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Photo degradation of Olive Mill Wastewaters Using Graphene-Tio2 and Recovery of Graphene-Tio$_2$

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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-TiO$_2$ 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 peaksshowed 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-TiO$_2$were investigated under photocatalytic oxidation. The effects of increasing Graphene-TiO$_2$ 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-TiO$_2$ concentration (3 g/L). The maximum recovery capacity of Graphene-TiO$_2$ was found between 90 and 95% after sequential six cycles.

Keywords: *Graphene-TiO$_2$, Photocatalytic degradation, Olive mill Wastewater, UV Irradiation.*

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I. 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 materialsarethemostcommonlyusedsemiconductoroxidephotocatalystsduetotheirlowenvironmentalimpact.However, therearenumerousobstaclesimpedingthemaximizationof photocatalyticactivity in thesematerials, includinglowadsorptionability, detrimentalrecombination of chargecarriers,andlight utilization.TiO2/carbonnanotubecompositeshavebeenestablished as viablepotentialphotocatalystsforuse in bothwaterandairpurifications(1-4). Thesynergeticeffect of carbonnanotubes on photocatalystenhancement, in whichcarbonnanotubesact as theelectronsinkforthehindrance of chargecarrierrecombination [1-2or as thephotosensitizertogenerate a greaterdensity of electron/hole pairs ,hasbeenpreviouslydemonstrated. Carbonnanotubesalsobehaveas impurities, resulting in theformation of Ti–O–C bondsand,therefore, expandingthelightabsorptiontolongerwavelengths4-6)).

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 photocatalystscombinedwithtwo-dimensional GO (GO–TiO2) hybrids, theoxygenatedfunctionalgroups on the GO sheetsfacilitatethebinding ofTiO2 and GO andGOs can serve as electronsinksunderultraviolet (UV) illuminationorelectrondonorsundervisiblelightilluminationforretardation of electron-hole recombination(3-4). Additionally, thesurfaceareas of GO–TiO2 hybrids(e.g., 80m2 g−1) arehigherthanthat of uncoupled TiO2 (e.g.,57m2 g−1) [5,6].

Thecombination of TiO2 andgrapheneoxideand/orgraphene is predictedtogenerate a synergisticeffectthatpotentiallyenhancesthephotodegradation of organicandinorganiccontaminants in aqueousmediaduetothepossibleimprovements in theadsorbability (sevil 2 of organics (dyes)(7) andinorganics (Pb)(8) andCo (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-TiO_2 under photocatalytic oxidation.Photo-degradation under UV irradiation was studied for different irradiation times, pH and concentrations of Graphene-TiO_2.Reuse of Graphene-$TiO_2$was also investigated.

II. MATERIAL AND METHODS

2.2 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 TiO_2 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 ^{0}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 AquamateThermo at 420 nm wave length (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-TiO_2under laboratory conditions

In a typical preparation, an aqueous dispersion of graphene (8.4 mg/mL) was dissolved in 200 mL of deionized water. TiO_2powder (P25, Degussa) was dispersed in deionized water and subsequently added to the graphene oxide solution. The mixture wassonicated for 1.5 h and further stirred for 12 h at room temperatureto obtain a homogeneous solution. The product was filtered anddried in a vacuum at 50 ◦C for 4 h.

2.5 Reuse methods of Graphene-TiO_2

After first use the Graphene-$TiO_2$was filtered after photocatalytic degradation, washed three times by water and ethanol and dried.The washed Graphene-TiO_2 was used for fivesequential times to threat the raw OMW in each step with UV irradiation. Under sunlight treatment the first used Graphene-TiO_2 was used threat the raw OMW.

III. 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-TiO_2 concentrations, pH values and irradiation times.

3.2.1.1. The Effect of Concentration of Graphene-TiO_2on Treatment of OMW

Graphene-TiO_2concentration is an important parameter for the photo-treatment of OMW(11,12). In order todetermine the maximum photocatalytic treatment efficiencies of OMW 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/LGraphene-TiO_2concentrations 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% and79% at0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/LGraphene-TiO_2, respectively (Fig.1.a).The TS removal yields were obtained as 57%, 79%, 95%, 93% and85% at 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/Lgraphene, 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/LGraphene-TiO_2, respectively(Fig.1.c). The results showed that the removal efficiencies were not changed with increasing Graphene-TiO_2concentrations from 3 g/L up to 10 g/L, significantly (Fig.1).Among the Graphene-TiO_2 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/LGraphene-TiO_2 composite concentration. The maximum COD, TS, phenol removal yields were obtained 88%, 95% and 92%, respectively (Fig.1.d).

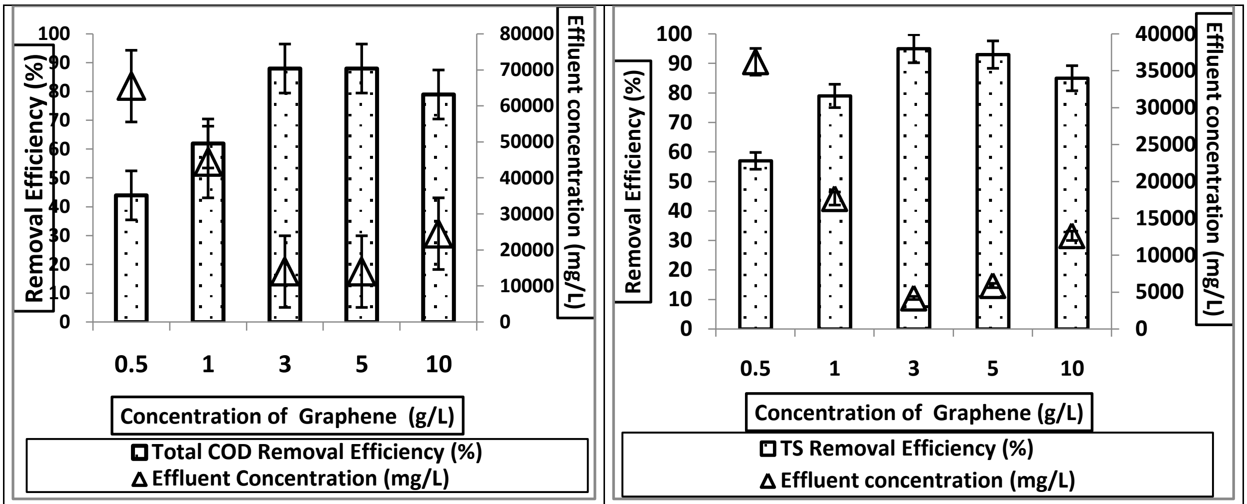

Fig.1.a. Effect of increasing Graphene-TiO_2concentrations on COD removal from OMW (pH 4, T: 20°C,Irradiation time: 30 min)

Fig.1.b. Effect of increasing Graphene-TiO_2concentrations on TS removal from OMW (pH 4, T: 20°C,Irradiation time: 30 min)

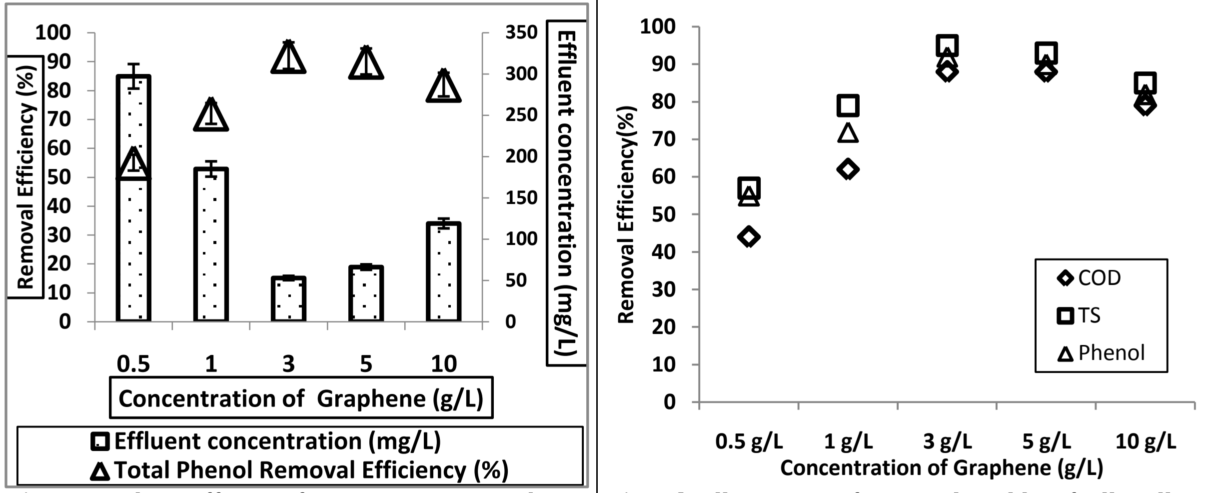

Fig.1.c. The effect of increasing Graphene-TiO_2concentrations on Phenol removal from OMW (pH 4, T: 20 °C, Irradiation time: 30 min)

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. The Effect of Irradiation Time on Treatment of OMW

OMW treatment with Graphene-$TiO_2$was investigated at different irradiation times. Irradiation times were chosen as 15, 30, 60 and 90 min. The concentration of Graphene-TiO_2 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 minirradiation times, respectively.When the irradiation time was increased from 30 min to60 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 minirradiation times, respectively (Fig. 2.b.). Increasing the irradiation time from 30 min to 90 mindecreased 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.).

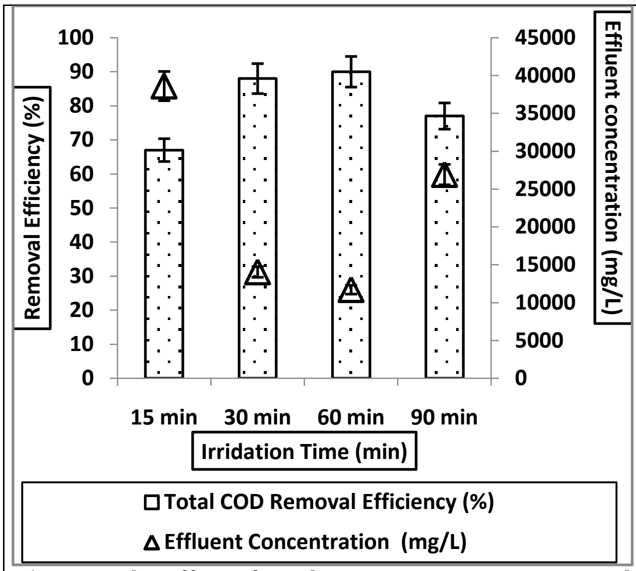

Fig. 2.a. The effect of irradiation time on COD removal efficiency (pH 4, Graphene-TiO_2concentration:3 g/L, T:20 °C)

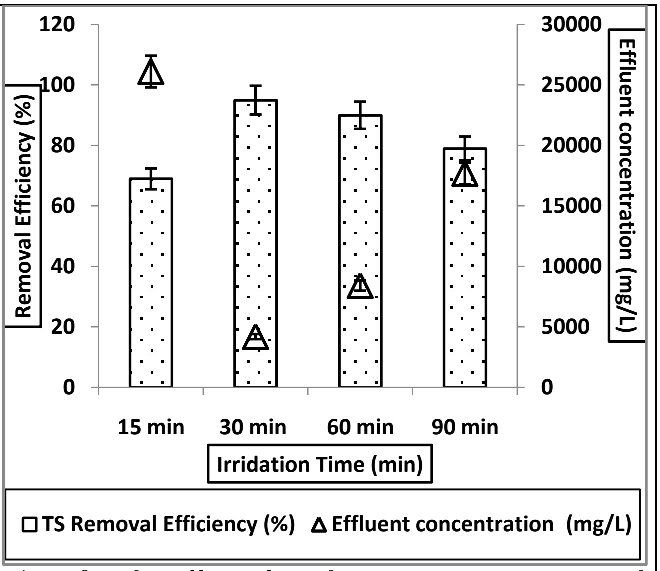

Fig. 2.b. The effect of irradiation time on TS removal efficiency (pH 4, Graphene-TiO_2concentration: 3 g/L, T: 20 °C)

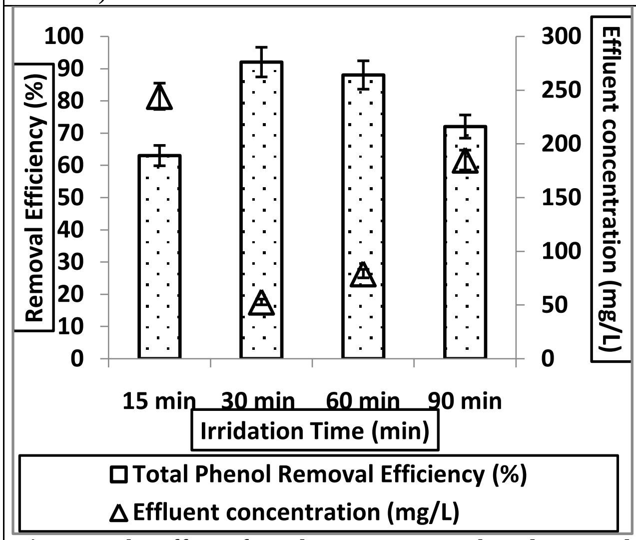

Fig. 2.c. The effect of irradiation time on Phenol removal efficiency (pH 4, Graphene-TiO_2concentration:3 g/L, T:20 °C)

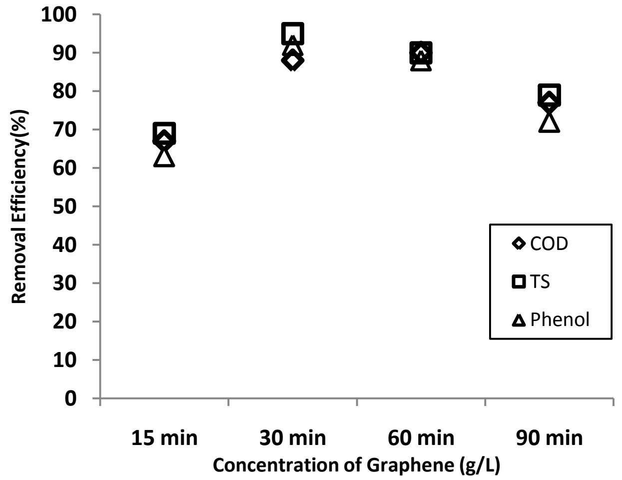

Fig. 2.d. Illustration of removal yields of all pollutant parameters (pH 4, Graphene-TiO_2concentration: 3 g/L, T: 20 °C)

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

3.2.1.3. The Effect of pH of OMW on Treatment of Olive Mill Treatment with Graphene-TiO_2

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 onOMWwith Graphene-TiO_2. (Fig. 3). All experiments were realized with 3 g/L Graphene-TiO_2at 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.

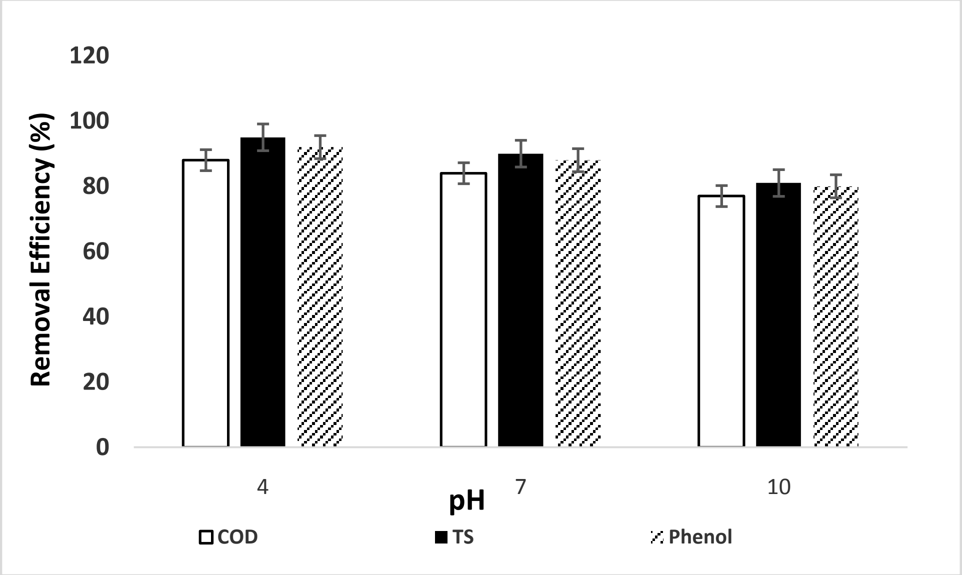

Fig.3. Effect of pH on the treatment of OMW with Graphene-TiO_2composite on COD, TS, and Phenol yields in the OMW

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 6,8nm(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.

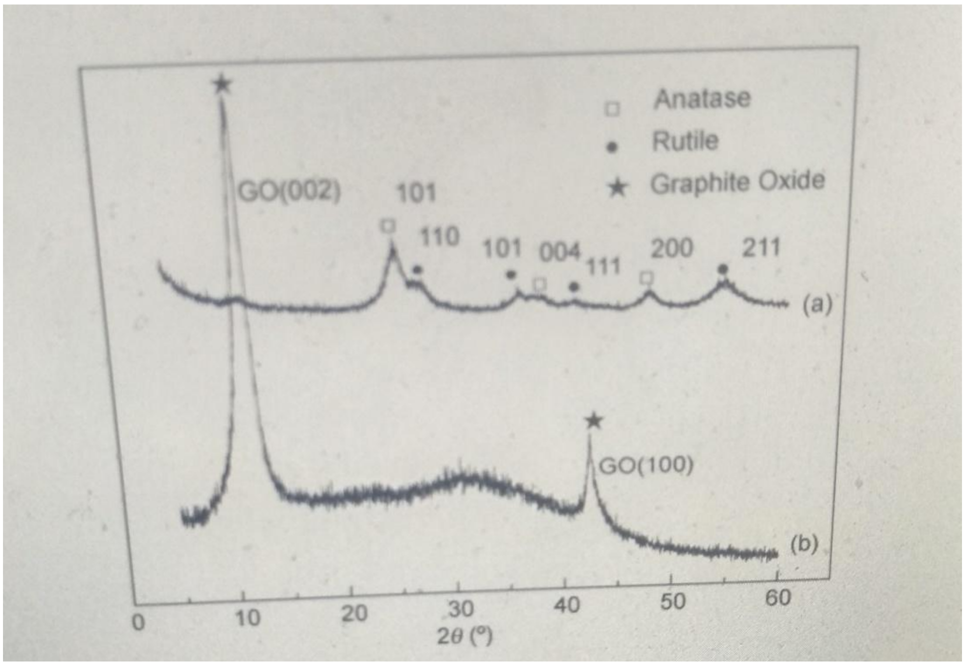

Figure 4. XRD disturbances of GO and TiO2

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).

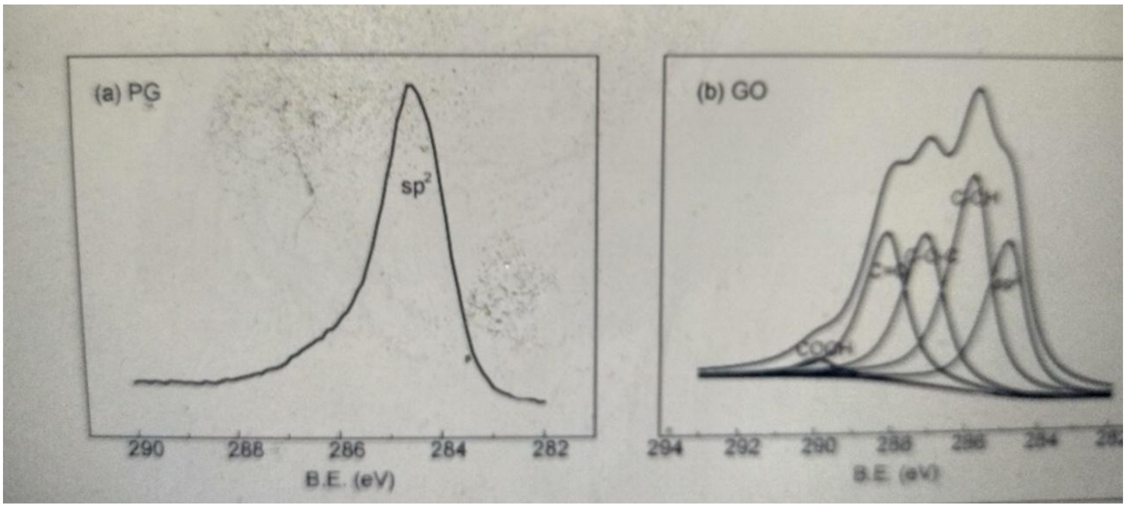

Figure 5 a. XPS analysis in PO; 5b. XPS analysis in GO

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 nano-particles 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.

FIG 6.FE-SEM analysis in GO- TiO2 nanocomposite

3.4. *Reuse ofGraphene-TiO$_2$after treatment of OMW*

In this study, six sequential treatment steps were investigated for determination of reusability of Graphene-TiO$_2$. Six treatments of OMW without change the Graphene-TiO$_2$ under same operational conditions (pH 4, Graphene-TiO$_2$ concentration: 3 g/L, T:20 °C).After the first treatment of the OMW, the polluted 3 g/L Graphene-TiO$_2$were centrifugedand washed with distilled water and ethanol to use again.After 2ND and 3THsequential it was found that with 3 g/L Graphene-TiO$_2$ the COD, phenol and TS yields were not changed compared to first use of Graphene-TiO$_2$ (Fig. 7a). It was found thatthe removals of all parameters decreased slightly after 5 TH and 6TH steps of treatment. As a consequence, the yields of Graphene-TiO$_2$ recoveries for each treatment steps (1, 2, 3, 4, 5 and 6 TH) were obtained as 95%, 95%, 94%, 93%, 93% and 90%, respectively (Fig.7b).

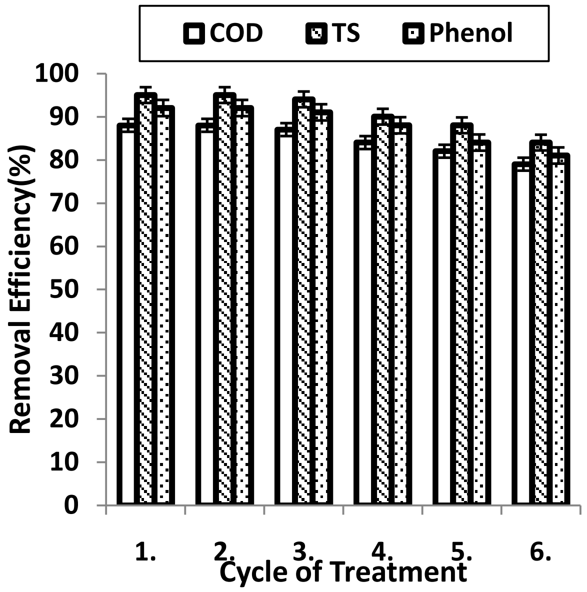

Fig.7a. Reuse cycles of treatment of OMW with UV (pH 4, concentration of Graphene-TiO_2: 3 g/L, T: 20 °C, irradiation time: 30 min)

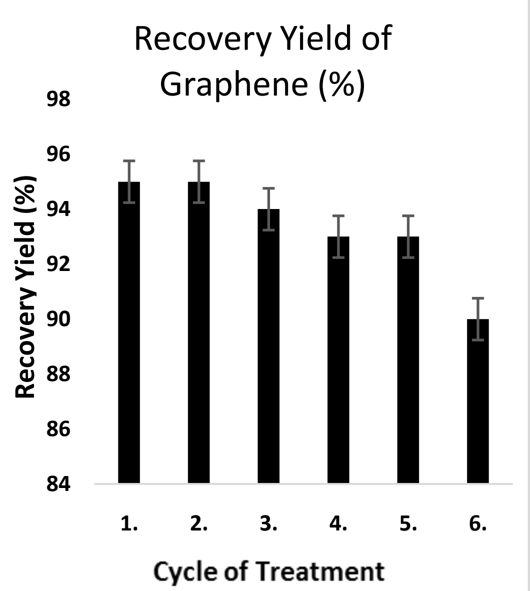

Fig.7b. Recovery yield of Graphene-TiO_2 under same operational conditions (pH 4, concentration of Graphene-TiO_2: 3 g/L, T: 20 °C, irradiation time: 30 min)

IV. CONCLUSION

The maximum COD, TS and phenol yields were 88%, 95% and 92% with 3 g/LGraphene-TiO_2under 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 pollutedGraphene-TiO_2 can be effectively used again after treated for 3 sequential to treat the OMW pollutants as its in first used.

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