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RESEARCH PAPER

Synthesis and Application of TiO_2/SWCNTs/Pt Nanocomposites as a Good Photocatalyst for Hydrogen Production

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ABSTRACT

Titanium dioxide Hombickat UV100 was used as semiconductor for hydrogen production reaction without and with modification by 0.5% single walled carbon nanotubes SWCNTs and platinum Pt. the modification includes synthesize binary composites with SWCNTs by sonochemical addition while with Pt was accrued by photo deposition method. Structural properties and morphology of the synthesized materials SWCNT/UV100, UV100: Pt and ternary composites SWCNT/UV100: Pt with pristine UV100 were characterized by x-ray diffraction, UV-visible diffraction and Fourier transform infrared spectroscopy FTIR. The results showed that SWCNTs reduce the activities of UV100 in producing H_2 from solution 10% MeOH/H_2O while in the ternary composites SWCNT/UV100: Pt the SWCNTs play very important roles in increase the activity of UV100 with Pt to more than 20%. The role of SWCNTs was related to dispersion Pt with less agglomerates as compare with UV100: Pt and that create more active cites on the surface of UV100-TiO_2.

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INTRODUCTION

Nano composites refers to all the materials that exist together in Nano scale with real connections to improve the total physical and chemical properties for mixture which make it more activities in specific applications as compare with the materials that make up the compound if used alone. Nanocomposites characterized by rare properties such Nano size, large surface area, and many active sites which encourage to develop performance of huge amounts and types of materials in the fields of drugs, biomaterials and other application [1]. many literatures reported that all the martials when reach to nanoscale the interactions at outer phases increase in very large value [2].Titanium dioxide TiO_2 one of common materials that is synthesized in nanoscale and inter in many applications such as hydrogen production

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which represent the future fuels and the best sample for clean and friendly energy [1, 2].

TiO_2 behaves three crystalline structures: rutile, brookite and anatase, which is the best in photocatalytic reactivates and most widespread for hydrogen evolution. Titanium dioxide TiO_2 mostly refer to it by commercial names such as Degussa (Evonik) P25 and hombikate UV100. The first one Degussa is composed of anatase and rutile crystallites, with two common ratios 70:30 and 80:20 respectively while the second types is completely including anatase phase only which shown higher activities from the ether[3]. Maybe TiO_2 characterized by many physical and chemical properties make it the best alternative for many applications compared to many nanomaterials in addition to the safety and cost but still the band gap for activation one of problems that reduce the activates. Many efforts were done to enhance the abilities for used TiO_2 with all phases and types in many fields of applications such combines with many components of what is known composites which could be binary, ternary or more according to the number of addition materials in matrix. Carbon nanotubes CNTs with two types single SWCNT and multi-walled carbon nanotubes MWCNT and platinum Pt represent the best adding materials with TiO_2 [4, 5].

Compared nanoparticles with to micro-particles, the first behave a higher photocatalytic activity, due to required minimal value of energy to transfer the charge to the surface. Generally, the Nano size characterized by reduce the distance that photo generated electrons / holes need to travel to the surface with reducing the probability of recombination [5-7]. Until know and for unknown time in the future the research in the field of hydrogen production still continues by using composites as photocatalytic which include CNTs and Pt with TiO_2 because experimentally shows variance in activities form system to ether. The variance was reported in many literatures which published in this sections [8]. In this work UV100 – TiO_2 was used to produce hydrogen from 10% Methanol/ H_2O solution in 4 conditions: i-pristine UV100, ii-modified with SWCNTs and Pt in binary composites, iii- ternary composites with SWCNT/Pt.

MATERIALS AND METHODS

Materials

The SWCNTs used in this study were purchased from Aldrich which fabricated by chemical vapor deposition and purities 70% with average diameter of 0.9 nm. The metal salt precursor, was dihydrogen hexachloro palatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), which supplied from Alfa Aesar. Nitric acid (65 wt% HNO_3) and sulfuric acid (37 wt% H_2SO_4) were obtained from Fluka. The scavenger agent Methanol was purchase from Merck with purities 99%.

Functionalization of carbon nanotubes

The oxidation process was done as reported in litureture , 100 mL of HNO_3/H_2SO_4 (1/3) in 250 mL of conical flask with condenser were used as oxidation agent for 50 mg of SWCNTs which mixing under magnetic stirring for 5 h at 50˚C. After washing until reach to neutralization at pH equal to 7 the product was drying at 120 for 3h at inner atmosphere by N_2 gas.

Preparation of 0.5%SWCNT/TiO_2 (UV100) by sonochemical method

The equivalent weight of functionalized SWCNTs were dispersed in 250 m L of distilled water using ultrasonic water bath for 30 min. (solution A). 0.5g of UV100- TiO_2 was dispersed in the same condition of SWCNTs (solution B). Solution B was drop wise to solution A in excite ultrasonic water bath for 30 min. Then filtered and drying the product at 100˚C overnight.

Preparation of UV100:0.5%Pt by photodeposition method

The second types of binary composites UV100:0.5%Pt was prepared by the photo-deposition method which includes dispersion of 1 g of UV100 nanoparticles in 100 mL H2PtCl6/ aqueous solution that containing the equivalent ratios of 0.5%Pt with stirring for 1 h. The resulting mixture was irradiated with intensity light 2. mW cm^{-2} UV(A) for 3 h under an Ar atmosphere, then 1 mL methanol was injected into the solution with continues illumination for 5 h. The powder was filtered and washed with water, before dried at 100 °C overnight.

Preparation of 0.5%SWCNT/UV100:0.5%Pt composites

The ternary composites 0.5%SWCNT/ UV100:0.5%Pt was prepared by two steps the first preparation 0.5%SWCNT/UV100 include the same dateless which mentions in the first part without

drying. The second steps required forming mixture of 100 mL aqueous with stirring for 30 min. to ensure forming homogenous dispersion for mixture then inject the equivalent weight H2PtCl6 solution with starting illumination for 9 h, at the end of third hours 1 m L of methanol was injected to the mixture under the same conditions of photo-deposition. Finally, the powder was filtered and washed with water, before dried at 100 °C overnight.

Photocatalytic activity for H_2 production

The reactor of hydrogen production consists of a xenon lamp (Osram XBO) with a 1000-WattUV-B light at the 240-1000nm wavelength and light intensity 40 mW cm^{-2} which fixed horizontally to the glass reactor. The reactor vessel consisting of a double-jacket Pyrex-glass reactor (110 mL volume) equipped with a quartz disc for light penetration.

After reach the lamp for stability of light intensity and Argon gas was purged through the suspension for 30 min at 298˚C which kept constant by a Land Nds. Uni Hancooler system. During irradiation, the headspace gas (40 mL) of the reactor was intermittently sampled (0.5 µL) and analyzed for H_2 using a gas chromatograph (Shimadzu GC – 8A) equipped with a thermal conductivity detector and a carboxen 1000 packed column. The photocatalytic reactions of hydrogen production from 10 % of an aqueous methanol solution were carried out using 80 mg of pristine UV100 and different composites of 0.5%SWCNT/UV00, UV100:0.5%Pt and 0.5%SWNT/UV100;0.5%Pt.

Characterization

The pristine UV100 and binary composite 0.5%SWCNT/UV100 and UV100/0.5%Pt with ternary composites 0.5%SWCNT/UV100/0.5%Pt were characterized by thee techniques x-ray diffraction XRD, Fourier-transform infrared spectroscopy FTIR and UV-visible reflectance. XRD measurements were carried out by X-Ray diffractometer (Philips APD 15) with CuKα radiation. Fourier transform infrared spectroscopy FTIR were carried out in the 400–4000 cm^{-1} wavenumber when formed into pellets with KBr and the spectra were recorded on a BRUKER FTIR Spectrometer. The absorbance (220–800 nm) of pristine UV100 and modified with SWCNTs or/and Pt in binary and ternary composites were done by UV–Vis diffuse reflectance spectra of the powder on a JASCO V-560 UV–Vis spectrophotometer, with a double monochromator with an integrating sphere attachment (JASCO ISV-469).

RESULTS AND DISCUSSION

Fig. 1, include the diffraction pattern of UV100 exhibited reflections of anatase phase, at (101) 25.21°, (004) 37.95°, (200) 48.2°, (105) 53.91°, and (200) 62.9 corresponding to a tetragonal anatase

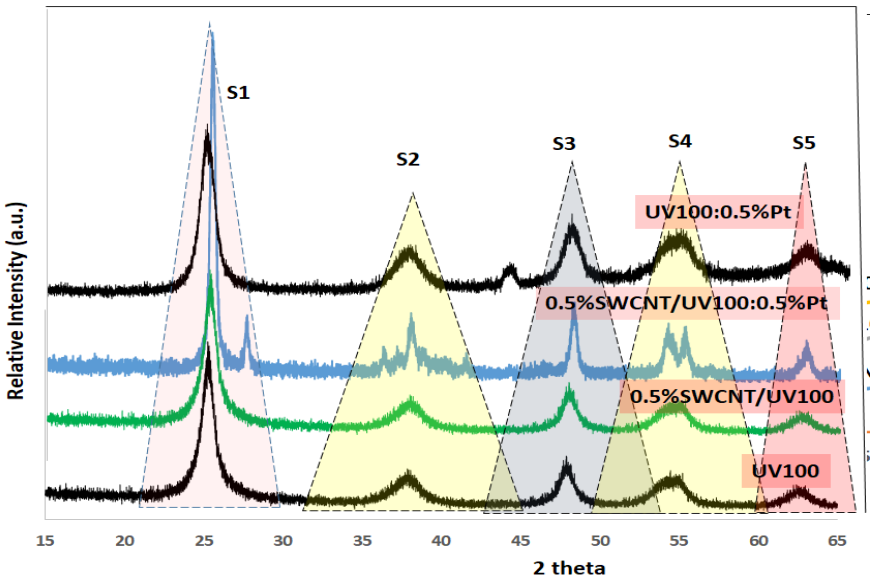

Fig. 1. The XRD patterns of the photocatalysts Hombikat UV100, 0. 0.5%SWCNT/UV100 , UV100:0.5%Pt and 0.5%SWCNT/UV100:0.5%Pt.

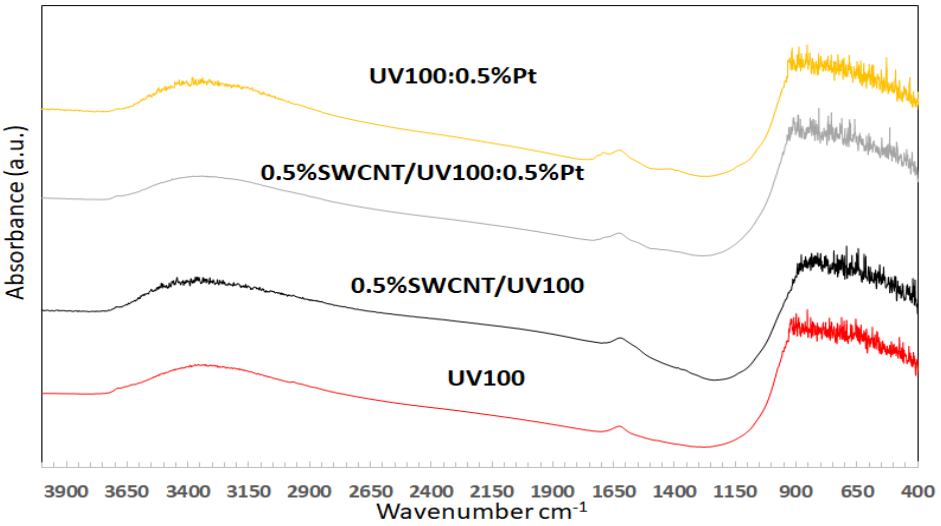

Fig. 2. The FTIR spectrum of the photocatalysts Hombikat UV100, 0. 0.5%SWCNT/UV100, UV100:0.5%Pt and 0.5%SWCNT/UV100:0.5%Pt.

structure, mostly the pristine UV 100 which is pure anatase phase showed wide peaks due to small nanoparticles and lower crystallinity. The binary composite 0.5%SWCNT/UV100 patterns did not witness clear change in peaks the change was limited to reduce the wide of peaks due to forming many agglomerate particles [9]. The patterns for UV100:0.5%Pt include two properties the first reduce the wide of peaks which refers to increase in particle size with increase the agglomerates , while the other was appears new peaks at 45˚ which related to Pt species that precipitation on the surface of TiO_2. The patterns for ternary composite 0.5%SWCNT/UV100:0.5%Pt where characterized by new peaks at 27.8˚ , 36.2˚, 42.3˚ and 53.7˚ that can be related to Pt species that precipitation with homogenous dispersion on the surface of TiO_2 with less agglomeration as compare with binary composites. The value of particle size was estimated by Sheerer equation and that shown 5 nm, 12 nm, 19nm and 15 nm for pristine UV100, SWCNT/UV100, UV100: Pt and SWCNT/UV100:Pt respectively [10].

Fig. 2 represent the FTIR spectroscopy in the absorbance mode which estimated qualitative analysis for the nature bonded to the surfaces. The band at 1440 cm^{-1} was attributed to Ti–O–Ti vibration, observed very weak for UV100- TiO_2 and that increase in intensity of absorbance when change the structure to binary composites and ternary composites. The band at 1650 cm^{-1} was assigned to the O–H bending vibration of the chemisorbed water and that also increase in UV100 after modification and shown the largest influence with UV100: Pt which may related to increase the hydrophilic behavior with Pt more than in excite SWCNTs. the broad band around 3400 cm^{-1} was due to O–H stretching bond mode of the free water, which increase after impregnation with SWCNTs and Pt due to the hydrophilicity for impregnated materials. The vibration of C=C stretching bond for the aromatic ring at about 1600 cm^{-1} refers to sp2 hybridization in SWCNTs was not clear which may had related to the bit ratios and homogenous distribution thus did not appears. The absorbance which refers to Pt bond and that may had formed with Ti or with C (in SWCNTs) also did not shown because it accrued in figure print region between 730-470 cm^{-1}.

the absorption spectra were plotted in Fig. 3, which witness shift in absorbance from 384 eV near ultraviolet with pristine UV100 to visible part at 409 eV, 445 eV and 474 eV for SWCNT/UV100, UV100: Pt and MWCNT/UV100: Pt respectively. The absorption of light witness large shift after impregnated with Pt and that was increased in excite of SWCNTs with Pt. The large shift in ternary composite can be related to co-enhancements between Pt nanoparticles and SWCNTs which forming together bridge of electrons dispersed with TiO_2-UV100 causing new active sites with high activities to absorb the light which shifted

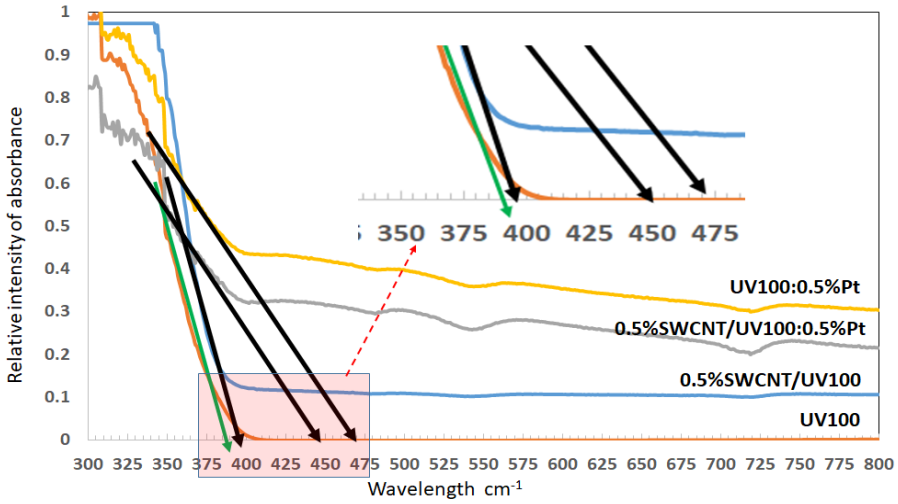

Fig. 3. UV–vis absorption spectra for pristine UV100 and modified in ternary and binary composites 0. 5%SWCNT/UV100 , UV100:0.5%Pt and 0.5%SWCNT/UV100:0.5%Pt

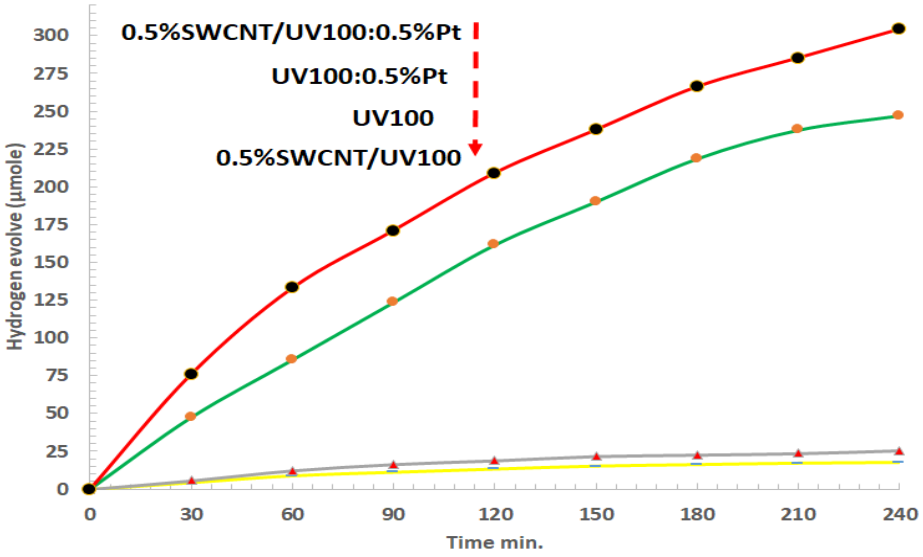

Fig. 4. Time dependency of H_2 gas concentrations as a function of illumination time on 80 mg of pristine UV100, 0.25%MWCNT/UV100 and 0.5%MWCNT/UV100 from 10% methanol aqueous solution under light intensity 40 mW cm^{-2} of UV illumination at 298K.

mostly to visible part [11-18]. The two composites with Pt in ternary and binary matrix showed two absorbance region in the visible part at 550 e V and 725 e V which means the active absorbance at visible part of light.

The photocatalytic activates for UV100 before and after modifying were tested in hydrogen production reaction by using MeOH/solution as mentions in experimental section, and the results were reported in Fig. 4. The best catalyst produce hydrogen was ternary composites SWCNT/ UV100:Pt with rate constant 1.89 µmole/min then binary composites UV100/Pt with rate constant 1.37 µmole/min. Fig. 5, shown the last two

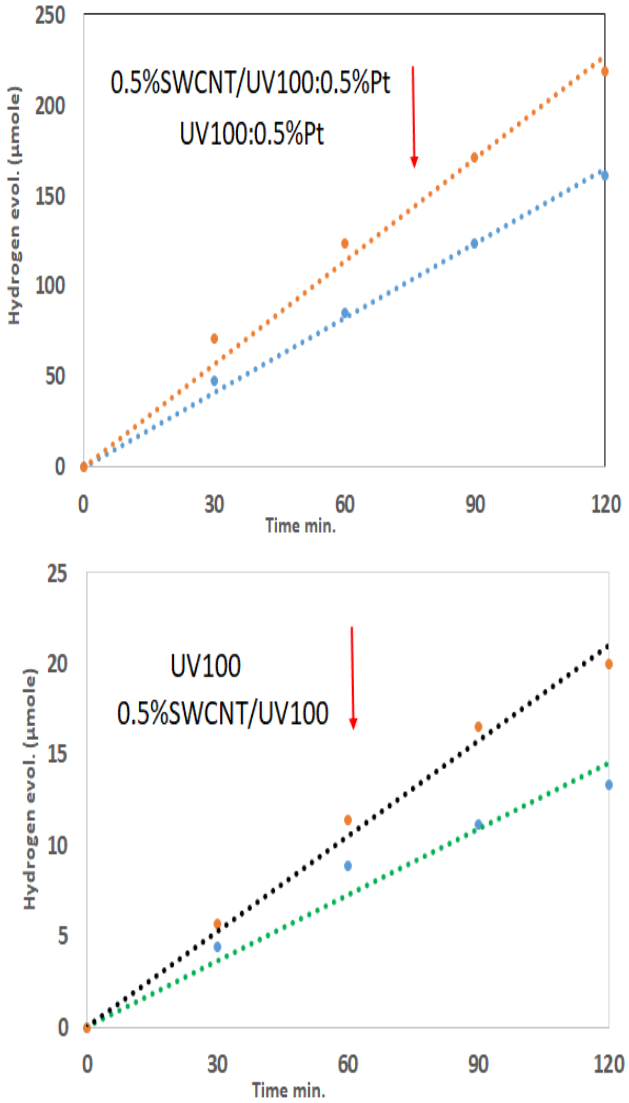

Fig. 5. Rate constant of evolve H_2 gas for the photocatalytic reaction on the right pristine UV100 and 0.5%SWCNT/UV100, on the left 0.5%SWCNT/UV100:0.5%Pt and UV100:0.5%Pt.

composites were more active as compare with pristine UV100 which active with 0.17 µmole/min and the binary composites SWCNT/UV100 when reduce the activities of pristine UV100 to the activities 0.12 µmole/min.

The results show that SWCNTs succeed to enhance the activists of UV100 in ternary composites with Pt species while alone was failed to increase the activities and that can be related to act the SWCNTs as retardation agent when prevent UV-light to penetration to the solution and reach to UV100 surface.

The role of SWCNTs was invers in ternary composites with Pt when shows increase in activates reach to about 20% as compare with UV100: Pt and that can be related to related to many causes such : SWCNTs characterized by high specific surface area with many function carboxylic group can interaction with TiO_2 and Pt. Second, CNTs as large surface area can accept high ratios of Pt species without making large agglomerations a rata least reduces the agglomeration. The two

reasons able to create many active cites to easy transfer the charges on surface and that prevent the re-combination h^+/e^-.The mechanism of activities for UV100 after modification which is not consumed during the entire process can explain by highlight on the principles of Photo catalysis which is consisting of light absorption to produce charge carriers up to surface catalytic. After absorption of light by the photocatalyst, the double active charges (h^+ VB /e^- CB) should provide some reason to prevent recombination and that absolutely increase the activity. thus if change the condition of absorbance of light from UV- part to visible that absolutely make the recombination effect removed or reduce in very large ratios .

When presence of SWCNTs in ternary composites SWCNT/UV100/Pt extend the photo-response of TiO_2 and narrow its bandgap energy while Pt in addition to increase the conductivity it makes as reflection part to re absorb from the matrix. Thus the hybrid between Pt and SWCNTs within UV100-TiO_2 make the best enhance for the larger value of hydrogen production [19, 20].

CONCLUSION

In this study, UV100- TiO_2 successfully impregnated with Pt and SWCNTs with the same ratios in binary composites 0.5%SWCNT/UV100, UV100:0.5%Pt and ternary composites SWCNT/UV100:Pt and determined the activity in photocatalytic by reaction of hydrogen production with irradiation under UV light. According to analysis by XRD, FTIR and uv-visble spectroscopy the UV100- TiO_2 particle was increase in size after modifying with increase the agglomerations but that did not prevent the modifying martials to show increase in activities. Create huge amount of active site with homogenous dispersion for Pt and SWCNTs were the critical parameters which enhance the hybridization for the mixture and that responsible for the new activity. The external results when reduce the activities for SWCNT/UV100 was related to homogenous dispersion of SWCNTs with very light density make the dispersion of it caver the most surface which responsible on prevent the penetration of UV-Light .

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Liqaa H.Abd RA, Aseel M.Aljeboree, Firas H.Abdulrazzak, Falah H. Hussein and Ayad F. Alkaim. Role of Semiconductors (Zinc Oxide as a Model) for Removal of Pharmaceutical Tetracycline (TCs) from Aqueous Solutions in the Presence of Selective Light. International Journal of Recent Technology and Engineering (IJRTE). 2019;8(2S3):DOI : 10.35940/ijrte.B31270.30782S35319.
2. Falah H. Hussein AMA, Zeyad O. Musa, Firas H. Abdulrazzak, Mohammed Bassim Alqaragoly and Ayad F. Alkaim. Is it Photocatalytic Degradation of Textile Dyes a Friendly Method? Methyl Violet Dye as a Model for Application in Aqueous Solutions in the Presence of Commercial TiO_2. International Journal of Recent Technology and Engineering (IJRTE). 2019;8(2S3).
3. Aseel M. Aljeboree AFA, Ali loay ,hanadi m algburi. Photocatalytic Degradation of Textile Dye Cristal Violet Wastewater using Zinc Oxide as a Model of Pharmaceutical Threat Reductions. Journal of Global Pharma Technology. 2019;11(3):138-143.
4. Abdulrazzak FH. Enhance photocatalytic Activity of TiO_2 by Carbon Nanotubes. International Journal of ChemTech Research. 2016;9(3):431-443
5. Aseel M. Aljeobree ATB, Ayad F. Alkaim,Falah H. Hussein. ZNO Nanoparticles as a Model for Removal of Pharmaceutical Compounds (Vitamin B12)in the Presence of UVA Light. International Journal of Recent Technology and Engineering (IJRTE). 2019;8(2S3):DOI : 10.35940/ijrte.B31261.30782S35319.
6. Ali M.Jassm BAJ, Firas H. Abdulrazzak, Ayad F. Alkaim and Falah H. Hussein. Synthesis and Characterization of Carbon Nanotubes by Modified Flame Fragments Deposition Method. Asian J Chem. 2017;29(12):2804-2808.
7. Aseel M Aljeboree HYA-G, Mohammed H Said, Ayad F Alkaim. The effect of different parameters on the removal of vitamin B12 drug (as a model biochemical pollutants) by AC/clay. Biochem Cell Arch. 2019;19(1):755-759.
8. Buser H.R. PT, Muller M.D. Occurrence and fate of the pharmaceutical drug diclofenac in surface waters: rapid photodegradation in a lake. Environ Sci Technol 1998;32 (22):3449.
9. Merry Sianipar SHK, Khoiruddin, Ferry Iskandar ad and Gede Wenten. Functionalized carbon nanotube (CNT) membrane: progress and challenges RSC Adv. 2017;1:51175-51198. .
10. L. Huang QC, X. Wu , H. Wang and Y. Liu, . The simultaneous photocatalytic degradation of phenol and reduction of Cr(VI) by TiO_2/CNTs . J Ind Eng Chem. 2012;1:18 574-580.
11. M.J. Gómez CS, M. Mezcua, A.R. Fernández-Alba, A. Agüera. Photodegradation study of three dipyrone metabolites in various water systems: identification and toxicity of their photodegradation products. Water Res. 2008; 42 2698-2706.
12. Safa A. Yassin AHAk, and Firas H. Abdulrazzak,. Enhance the Growth of Multi- walled Carbon Nanotubes from Coal by Catalytic Chemical Flame Deposition . IOP Conf Series: Materials Science and Engineering 2019;571.
13. Zhang Y X, Yongjun Z,Yang L. Comparison of amoxicillin photodegradation in the UV/H_2O_2 and UV/persulfate systems: Reaction kinetics, degradation pathways, and antibacterial activity. Chem Eng J. 2019;372:420-428.
14. Andreozzi RR, Nicklas,P. Pharmaceuticals in STP effluents

and their solar photodegradation in aquatic environment. . Chemosphere 2003.;50 1319-1330.
15. Trovó AG, Nogueira, R.F.P.,Agüera, A., Sirtori, C.,Fernández-Alba, A.R. Photodegradation of sulfamethoxazole in various aqueous media: persistence, toxicity and photoproducts assessment. Chemosphere. 2009;77:1292-1298.
16. Luo S. ZnO nanorod arrays assembled on activated carbon fibers for photocatalytic degradation: Characteristics and synergistic effects. Chemosphere. 2020;261:127731.
17. Ayad F. Alkaim AMA. Adsorption and Photocatalytic Degradation of Pharmaceutical Amoxicillin using TiO_2 Nanoparticles in Aqueous Solutions: Oxidative Coupling as Spectrophotometric Method International Journal of Advanced Science and Technology 2020;29(5):5480 - 5487
18. Ahmed H, R,Raheem, S,J, Aziz, B, K,. Removal of Leishman stain from aqueous solutions using natural clay of Qulapalk area of Kurdistan region of Iraq. Karbala International Journal of Modern Science. 2017;3(3):165-175.
19. Fabrao RM, Brito, J. F. Silva, J. L.,Stradiotto, N. R.,Zanoni, M. V. B. Appraisal of photoelectrocatalytic oxidation of glucose and production of high value chemicals on nanotube Ti/TiO_2 electrode. Electrochimica Acta. 2019;222:123-132.
20. Ye Y, Y. Feng, H., Bruning, D. Yntema, H.H., Rijnaarts, M Photocatalytic degradation of metoprolol by TiO_2 nanotube arrays and UV-LED: Effects of catalyst properties, operational parameters, commonly present water constituents, and photo-induced reactive species. . Applied Catalysis B: Environmental. 2018;220:171-181.