric measurement results, antibiotic removal rate, for Lüleburgaz domestic WWTP's effluent water sample, was 96,536% for 3 h *NFC*-doped photocatalytic oxidation process. It was increased to 99,963% whenever the oxidation process time was extended to 7 h, as it is presented in Fig. 6.

As seen in Fig. 7 and Fig. 8; antibiotic removal rates were 99,982% and 99,956%, 99,954% and 99,789% respectively for Malkara, Karpuzlu, Kırklareli domestic and Çerkezköy Industrial WWTP's effluent

Table 4
NFC-doped TiO_2 Photocatalytic activity results for removal antibiotics.

	Before AOPAntibiotic Contents			After AOPAntibiotic Removal		
	CIP ng/L	**ERY ng/L**	**SMX ng/ L** 	**CIP (ng/L)**	**ERY ng/ L** 	**SMX ng/ L** 
Malkara Domestic WWTP	38,800	263	6120	0,96	< 0	< 0
Kırklareli Domestic WWTP	13,800	4680	10,100	0,27	< 0	3,79
Lüleburgaz Domestic WWTP	16,100	2950	5140	< 0	< 0	289[a] 2,32[b]
Karpuzlu Domestic WWTP	14,000	5430	4970	0,89	< 0	3,21
Çerkezköy Industrial WWTP	< 0	< 0	5100	< 0	< 0	6,08

[a] a 3 h advanced oxidation process results.
[b] a 7 h advanced oxidation process results.

waters.

Fig. 7. (Please see Supplementary document).

As seen in Fig. 8, results of UV–Vis spectrophotometre measurements for the removal of antibiotic residue concentrations were supported by the results measured by HPLC MS-MS results given in Table 4.

3.6. *Re-use evaluation of NFC-doped TiO_2 photocatalytic treated effluents, for agricultural irrigation*

The reuse of treated effluents, aimed for agricultural irrigation purpose in this study, is evaluated in Table 7.

As illustrated in Table 7; IVth quality class of Malkara, Lüleburgaz and Karpuzlu domestic WWTP's raw influent water qualities have been enhanced to IInd quality class after biological conventional treatment. IVth quality class of Kırklareli domestic WWTP raw influent water quality has been enhanced to Ist quality class after biological conventional treatment. The advanced oxidation process was effective at this point all domestic WWTP raw influent water qualities have been increased to Ist quality class by means *NFC*-doped photocatalytic oxidation process.

According to the all these results, domestic and industrial wastewater samples, taken from the biological treatment effluent points of the mentioned plants, are become available for agricultural irrigation after the photocatalytic oxidation process with *NFC*-doped TiO_2, efficiently regarding “a) Classifications for usage purposes of water” in “Turkish regulation on the Amendment of the Regulation on the Water Quality of the Surface” published in the Official Newspaper dated August 10, 2016 and numbered 29,327.

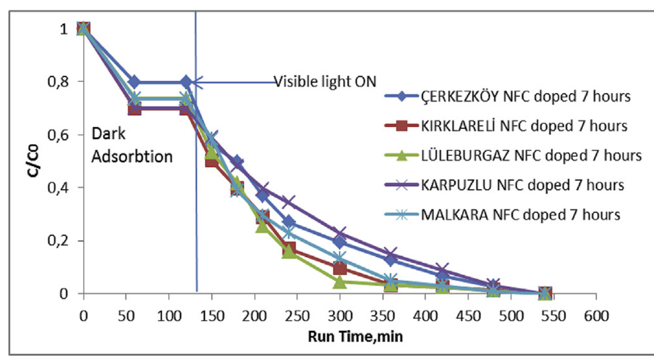


Fig. 8. Comparison of UV–Vis spectrophotometer measurement results after *NFC*-doped TiO_2 photocatalytic advanced oxidation processes of all domestic and industrial wastewater treatment plant effluents.

Table 7
Use of *NFC*-doped TiO_2 photocatalytic treated water in agricultural irrigation.

	Before AOP	After AOP by *NFC* Doped
	Quality Class	Quality Class
Malkara Domestic Effluent Water	II. class	I. class
Lüleburgaz Domestic Effluent Water	II. class	I. class
Karpuzlu Domestic Effluent Water	II. class	I. class
Kırklareli Domestic Effluent Water	I. class	I. class
Çerkezköy Industrial Effluent Water	IV. class	II. class

Table 6
NFC- doped TiO_2 Photocatalytic activity for COD and TOC removal.

Sampling in March 2017	Before AOP	After AOP	COD Removal %	Before AOP	After AOP	TOC Removal %
	COD mg/L			TOC mg/L		
Malkara Domestic WWTP	94	21	78	83	20	86
Karpuzlu Domestic WWTP	160	33	79	60	13	78
Lüleburgaz Domestic WWTP	67	18	73	48	10	79
Kırklareli Domestic WWTP	70	16	77	52	14	73
Çerkezköy Industrial WWTP	229	87	62	208	80	62

Table 8
Comparison of this study results with similiar studies published in scientific literature.

Wastewater characterization	Experimental study	Conclusion	Reference
Synthetic wastewater; the CIP, C17H18FN3O3, (CAS No.85,721-33-1 and Mw = 331.346 g/mol), was investigated as a model pollutant.	In 2016 Parsa J-B et al. were studied on the performance and modelling of the electro-coagulation process for CIP removal.	%77 COD removal and %49 TOC removal were reported in this study. Comparing it with this study, %73–79 COD removal, %73–86 TOC removal were obtained by NFC-doped TiO_2 photocatalytic oxidation process	Parsa et al., 2016
Synthetic wastewater; wastewater prepared in laboratory scale.	In 2014, Vignesh K., et al., focused on photocatalytic degredation of ERY under visible light by zinc phtalaocyanine – modified titania nanoparticles prepared by chemical impregnation method to improve the photocatalytic activity of TiO2 under visible light.	Degradation yield of ERY was reported as 74, 21%.	Vignesh et al., 2014
Synthetic wastewater; wastewater prepared in laboratory scale.	Jihyun R. K., et al., were used biochar-supported TiO_2 (biochar/TiO_2) for the removal of SMX under UV light from wastewater prepared in laboratory scale.	It was reported that photocatalytic oxidation of SMX using the biochar/TiO_2 resulted in the high removal and mineralization of SMX and negligible toxicity	Jihyun and Eunsung, 2016
Synthetic wastewater; acid blue 92 (anionic dye) as water pollutant.	Beshkar F., et al prepared photocatalytically active copper chromite via a hydrothermal reaction in 2017.	Anionic dye degradation yield of the photocatalyst was informed as %87. The energy gap amount of the copper chromite was determined to be 3,38eV	Beshkar F., et al., 2017
Real wastewater (industrial and domestic) which was sampled from Meriç-Ergene Basin	Photocatalytic degradation of antibiotic residues by using N-F-C doped photocatalyst under UV–Visible light.	99%–100% antibiotic residue removal, 62%–79% COD and 62%–86% TOC removal was provided by means of 7 h NFC-doped photocatalytic oxidation under visible light,	This study

Moreover, this study results were compared with similiar studies published in scientific literature on Table 8. As it is quite known, antibiotic residues inhibit the biological treatment systems and cause endocrine distributing effects through food chain by irrigation water (Despo et al., 2011). So, this study will contribute a novel method to scientific literature for the degradation of three important and widely used antibiotic residues from real Meriç-Ergene Basin waste water through doping TiO_2 with N-F- C elements without heating process which had never studied before.

4. Conclusion

As a conclusion, firstly according to the pollutant characterization; very high COD, TOC, SS and color removal efficiencies were obtained by using conventional biological treatment method, but on the other hand it has been determined that antibiotic elimination can not be achieved by these biological conventional methods.

Successfully, by means of 7 h *NFC*-doped photocatalytic oxidation under visible light, %99 to %100 removal of antibiotic residue was provided with approximately 73%–79% COD removal, 73%–86% TOC removal at the same time in Malkara Kırklareli, Lüleburgaz ve Karpuzlu Domestic and 62% TOC and COD removal in Çerkezköy Industrial WWTP's secondary effluent water.

For the reuse assessment of treated water; domestic wastewaters were improved to I^{st} class water quality, industrial waste waters were improved to 2nd class water quality by photocatalytic oxidation process with *NFC*-doped TiO_2 photocatalyst according to the" Turkish Surface Water Quality Regulations" and can be used in agricultural irrigation. This study has proved that it is possible to treat the secondary effluent waters, at the level to be reused for irrigation, with advanced oxidation process by using effective *NFC*-doped photocatalyst. In the near future, environmentally friendly type of three-doped photocatalytic oxidation processes can compete with conventional treatment methods, by designing effective and cheap photocatalytic reactors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2018.11.095.

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