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EVALUATION AND PHOTOCATALYTIC DEGRADATION OFPOLYAROMATIC HYDROCARBONS IN PETROLEUM REFINERY WASTEWATER

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ABSTRACT

Due to the importance of Gulf area, the present study was performed indischarge basin around the Coastal area of petroleum Suez Company, which is located in the northwest of the Gulf. In our previous work, Sediment samples were collected from five stations at different distances along discharge basin of the company and the concentrations of Poly-aromatic Hydrocarbons (PAHs) were determined in sediment samples. At all of the stations, the concentration of ΣPAHs was higher than the guideline value **(4022ng g^{-1})**. The concentration of PAHs in the sediments ranged between 22333.983 up to 73597.864ng g^{-1} .

In this work, different wt. % of Copper/$TiO_2$was prepared by wet impregnation method. The prepared materials were studied by nitrogen adsorption-desorption isotherm, X-ray diffraction, FTIR and Raman spectroscopy and high resolution transmission electron microscopy. The prepared materials were used to remove the Polyaromatic Hydrocarbons of the discharge basin of petroleum Suez Company by photocatalysis technique using batch reactor equipped with UV-vis solar light. Our results showed that the 0.09wt. % Cu/TiO_2 has a higher photocatalytic activity in the photocatalytic degradation than 0.04wt. %. The polyaromtichydrocarbons in water were successfully removed after 240 min of irradiation

Keywords- discharge basin, petroleum Suez Company, PAHs, guideline value, photocatalysis, TiO2, cupper phthaocyanine

I. INTRODUCTION

Oil pollution of aquatic ecosystems is a serious problem inmany parts of the world. The released oil undergoes severalweathering processes (biotic and abiotic) that alter its physical and chemical composition [1,2]. Themain weathering processes that contribute to the fate of oil inaquatic ecosystems include evaporation, spreading, dissolution,dispersion, emulsification, photodegradation, biodegradation andsedimentation. Although evaporation and cleanup activities mayreduce the amount of oil released into the water, a fraction of thisoil dissolves in seawater and continues to exert adverse effects onthe marine environment [3].It has been establishedthat the dissolved rather than the emulsified or theabsorbed fraction of the oil that is acutely toxic to marine life. The traditional treatment of refinery wastewater is based on the physicochemical andmechanical methods and further biological treatment in theintegrated activated sludge treatment unit. With respect to thefact that different concentrations of aliphatic and aromaticpetroleum hydrocarbons are present in the wastewater, amongwhich the aromatic fraction is not readily degraded by the conventionaltreatments and is more toxic, there is still a need foradvanced techniques to remove this sort of pollutants as much aspossible.

Several solutions are proposed in this regard; including useof coagulants [4,5], coagulation enhanced by centrifugation [6],ultra filtration [7,8] or sorption on organo-minerals [9]; with alevel of advantage for each of them.

Photodegradation may play distinctlyimportant roles in oil breakdown in the marine environment.Biodegradation may be slow in tropical and subtropical latitudeswhen nutrients are limited. On the other hand,Photodegradationmay be of greater importance in environments with intense solarradiation such as those in Egypt. Photo-oxidation may most likelyenhance the dispersion of the oil spills by transforming the oilcomponents into more water-soluble oxygenated ones. Thisprocess may also be responsible for changes in physical propertiesof the exposed oil [10, 11].

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The photocatalysis is one of the techniques, which are socalled "advanced oxidation processes (AOPs)". These processescan completely degrade the organic pollutants into harmlesssubstances such as CO_2 and H_2O under moderateconditions. The AOPs are characterized by the production ofOH• radicals which are extraordinary reactive speciesand capable of mineralizing organic pollutants[12]. They are also characterized by a little selectivity of attack,which is a useful attribute for an oxidant used inwastewater treatment.They attack most of the organic molecules with differentrates; therefore, providing a valuable technique when multicontaminatedwastewater,e.g. refinerywastewater is considered.The photocatalysis has been tested onmany different compoundsincluding environmentally relevant organic compounds and inmany different processes [13-15].

Due to the large band gap such asband gap of TiO2 (anatase: 3.2 eV; rutile: 3.0 eV), many semiconductorsordinarily used can generate electron–hole pairsonly when illuminated by ultraviolet light, which is a limit tothe photo-electronic transition efficiency of solar photo catalysisbecause the portion of UV-light in the solar spectrum isonly about 3–5% of total sunlight [16,17]. Therefore, the developmentof visible-light-driven photocatalysts is indispensableIn this study, we interest to apply a photocatalysis technology for refinery wastewater treatment through simple synthesis and characterization of photoactive material. to make adequate use of solar energy in decontaminatingwater[18-20].

II. METHODOLOGY

Area of study

Laboratory treatment was performed using the sediment ofdischarge basin of Suez Oil Processing Company, which is located in the northwest of the Gulf.Sediment sample was collected from station of the discharge basin of thecompany. The oil was extracted and concentrated to approximately 0.2 ml using dry nitrogen. The oil content in sediment was then calculated after removing the solvent till constant wt. and the concentrations of Poly-aromatic Hydrocarbons (PAHs) were determined in sediment samples using High Performance liquid chromatography. The concentration of ΣPAHs was higher than the guideline value (4022ng g-1) due to the aromatic outlet to discharge basin of petroleum Suez Company [21]. The extracted oil was weighed and dissolved in a small volume of methanol and then diluted with distilled water to a known volume to carry out the photocatalytic degradation process.

Catalyst preparation

Pure TiO_2 and Cu /TiO_2 in different wt. % 0.04 and 0.09 were prepared by sol-gel methodat ambient pressure and temperature asfollows; TiO_2 was prepared by dissolving titanium isopropoxide in isopropanol. Ammonia solution was added dropwise with constant stirring to adjust pH at 9. The precipitate was then centrifuge and dried at 120 ^oC then calcined at 500° C for 2hours. Doping TiO_2 with copper phthalocyanine was carried out as follows:
A calculated weight of solid TiO_2 was stirred overnight in known concentration of copper phthalocyanine in a solution containing poly (dialyldimethylammonium chloride) conductive polymer. The powder was filtered, dried at 120° C and calcined at 250° C for 2 hours.

Catalyst characterization

Nitrogen adsorption/desorption isotherms of the synthesized samples were measured on ASAP2010, at -196°C after degassing at 200 °C for 4 h. X-ray diffraction patterns were recorded with a Pan Analytical Model X' Pert Pro, which was equipped with CuKα radiation (λ = 0.1542 nm). High Resolution Transmission electron microscopy (HRTEM) analysis was carried out using a JEOL JEM-1230 electron microscope operating at 120 kV. Raman spectra were collected using a Renishaw Via 2000 system with an argon ion laser emitting at 100 and 800 nm. FT-IR spectra of the samples were carried out using ATI unicam (Mattson 936) Bench Top spectrometer.

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Photocatalytic degradation of polyaromatic hydrocarbons extract

Experiments were carried out in vertical reactor, resemble to the published previous work [22] with capacity ofabout 500 ml (Figure 1). TheUV-Vis lamp with the highest irradiationpeak at 365 nm was immersed in a silica jacket which allows the circulation of water to remove any thermal effect due to the irradiation. The silica jacket was placed in a jar containing polluted water. For well-mixing of the catalyst and polluted water a magnetic stirrer was used. At different irradiation time intervals, samples of the irradiated water were withdrawn for the analysis using HPLC (PerkenElmr series 200) equipped with photo-diode-array detector and at λ = 245 nm and Brownlee Analytical PAHs 5 μ m (250×4.6 mm) column. The mobile phase was acetonitrile / water witha gradient elution in which a change in the ratio of acetonitrile to water from 60/40 to 100%within 15 min was usedat flow rate of 1.2 ml min^{-1}.

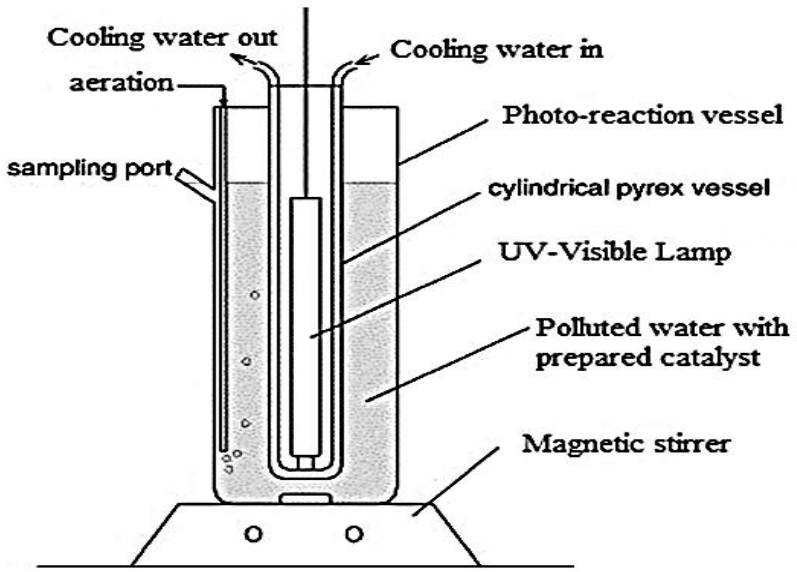

Figure 1: Schematic diagram of photo-reactor

III. RESULTS & DISCUSSION

N_2 adsorption desorption isotherm

The prepared samples display Type IV isotherm according to the IUPAC classification, which are typical for mesoporous solids [23] (Figure 2A&B). In Table 1the surface and structural properties of pure $TiO_2$and different wt. % Cu/$TiO_2$are summarized. From BET results, it is clear that the presence of polymer leads to a certainstabilization of the surface area. The BET surface area, the pore volume and pore size have not change significantly with increasing the Cu loading.

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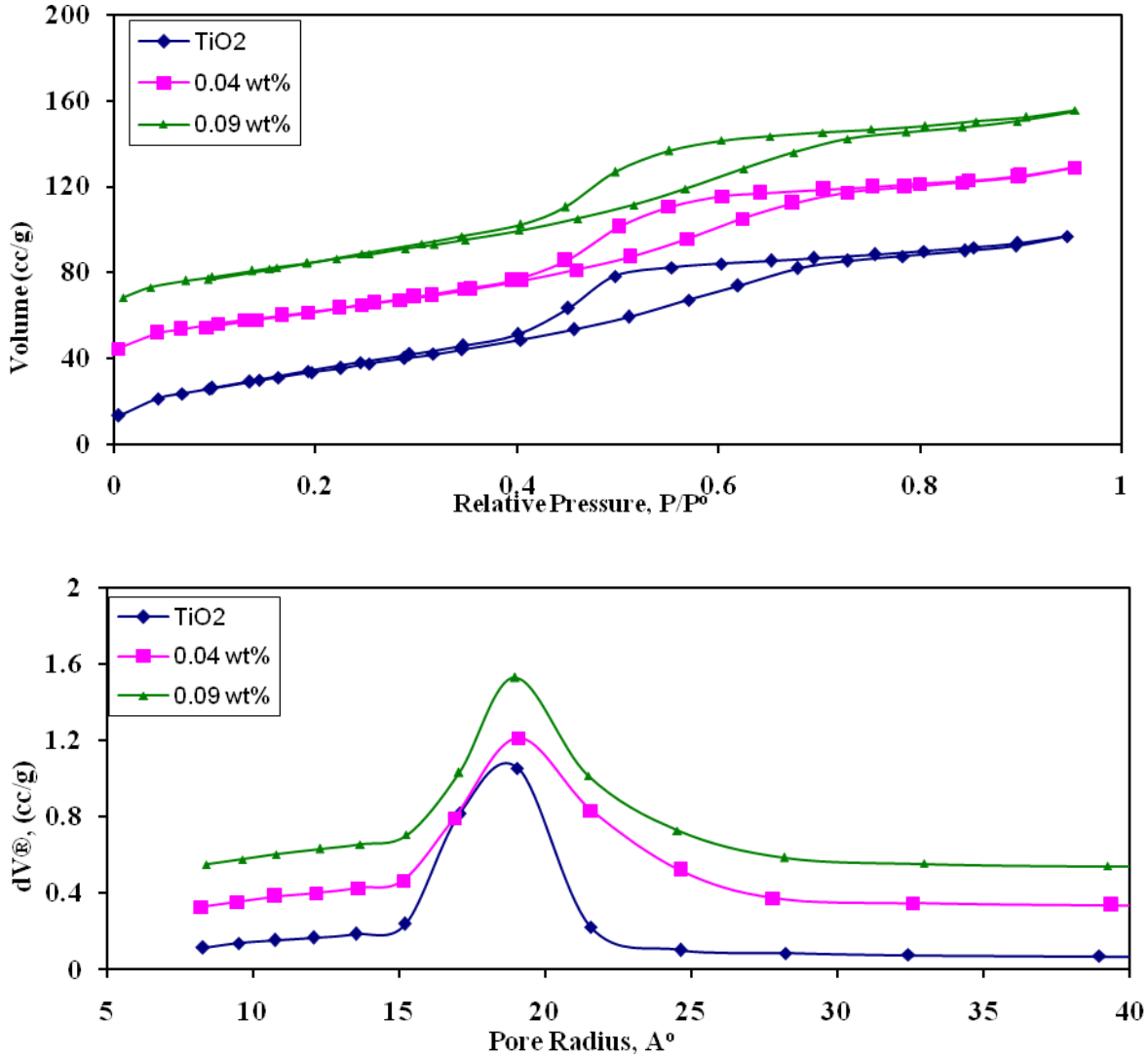

Figure 2: ***N_2 adsorption-desorption isotherm of TiO_2, 0.04 and 0.09 wt.% Cu/TiO_2 (A) and the corresponding pore size distribution (B).***

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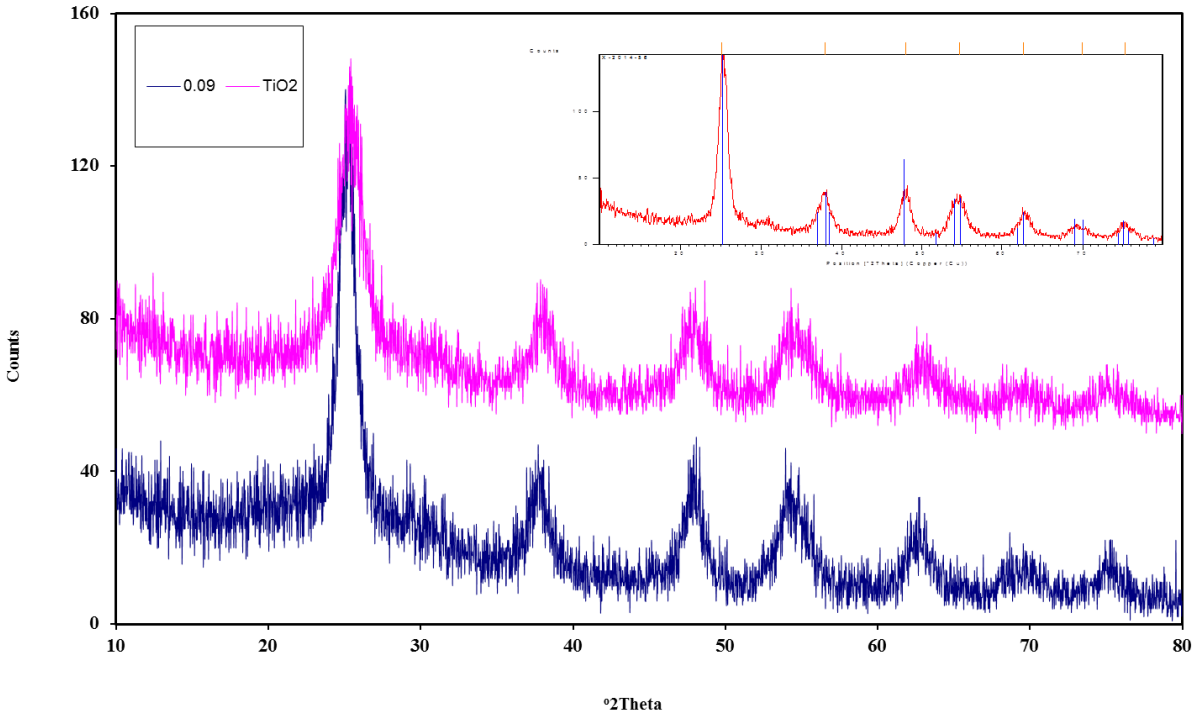
Table 1: Surface properties and crystallite size of TiO_2, 0.04 wt.% Cu/TiO_2 and 0.09 wt.% Cu/TiO_2

catalyst	BET Surface area,m^2/g	Average Pore radius, nm	Total Pore volume,cc/g	Crystallite size, nm
TiO_2	131.8	2.30	0.15	3.2
0.04 wt.% Cu/TiO_2	121.9	2.51	0.15	2.86
0.09 wt.% Cu/TiO_2	132.0	2.44	0.16	1.66

X-ray diffraction

Figure 3 shows the XRD of bare TiO_2 and Cu/TiO_2 in different wt. %. Thediffraction peaks observed at the 2θ values of 25.42, 38.68,48.15, and 74.4 correspond to the anatase phase of TiO_2 and wereassigned to the (101), (004), (200), and (215) crystallographicplanes, respectively. No characteristic peaks for copper was found in the XRD. This indicates that, copper is highlydispersed on the TiO_2 surface. A decrease in intensity of the (101) peakand increase in the broadness withincreasing in the concentration of copper. This is due to the presence of polymer which suppresses the increasein size of the crystal.Due to the large atomic radius of Cu^{+2}(1.57 Å) compared toTi^{4+} (0.68 Å), it is impossible for Cu ions to act as interstitial ionsin the TiO_2 matrix. Hence Cu^{2+} ions may only replace Ti^{4+} in the latticesites.Table 1 shows the calculated crystallite size using scherrer's equation.The results shows that the crystallite size was 3.2 nm, 2.86 nm and 1.66 nm for bare TiO_2, 0.04 and 0.09 % wt. % Cu/TiO_2, respectively.



Raman spectroscopy

Figure4 shows the Raman spectroscopy in the range of 100–1000 cm^{-1}.The anataseTiO_2phase was observed at 156 (E_g), 428 (B_{1g}), 533 (A_{1g}), and659 cm^{-1} (Eg). The inset at the top of Figure4 showsblue shift inthe lowest frequency (Eg) mode upon impregnation with copper.No signals corresponding to copper particles were identified in the

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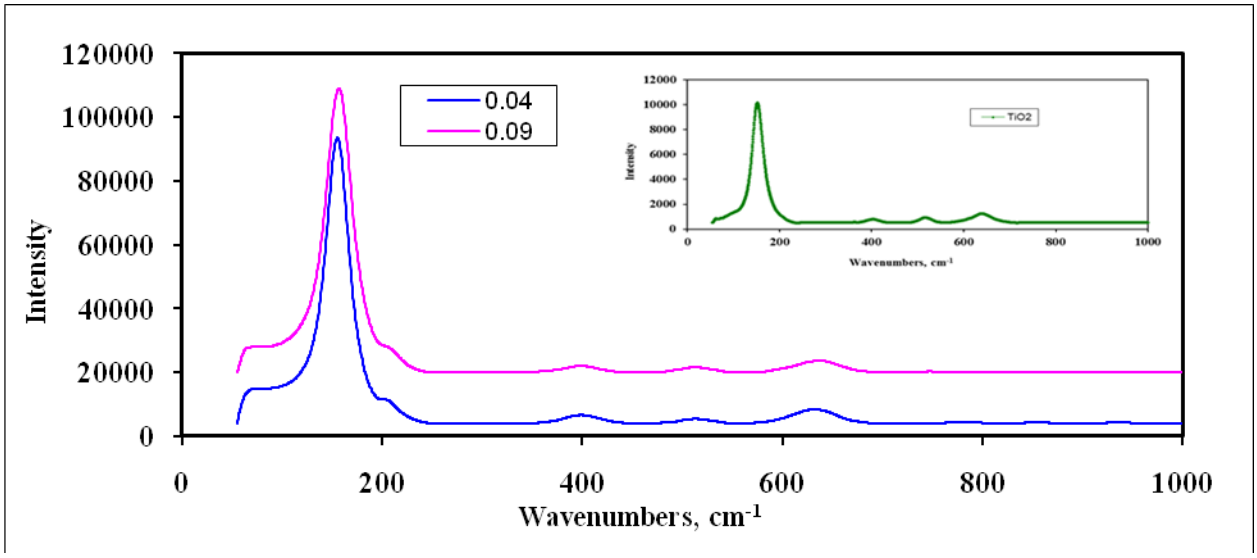
samples. This may be attributed tothe relatively low concentration of copper loaded onto the $TiO_2$and its weak Raman scattering. The peak intensities were decreased by the copper loading, this indicates that the interactionbetween copper and TiO_2 affected the Raman resonance ofthe TiO_2[24] without phase transition due to the change in the electronic structure of TiO_2 with scandiumdoping [25].



Figur4: Raman spectroscopy of TiO_2, 0.04 and 0.09 wt.% Cu/TiO_2

FTIR spectroscopy

Figure 5 shows the FTIR of the prepared samples. The bare TiO_2 display the presence of absorption bands at 594 cm^{-1} due to the presence of stretching vibration of Ti-O-Ti. A band at 1400 cm^{-1} could be attributed to N-O asymmetric stretching bond. A vibrational band at 1636 cm^{-1} could be assigned to O-H bending of hydroxyl group. The broad band at 3418 cm^{-1} is due to stretching mode of surface hydroxyl group. The same groups appear in 0.04wt.% and 0.09wt.% Cu/TiO_2.

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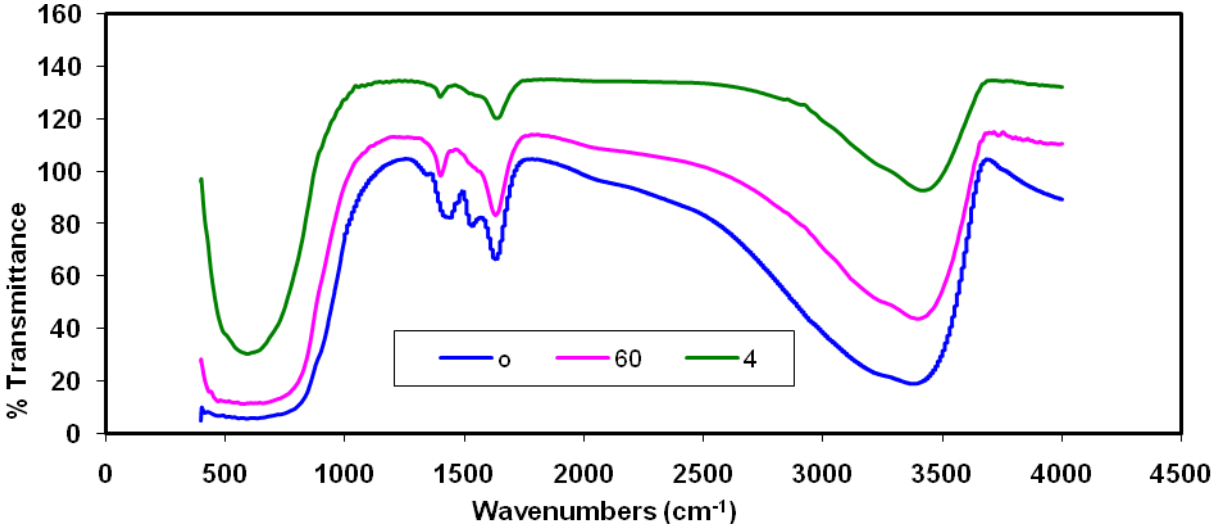
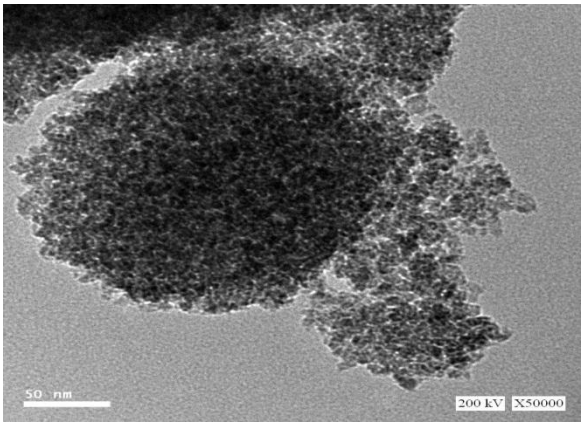
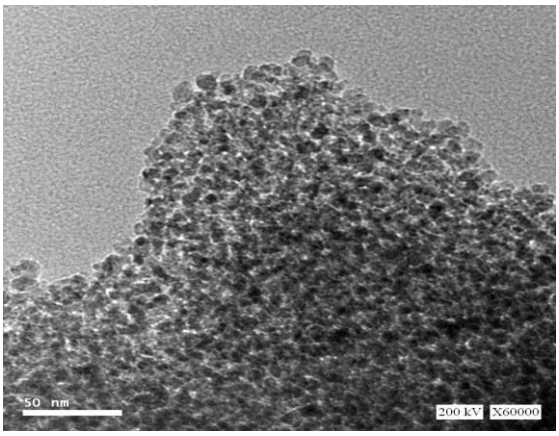


Figure 5: FTIR of TiO_2, 0.04wt.% Cu/TiO_2 and 0.09wt.% Cu/TiO_2

High Resolution transmission electron microscopy (HRTEM)

Figure 6 (A-C) shows the HRTEM of TiO2, 0.04wt.% and 0.09wt.%. The Figure shows the change in crystallite size according to the copper doping. The samples display a cubic morphology with different sizes; in case of TiO_2 the particle sizewas 3.2 nm. The particle size decrease as the copper loading increases.





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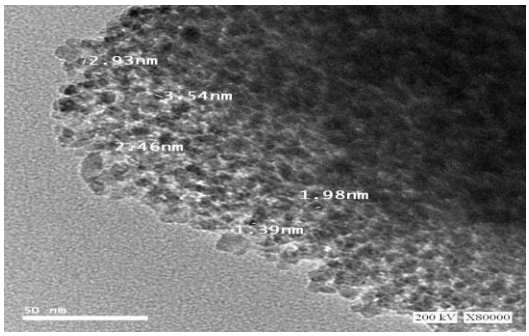

Figure 6: HRTEM of TiO_2(A), 0.04 wt.% Cu/TiO_2 (B) and 0.09 Wt.% Cu/TiO_2(C)

***Photocatalytic degradation*:**

The photocatalyticexperiments were carried out using extracted oil from sediment of Suez company drainage. The sample under study represents the outlet of Suez oil Petroleum company at <50m/west.Figure 7 shows themap of stations along the drainage basin of Suez Oil Petroleum Company (SOPC).The sample was extracted and diluted with distilled water. The extracted oil from different stations of the Companycontains2-3 rings and 4-rings, beside5-6-ring[21], the PAHs in sediment were Acenaphthylene (A), Acenaphthene (Ace), Flourene (F), phenanthrene (Phe), anthracene (Ant), Fluoranthne (Flu), pyrene(Py), benzo(a)anthracene (BaA),benzo(b)flourancene (BbF), Benzo[a] Pyrene (BAP) , indeno[1,2,3-] pyrene. Figure 8 shows the chemical structure of PAHsin this study.Table 2 shows the concentrations of PAHs in the sample under consideration as indicated by HPLC.

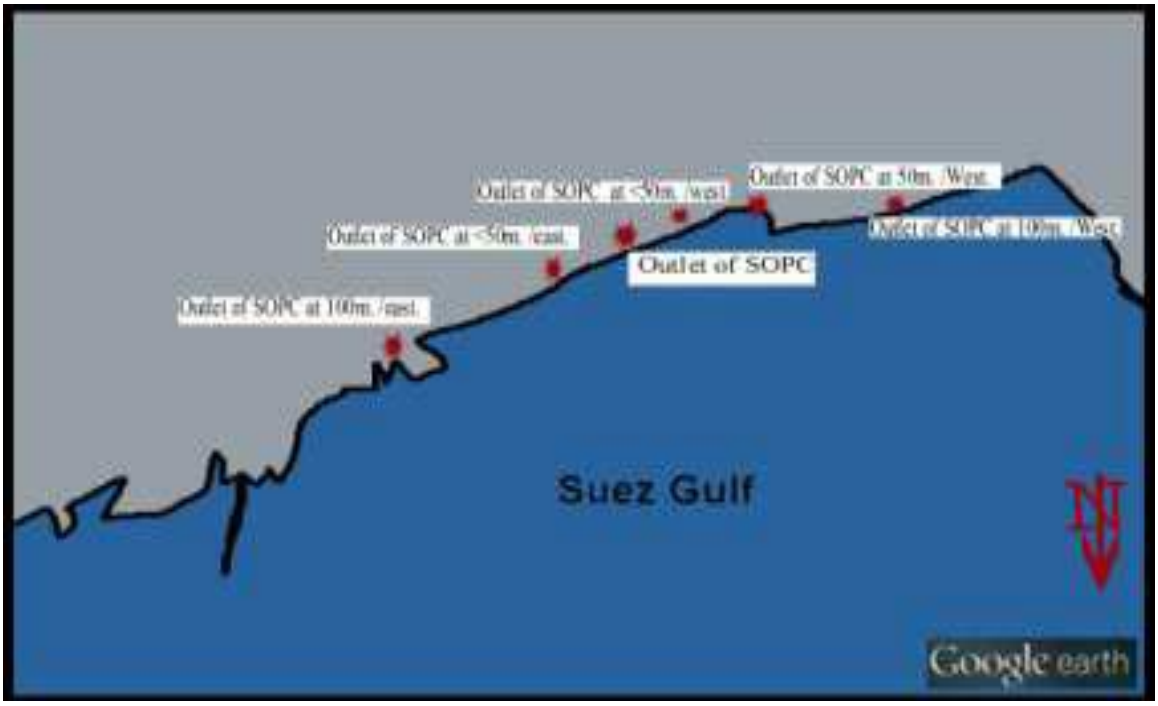

Figure 7: Map of stations along the drainage basin of Suez Oil Petroleum Company (SOPC)

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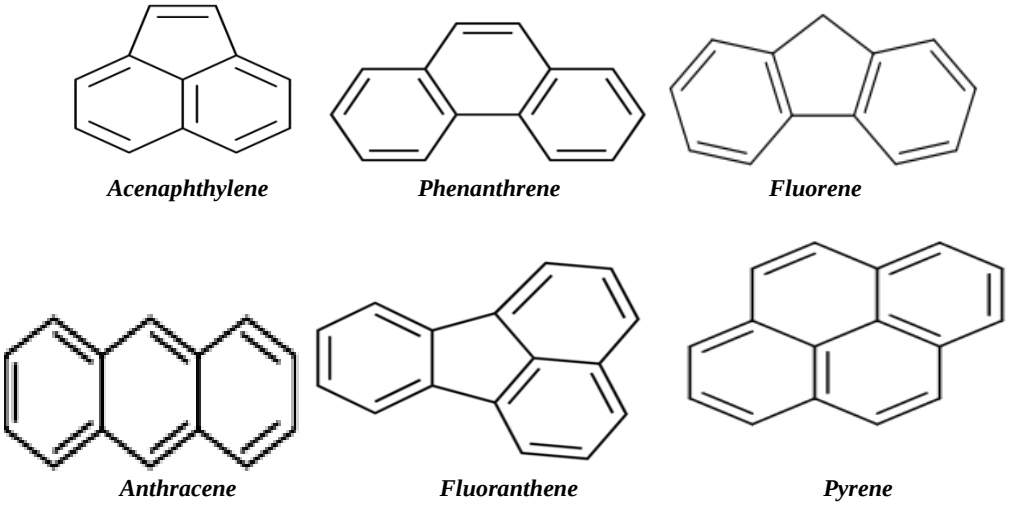

Figure 8: Chemical structure of the PAHs

Table2: The concentration of PAHs in the sample.

PAHs	Concentration, ppm
Acenaphthylene (A)	7.8
Phenanthrene (Phe)	1.0
Fluorene (F)	7.2
Anthracene (Ant)	1.8
Fluoranthene (Flu)	3.9
pyrene(Py)	10.6
Benzo(a)anthracene (BaA)	0.01
Benzo[b] flourancene (BAf)	0.03
indeno[1,2,3-] pyrene	0.01

Preliminary experiments were carried out to evaluate the effect of oxidation conditions on the removal of PAHs.The results confirmed that different aeration rates did not have significant effects on the PAHs removal under The normal condition at natural pH. The main role of air in the solution is to give sufficient oxygen in the polluted water. In presence of photocatalyst, as air is bubbled into solution, O_2 can scavenge the photon-produced electrons on the photocatalyst surface and produce super-oxide radicals. Super-oxide radicals are highly reactive species that could oxidize organic compounds adsorbed on the catalyst surface and the degradation process occurs and improves the degradation rate.

To study the adsorption capacity of the prepared samples, dark experiments were carried out for 15 min before illumination. Up to 14.6 ppm and 11.49 ppm of the total PAHs was disappeared using the samples 0.09 and 0.04wt.% Cu/TiO_2, respectively. Figure8a&b represents a comparison of the photodegradationof the identified compounds. Anthraceneundergoesfast degradation. It shows complete degradation after60 min of irradiation using 0.04 wt. % Cu/$TiO_2$and reaches 100% degradation after 30 min of irradiation using 0.09 wt. % Cu/TiO_2. Phenanthrene showed complete mineralization after 120 min of irradiation using 0.09 wt. % Cu/TiO_2 while the concentration of Phenanthrene reaches 0.23 ppm using 0.04 wt. % Cu/TiO_2. Fluoranthene (Flu)completely degraded after 240 min of irradiation over 0.09 wt. % Cu/TiO_2 while the concentration reaches 1 ppm using 0.04 wt. %

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Cu/TiO_2. Pyrene resists mineralization using 0.04 or 0.09 wt. % Cu/TiO_2. It is difficult to follow the degradation of Benzo(a)anthracene (BaA), Benzo[b] flourancene (BAf) and indeno[1,2,3-] pyrene due to their very low concentrations.

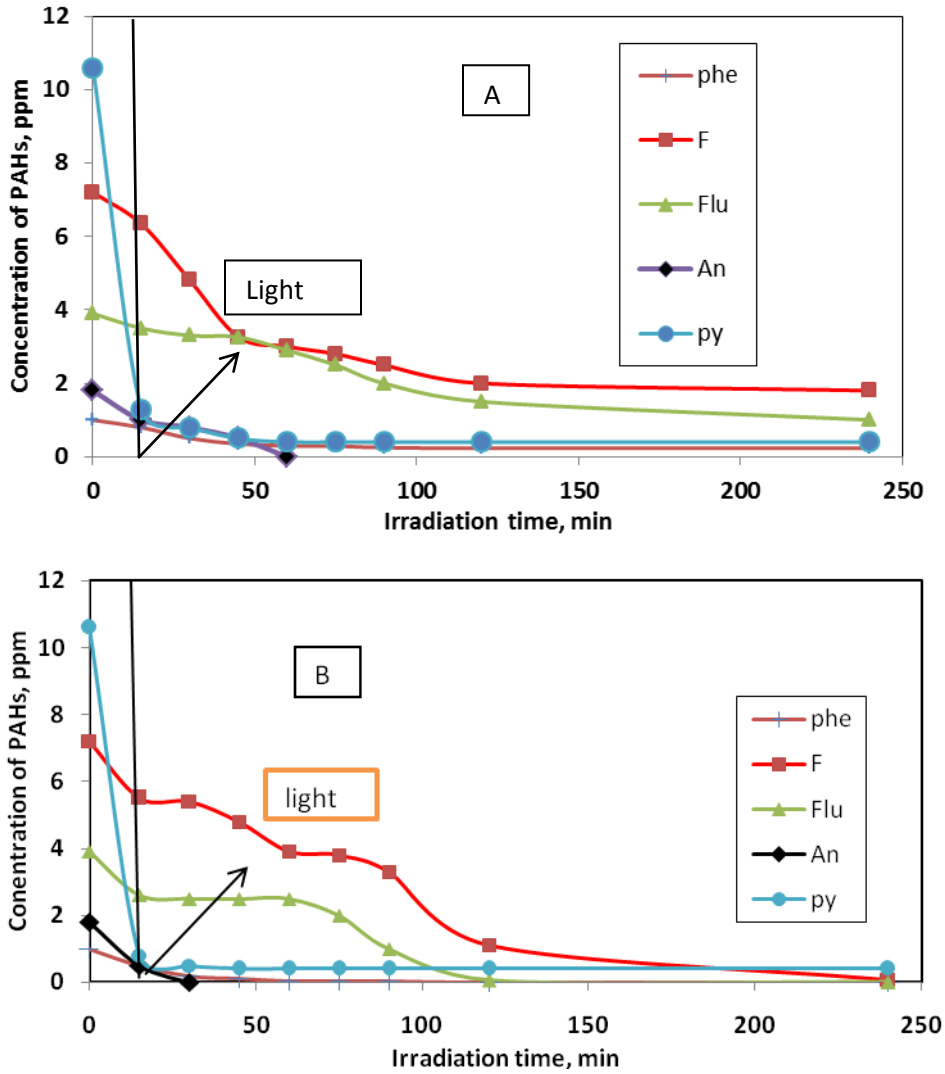

Figure 8: Photocatalytic degradation of PAHs using 0.04wt.% Cu/TiO_2(A) and 0.09 wt.% Cu/TiO_2(B) and UV-Vis light.

The photodegradationof the total PAHs displays in Figure 9. It shows that 0.09 wt.% Cu/TiO_2 is more active than 0.04 wt.% Cu/TiO_2. As the Copper particles loading increases the photocatalytic activity increases. The presence of copper particles on the surface helpsto increase the life time of the electron hole pairs by attracting theconduction band photoelectrons. The copperparticles on the surfacecapture the photoelectrons and are subsequently transferred to theadsorbed O_2 to yield highly oxidizing peroxy or superoxy species,leading to the effective separation of electrons and holesand thereforeenhance the rate of photocatalyticdegradation process.

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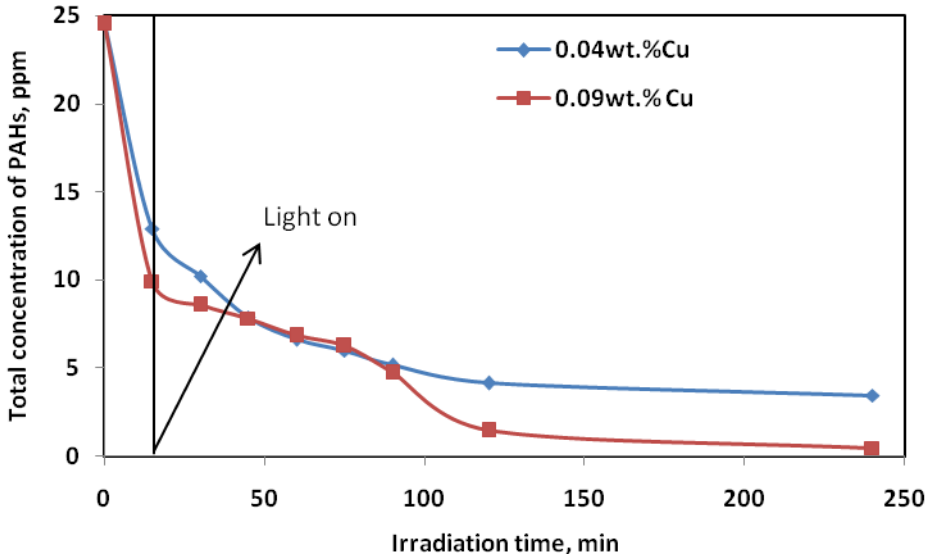

Figure 9: Photocatalytic degradation of total PAHs using 0.04 wt.% Cu/TiO_2 and 0.09 wt.% Cu/TiO_2.

IV. CONCLUSIONS

Different wt.% TiO_2 supported Copper was prepared by wet impregnation method and used as a photocalyst to remove the PAHs from refinery wastewater. The degradation efficiencyof 99% of the organic pollutants was achieved after 240 min of irradiation using 0.09 wt.% Cu/TiO_2while the degradation reaches 86.4% using 0.04 wt.% Cu/TiO2.This result has an industrial impact when this method is considered asan alternative process for biological degradation,having a minimum of 18 h residence time required to provideonly 77% removal.

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