

Research Article

Photodegradation of Olive Mill Wastewaters Using Graphene-TiO₂ and Recovery of Graphene-TiO₂

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Abstract: Olive oil mill wastewater contains high concentration of organic matter, acidic pH values, suspended solids and high content of phenols and polyphenols which are toxic substances. In this study, Graphene-TiO₂ was used to treat the pollutants from the olive mill industry wastewaters by photo-degradation. Graphene is an allotrope of carbon in the form of two-dimensional, atomic-scale, hexagonal lattices in which one atom form each vortex. It includes graphite, charcoal, carbon nanotubes and fullerenes. The large-scale production of functionalized graphene at low cost should result in good adsorbents for water purification. This is due to the two-dimensional layer structure, large surface area, pore volume and presence of surface functional groups in these materials; the inorganic nanoparticles also prevent aggregation of the adsorbent. XRD distribution peaks showed that GO existed in the XRD pattern which shows that a small quantity of GO and play a part in the intercalating process of TiO₂-Graphene Oxide. SEM analysis results showed that the graphene oxide layers consist from the connection of the graphene oxide flakes during the reaction between C=O in the edge of graphene oxide. In this study the photo-removals of COD, total solid and total phenol in olive mill effluent wastewater with Graphene-TiO₂ were investigated under photocatalytic oxidation. The effects of increasing Graphene-TiO₂ concentrations (0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L), photooxidation times (15, 30, 60 and 90 min) and pH (4, 7 and 10) were evaluated on the treatment of OMW pollutants. The photocatalytic reactions were performed under UV irradiation. The maximum pollutant removal efficiencies for COD, total phenol and TS obtained under 300 W UV light were 88%, 92% and 95% throughout photocatalysis at the optimum Graphene-TiO₂ concentration (3 g/L). The maximum recovery capacity of Graphene-TiO₂ was found between 90 and 95% after sequential six cycles.

Keywords: Graphene-TiO₂, Photocatalytic degradation, Olive mill Wastewater, UV Irradiation.

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1. INTRODUCTION

Agro-industrial wastewaters such as olive-oil mill effluent wastewaters (OMW) are amongst the most polluting industrial effluents since they cause considerable environmental problems (coloring of receiving waters, a serious threat to aquatic life, pollution of surface and ground waters, alterations in soil quality, phytotoxicity and odor nuisance) (1). OMW contains appreciable amount of organic materials with a high amount of toxicity/phytotoxicity-associated compounds, which resist biological degradation (2). Treatment of OMWs is of great importance and very difficult due to the high organic, phenol, fatty acids, and suspended solids content (2). Inadequate conventional treatment methods have led to alternative treatment methods such as treating OMW with nanoparticles.

TiO₂-based materials are the most commonly used semiconductor oxide photocatalysts due to their low environmental impact. However, there are numerous obstacles impeding the maximization of photocatalytic activity in these materials, including low adsorption ability, detrimental recombination of charge carriers, and light utilization. TiO₂/carbon nanotube composites have been established as viable potential photocatalysts for use in both water and air purifications (1-4). The synergetic effect of carbon nanotubes on photocatalyst enhancement, in which carbon nanotubes act as the electron sink for the hindrance of charge carrier recombination [1-2 or as the photosensitizer to generate a greater density of electron/hole pairs, has been previously demonstrated. Carbon nanotubes also behave as impurities, resulting in the formation of Ti-O-C bonds and, therefore, expanding the light absorption to longer wavelengths 4-6).

Graphene, a new member of carbon materials, has been used as a support material for photocatalysts owing to its unique physical structure, large surface area, superior electrical conductivity and excellent adsorption capacity (4). These properties make graphene a viable co-catalyst to accept electrons for exciton separation (3-4).

In TiO₂ photocatalysts combined with two-dimensional GO (GO–TiO₂) hybrids, the oxygenated functional groups on the GO sheets facilitate the binding of TiO₂ and GO and GOs can serve as electron sinks under ultraviolet (UV) illumination or electron donors under visible light illumination for retardation of electron-hole recombination (3-4). Additionally, the surface areas of GO–TiO₂ hybrids (e.g., 80m² g⁻¹) are higher than that of uncoupled TiO₂ (e.g., 57m² g⁻¹) [5,6].

The combination of TiO₂ and graphene oxide and/or graphene is predicted to generate a synergistic effect that potentially enhances the photodegradation of organic and inorganic contaminants in aqueous media due to the possible improvements in the adsorbability (several 2 of organics (dyes)(7) and inorganics (Pb)(8) and Co (III) Se (VI)(9)). Therefore, in this work, it was aimed to determine photo-removals of COD, total solid (TS) and total phenol in OMW with Graphene-TiO₂ under photocatalytic oxidation. Photodegradation under UV irradiation was studied for different irradiation times, pH and concentrations of Graphene-TiO₂. Reuse of Graphene-TiO₂ was also investigated.

2. MATERIAL AND METHODS

2.1. Effluent and Chemicals

Olive mill effluent from an olive mill industry located in the Aydın was collected and used without any pre-treatment, in November 2013. Graphene and TiO₂ were bought externally. Demineralized water was used for preparation of reagents solutions. 0.1 M HCl and 0.1 M NaOH are used to adjust pH values of olive mill wastewater.

2.2. Photocatalytic experiments

Treatment of OMW under UV experiments was conducted in an open batch system at room temperature of 20-25 °C. Quartz glass reactors and 20 UV lamps

each one having an irradiation power of 15 watt were used for experiments of treatment with UV. The effects of irradiation times (3, 6, 12, 24, 36 and 48 hours), pH (4, 7, and 10) on the treatment of olive mill wastewater were investigated. After experiments the supernatant were centrifuged at 9000 rpm for 10 min. All the experiments data were found from the duplicates analysis and the results presented as the mean values of the duplicates samples.

2.3. Analytical procedures

COD was measured by colorimetric method (5220 D) as explained in detail in APHA (2016) with a Spectrophotometer Aquamate Thermo at 420 nm wavelength (10). Phenols were measured using the Merck/WTW 14551 phenol reagent kits in a Photometer Nova 60/Spectroquant. TS measurements were performed according to method 2540B presented in Standard Methods (2016)(10).

2.4. Preparation of Graphene-TiO₂ under laboratory conditions

In a typical preparation, an aqueous dispersion of graphene (8.4 mg/mL) was dissolved in 200 mL of deionized water. TiO₂ powder (P25, Degussa) was dispersed in deionized water and subsequently added to the graphene oxide solution. The mixture was sonicated for 1.5 h and further stirred for 12 h at room temperature to obtain a homogeneous solution. The product was filtered and dried in a vacuum at 50 °C for 4 h.

2.5. Reuse methods of Graphene-TiO₂

After first use the Graphene-TiO₂ was filtered after photocatalytic degradation, washed three times by water and ethanol and dried. The washed Graphene-TiO₂ was used for five sequential times to treat the raw OMW in each step with UV irradiation. Under sunlight treatment the first used Graphene-TiO₂ was used to treat the raw OMW.

3. RESULTS AND DISCUSSION

3.1. Wastewater Characterization

The average COD, TS, and phenol contents of the raw olive mill effluent were 117000 mg/l, 84250 mg/l, and 660 mg/l respectively, while its average pH value was between 3.5 and 4.5 (Table 1). The samples were stored at room temperature and shaken well before all the experiments.

Table 1. Characterization of olive mill wastewater

Parameters	Initial Value
COD	117000 ± 200mg/L
TS	84250± 300 mg/L
Phenol	660±12 mg/L
pH	3.5-4.1

3.2. Photocatalytic studies

3.2.1. OMW Treatment with UV Irradiation

The photocatalytic experiments were carried out at increasing Graphene-TiO₂ concentrations, pH values and irradiation times.

3.2.1.1. The Effect of Concentration of Graphene-TiO₂ on Treatment of OMW

Graphene-TiO₂ concentration is an important parameter for the photo-treatment of OMW(11,12). In order to determine the maximum photocatalytic treatment efficiencies of OMW 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L Graphene-TiO₂ concentrations were researched. Preliminary experiments showed that among the irradiation times that are tested, the maximum OMW removal was obtained after 30 min irradiation time (data not shown). Therefore, all experiments were realized after 30 min irradiation time, at 21°C (room temperature) and at original pH (4) of OMW and under 300 W UV power.

The COD removal yields were obtained as 44%, 62%, 88%, 88% and 79 % at 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L Graphene-TiO₂, respectively (Fig.1.a). The TS removal yields were obtained as 57%, 79%, 95%, 93% and 85% at 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L graphene, respectively (Fig.1.b). The phenol removal yields were obtained as 55%, 72%, 92%, 90% and 82% at 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L Graphene-TiO₂, respectively (Fig.1.c). The results showed that the removal efficiencies were not changed with increasing Graphene-TiO₂ concentrations from 3 g/L up to 10 g/L, significantly (Fig.1). Among the Graphene-TiO₂ concentrations (0.5, 1, 3, 5 and 10 g/L), it was found that the maximum COD, phenol and TS yields were found at 3 g/L Graphene-TiO₂ composite concentration. The maximum COD, TS, phenol removal yields were obtained 88%, 95% and 92%, respectively (Fig.1.d).

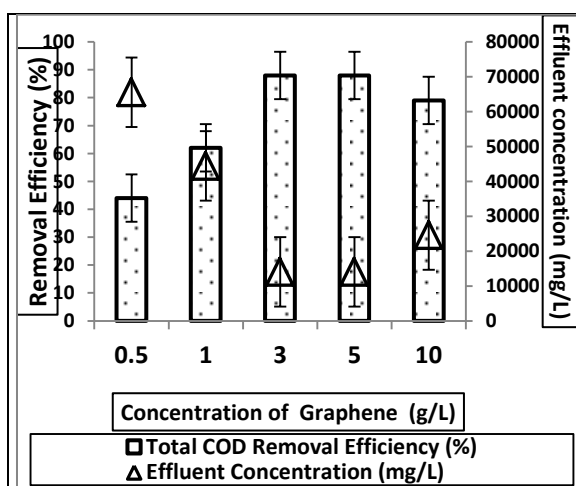


Fig.1.a. Effect of increasing Graphene-TiO₂ concentrations on COD removal from OMW (pH 4, T: 20°C, Irradiation time: 30 min)

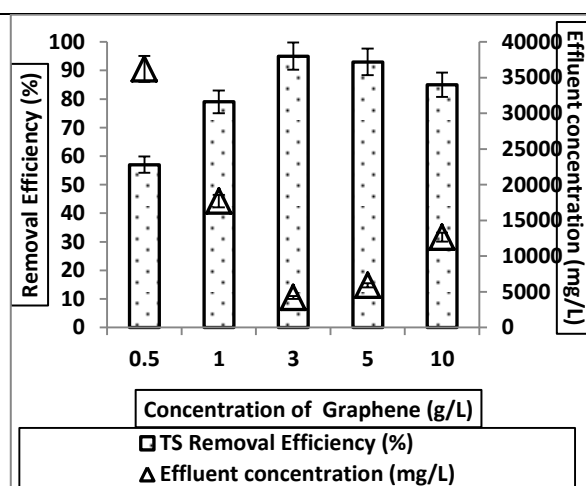


Fig.1.b. Effect of increasing Graphene-TiO₂ concentrations on TS removal from OMW (pH 4, T: 20°C, Irradiation time: 30 min)

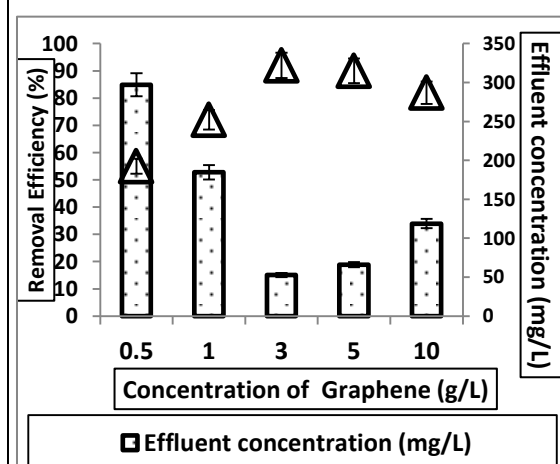


Fig.1.c. The effect of increasing Graphene-TiO₂ concentrations on Phenol removal from OMW (pH 4, T: 20 °C, Irradiation time: 30 min)

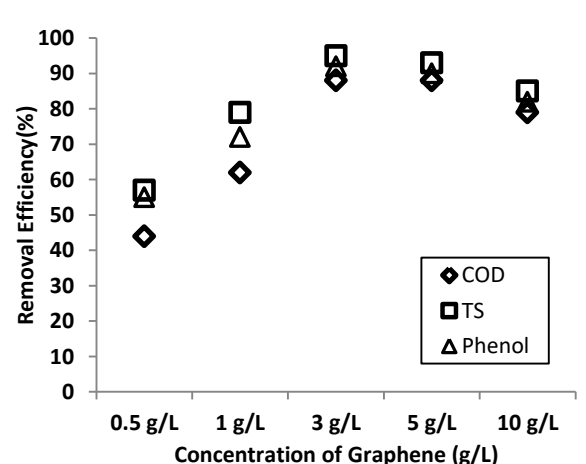


Fig.1.d. Illustration of removal yields of all pollutant parameters (pH 4, T: 20 °C, Irradiation time: 30 min)

Fig.1. The effect of concentration on COD, TS, phenol removal with UV irradiation

3.2.1.2.

3.2.1.3. *The Effect of Irradiation Time on Treatment of OMW*

OMW treatment with Graphene-TiO₂ was investigated at different irradiation times. Irradiation times were chosen as 15, 30, 60 and 90 min. The concentration of Graphene-TiO₂ was selected as 3 g/L to determine the optimum irradiation time. The irradiation time experiments realized in the original pH of OMW at 20 °C. The maximum removal efficiency of COD, TS and phenol were obtained at 30 min among the irradiation times used for experiments (Fig. 2). The COD removal yields were obtained as 67%, 88%, 90% and 77% at 15, 30, 60 and 90 min irradiation times, respectively. When the irradiation time was increased

from 30 min to 60 min, the COD removal efficiency was not increased significantly (Fig. 2.a). The TS removal yields were obtained as 69%, 95%, 90% and 79% after 15, 30, 60 and 90 min irradiation times, respectively (Fig. 2.b.). Increasing the irradiation time from 30 min to 90 min decreased significantly the removal efficiency of TS. The phenol removals were 63%, 92%, 88% and 72% at 15, 30, 60 and 90 min irradiation times, respectively (Fig. 2.c.). Fig.2.d summarizes all the removal efficiencies of pollutants in the OMW after treatment with UV. The maximum COD, TS, phenol removal yields were obtained after 30 min irradiation time (Fig. 2.d.).

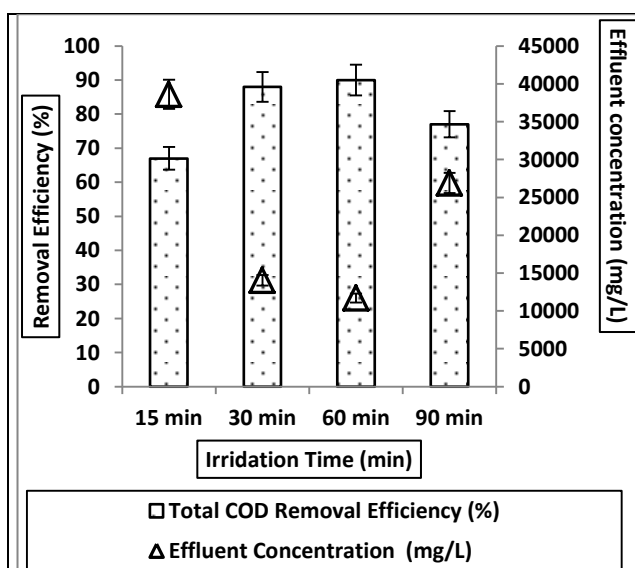


Fig. 2.a. The effect of irradiation time on COD removal efficiency (pH 4, Graphene-TiO₂ concentration: 3 g/L, T:20 °C)

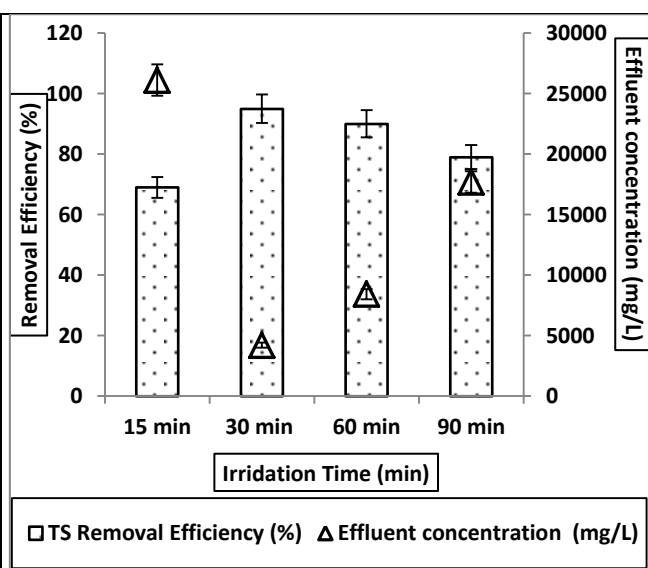


Fig. 2.b. The effect of irradiation time on TS removal efficiency (pH 4, Graphene-TiO₂ concentration: 3 g/L, T: 20 °C)

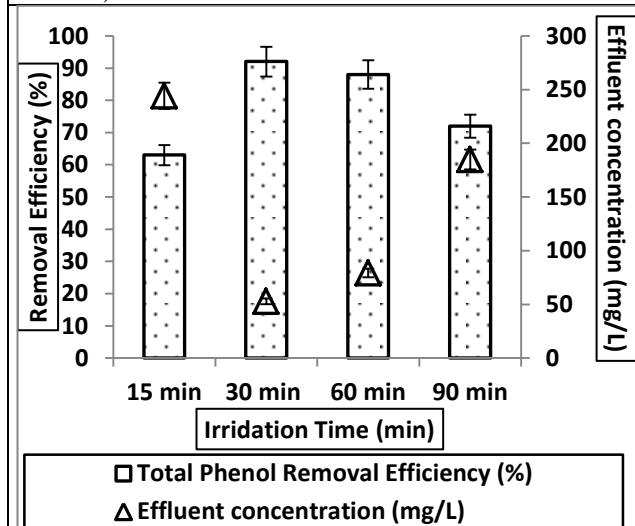


Fig. 2.c. The effect of irradiation time on Phenol removal efficiency (pH 4, Graphene-TiO₂ concentration: 3 g/L, T:20 °C)

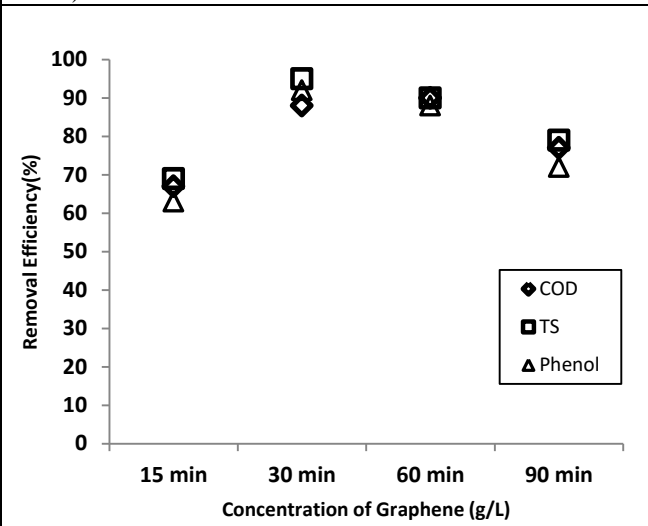


Fig. 2.d. Illustration of removal yields of all pollutant parameters (pH 4, Graphene-TiO₂ concentration: 3 g/L, T: 20 °C)

Fig.2. The effect of irradiation times on COD, TS, phenol removal with UV irradiation

3.2.1.4. The Effect of pH of OMW on Treatment of Olive Mill Treatment with Graphene-TiO₂

pH of OMW is an important parameter for the treatment mechanism of olive mill wastewater(13,14). In this study, the effect of acidic, neutral and alkaline pH was investigated on the treatment efficiency on OMW with Graphene-TiO₂. (Fig. 3). All experiments were realized with 3 g/L Graphene-TiO₂ at 30 min

retention times at 20 °C. Increasing of pH from 4 up to 10 did not significantly affect the COD, TS and phenol removal efficiencies. The maximum COD, TS, phenol removal yields were obtained as 88%, 95% and 92% at pH 4, respectively, therefore pH 4 was selected as the optimum pH for the photodegradation of all pollutant parameters among used pH values.

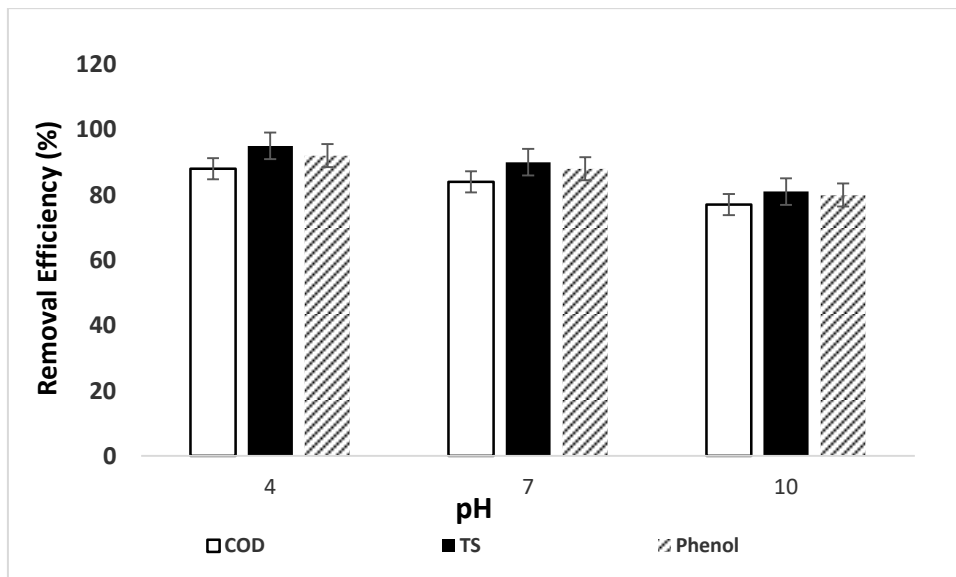


Fig.3. Effect of pH on the treatment of OMW with Graphene-TiO₂ composite on COD, TS, and Phenol yields in the OMW

3.3. Physicochemical characterization of GO- TiO₂ nanocomposite

3.3.1 XRD analysis in GO- TiO₂ nanocomposite

Figure 4 shows the XRD data of GO-TiO₂ nanocomposite. TiO₂ crystallites in the intercalated structure consisting of mixed anatase and rutile phase, in which anatase phase shows more content. (102), (005), (201) crystal surface diffraction peaks that are marked with square shapes are assigned to anatase, and the other four characteristic diffraction peaks of (111), (102), (112), (212) were marked with round shapes are

assigned to rutile phase. The average crystal size of TiO₂ in TiO₂-Graphene Oxide under different conditions is about 6,8 nm(data not shon) . Furthermore, a very slight diffraction peak which is marked with a pentagon shape at 2θ=12° belongs to (003) crystal of GO. The diffraction peak of GO which still existed in the XRD pattern which shows that a small quantity of GO was not exfoliated thoroughly, play a part in the intercalating process of TiO₂-Graphene Oxide.

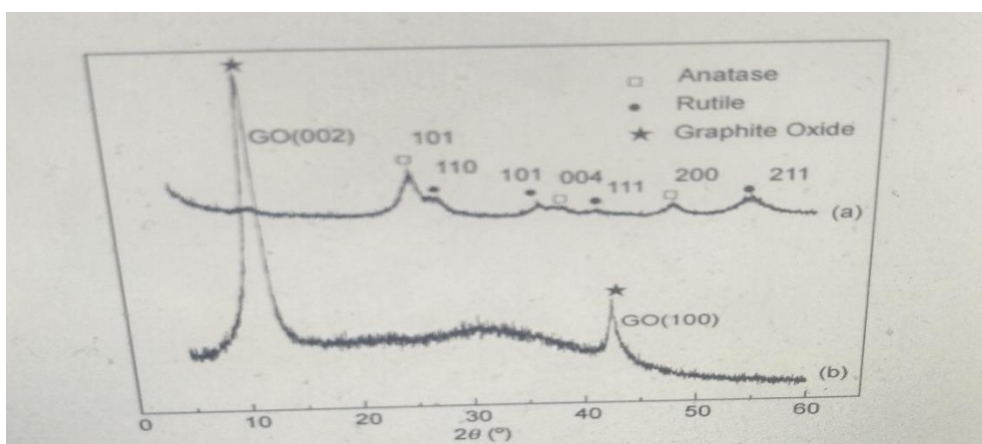


Figure 4. XRD disturbances of GO and TiO₂

3.3.2. XPS analysis in GO

Figure 5 show XPS analysis of graphite(PG) and GO. In figure 5a, the sp²-hybridized carbon peak appeared near 284.6 eV with a well-known asymmetric line shape. A few additional peaks after oxidation developed due to the functional groups. The spectra

were deconvoluted into five peaks of sp²(C–C, 285.1 eV), hydroxyl(C–OH, 286.1 eV), epoxide(C–O–C, 287.3 eV), conjugated carboxyl(C=O, 288.3 eV) and carboxyl(COOH, 290.0 eV) groups in the graphite oxide (Figure 5b).

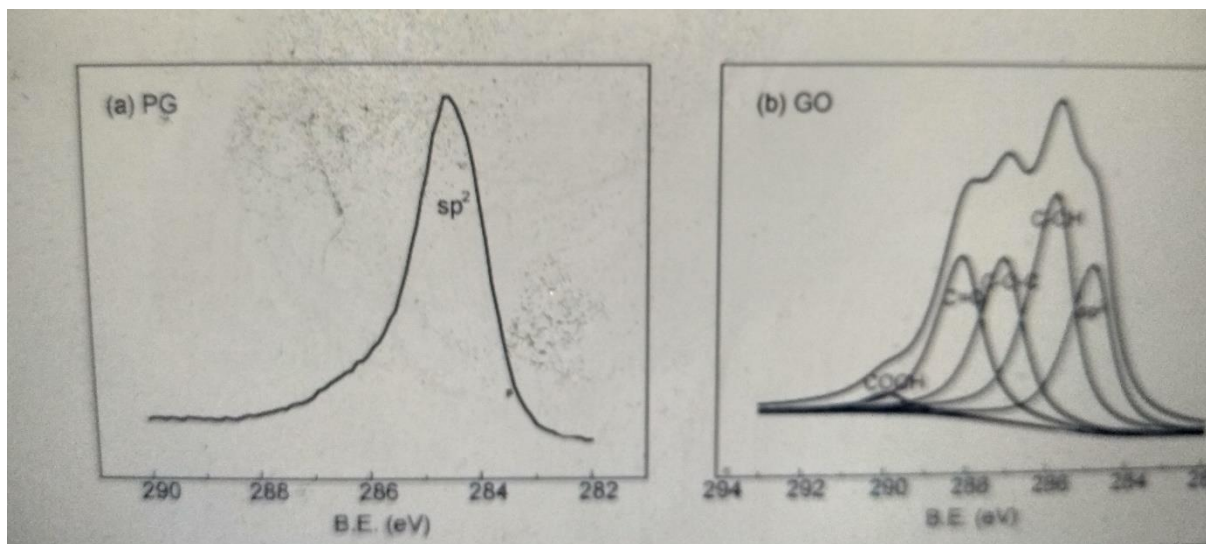


Figure 5 a. XPS analysis in PO; 5b. XPS analysis in GO

3.3.3. EM analysis in GO- TiO₂ nanocomposite

Figure 6 exhibited the SEM images of GO- TiO₂. It was found that large amounts of fine TiO₂ nanoparticles are located at graphene oxide flakes which own an area of about 200 nm. At the same time, large-scale pieces of graphene oxide can also be observed at which TiO₂ particles are located. These broader graphene oxide layers might be due to the connection of the graphene oxide flakes during the reaction between

C=O located at the edge of graphene oxide and [TiO]₂⁺ induced by the hydrolysis of Ti(SO₄)₂ (13,14). The formed graphene oxide flakes make [TiO]₂⁺ induced by the hydrolysis of Ti(SO₄)₂ diffuse from the edge of graphene oxide and the substitute the alkali metal ions existed in the interlayer. During the nucleation and growth of TiO₂ grains, a proportion of [TiO]₂⁺ groups may be consumed.



6. FE-SEM analysis in GO- TiO₂ nanocomposite

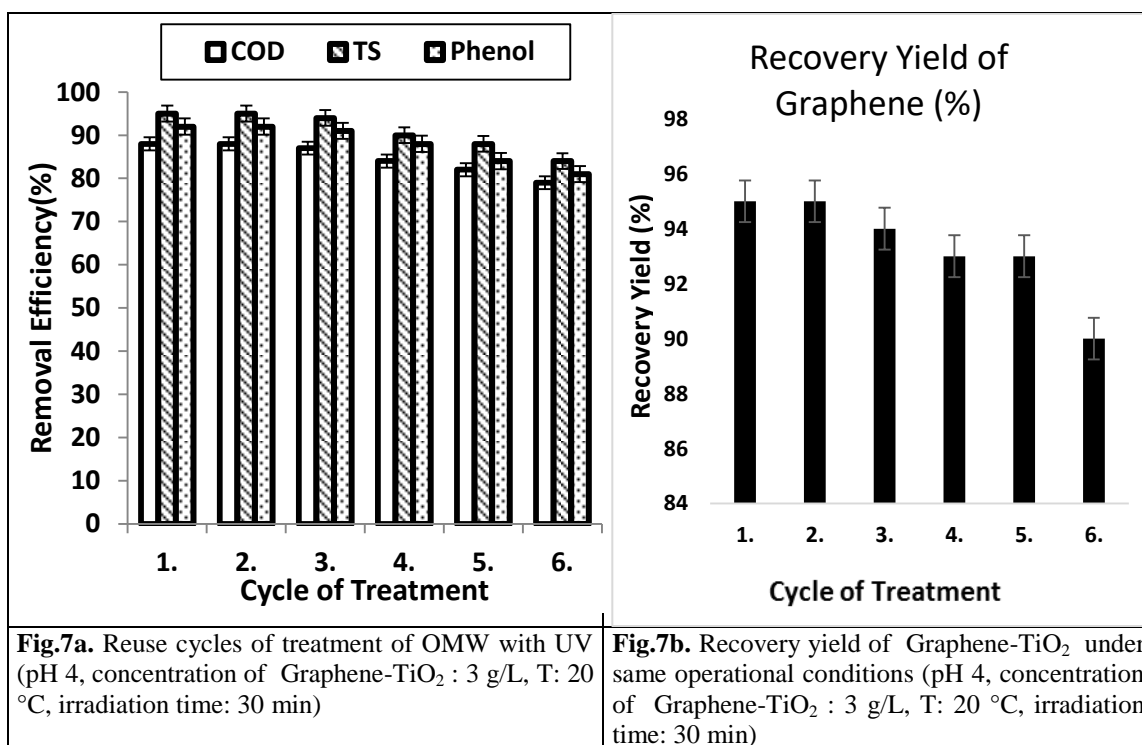
3.4. Reuse of Graphene-TiO₂ after treatment of OMW

In this study, six sequential treatment steps were investigated for determination of reusability of Graphene-TiO₂. Six treatments of OMW without change the Graphene-TiO₂ under same operational

conditions (pH 4, Graphene-TiO₂ concentration: 3 g/L, T: 20 °C). After the first treatment of the OMW, the polluted 3 g/L Graphene-TiO₂ were centrifuged and washed with distilled water and ethanol to use again. After 2ND and 3TH sequential it was found that with 3 g/L Graphene-TiO₂ the COD, phenol and TS yields

were not changed compared to first use of Graphene-TiO₂ (Fig. 7a). It was found that the removals of all parameters decreased slightly after 5th and 6th steps of treatment. As a consequence, the yields of Graphene-

TiO₂ recoveries for each treatment steps (1, 2, 3, 4, 5 and 6th) were obtained as 95%, 95%, 94%, 93%, 93% and 90%, respectively (Fig.7 b).



4.

5. CONCLUSION

The maximum COD, TS and phenol yields were 88%, 95% and 92% with 3 g/L Graphene-TiO₂ under 30 min UV irradiation at original pH of OMW. The results of all experiments showed that treatment of OMW under UV light irradiation has high removal efficiencies for all pollutant parameters. Since the maximum removal efficiencies of COD, TS and phenol were obtained at the original pH of the OMW (pH=4) operational cost significantly decreases. The old polluted Graphene-TiO₂ can be effectively used again after treated for 3 sequential to treat the OMW pollutants as its in first used.

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