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Photo-Degradation of Methamidophos (An Insecticide) in Water Using Dye-Modified Nano-Crystalline TiO_2 Supported onto Activated Carbon Surfaces

التحلل الضوئي للميثاميدوفوس (مبيد حشري) في الماء باستخدام اكسيد التيتانيوم النانوي البلوري المعدل بالصبغ المدعوم على أسطح الكربون المنشط

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Abstract: Anatase TiO2 surfaces have been treated with 2, 4, 6-triphenylpyrylium hydrogen sulfate (TPPHS) or tripyridylporhpyrinatomanganese(II) (MnP) dyes to yield the modified TiO2/ dye surfaces. The modified TiO2/dye surface was then supported onto activated carbon (AC) surfaces to yield a new class of catalytic system AC/TiO2/dye. The catalytic activities of naked TiO2, dye solution, TiO2/dye, and AC/TiO2/dye systems were examined in photo-degradation of Methamidophos (insecticide) in water, using both UV and visible light. All examined systems showed catalytic activity when used either in the UV or the visible regions, but the AC/TiO2/ dye showed the highest activity. The dye role, in enhancing activity of modified surfaces in UV degradation of the examined contaminants, is understandable by a charge-transfer catalytic effect. AC role can be explained by its ability to adsorb contaminant molecules and bringing them closer to catalytic sites. There was no significant temperature effect on catalyst efficiency in Methamidophos photo-degradation. Oxygen is essential for semiconductor photocatalytic degradation of Methamidophos, but higher oxygen concentrations lead to a downturn of the reaction rate.

Keywords: Photo-Degradation, Methamidophos, Nano-Crystalline, Activated Carbon Surfaces.

المستخلص: تمت معالجة أسطح Anatase TiO2 باستخدام الصبغة 2 ، 4 ، 6- triphenylpyrylium hydrogen sulfate (TPPHS) أو الصبغة tripyridylporhpyrinatomanganese (II) (MnP) للحصول على أسطح TiO2 / الصبغ المعدلة. تم بعد ذلك دعم سطح TiO2 / الصبغ المعدل على أسطح الكربون المنشط (AC) لإنتاج فئة جديدة من النظام التحفيزي (AC / TiO2 / صبغة). ثم تم فحص الأنشطة التحفيزية لثاني أكسيد التيتانيوم العاري ، محلول الصبغة ، TiO2 / صبغة ، وأنظمة AC / TiO2 / صبغ في التحلل الضوئي للميثاميدوفوس (مبيد حشري) في الماء ، باستخدام كل من: الأشعة فوق البنفسجية والضوء المرئي. أظهرت جميع الأنظمة التي تم فحصها نشاطًا تحفيزيًا عند استخدامها إما في الأشعة فوق البنفسجية أو المناطق المرئية ، ولكن أظهر (AC / TiO2 / صبغة) أعلى نشاط. يمكن فهم دور الصبغة ، في تعزيز نشاط الأسطح المعدلة في تحلل الملوثات التي تم فحصها بالأشعة فوق البنفسجية ، من خلال التأثير التحفيزي لنقل الشحنة. يمكن تفسير دور التيار المتردد من خلال قدرته على امتصاص جزيئات الملوثات وتقريبها من المواقع التحفيزية. لم يكن هناك تأثير معنوي لدرجة الحرارة على كفاءة المحفز في التحلل الضوئي للميثاميدوفوس. الأكسجين

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ضروري للتحلل التحفيزي للميثاميدوفوس بأشباه الموصلات ، لكن تركيزات الأكسجين الأعلى تؤدي إلى تراجع معدل التفاعل.

الكلمات المفتاحية: التحلل الضوئي، الميثاميدوفوس (مبيد حشري)، اكسيد التيتانيوم النانو بلوري، أسطح الكربون المنشط.

INTRODUCTION:

Semiconductor electrochemistry is a relatively new but mature branch of electrochemistry (Vione D. et al., 2005; Tiwari D. et al., 2008). Surface area of single crystal is increasing by subdividing it and making it more porous, as we reach the limiting case "the Ångström region" where further subdivision is not possible without breaking up the structure totally into small molecules and atoms; this is called nano-crystalline. TiO_2 is an example of nano-crystalline. It is the first nanoparticle semiconductor to be recognized, the key point which distinguishes TiO_2 from other semiconductors is the stability and ease of manufacturing polycrystalline electrodes. TiO_2 has three naturally occurring crystal phases: rutile, anatase and brookhite. A slightly distorted TiO_2 has an octahedral shape **Figure (1)**. The bond lengths for rutile and anatase are similar, but the anatase octahedral exhibit greater distortion in bond angles. Consequently, anatase has a somewhat more open structure with a higher molar volume and a lower density.

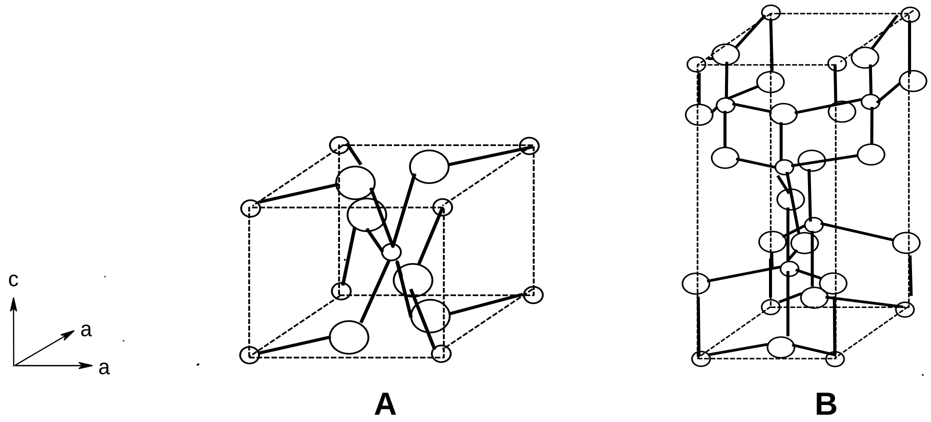
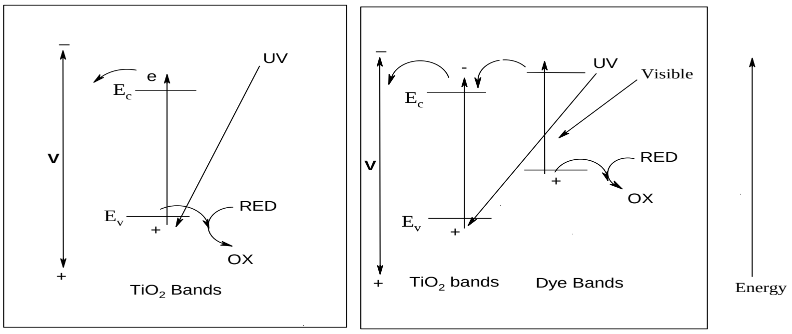


Figure (1): TiO_2 crystal structures. A: The unit cell for rutile, B: The unit cell for anatase. The small circles are the Ti cations and the large circles are the O anions.

Small cations and anions can migrate relatively rapidly through channels in the two lattices, a process that affects the uniformity of doping and the density of recombination centers .

Recently, devices combining to some extent properties of conventional TiO_2 films and those of powder or colloidal photocatalysts are attracting major interest. The highly porous nanocrystalline films which are consisting of a fine powder or colloid deposited on a conducting substrate have wide band gap (3.2 eV) sets. Only 3% of natural sunlight can be absorbed by TiO_2 (Karaire C. et al., 2004; Nazeerudin Md. et al., 2004; Granados G. Et al., 2005; Chatterjee D. et al, 2006) due to low ceiling. UV excitation is required in order that the photochemical processes may proceed conveniently. Electrical properties of TiO_2 necessarily refer to doped materials due to high resistivity of undoped TiO_2. TiO_2 has greatly been used for the purpose of water purification processes; it has been used widely as a naked semiconductor **(Fig.2 A)** in the photodegradation of organic and inorganic contaminants. TiO_2 surface can modified by using low bap dyes, such as 2,4,6-triphenylpyrylium hydrogen sulfate (TPPHS) **(Fig. 2B)** which has also been used in the degradation of organic and inorganic contaminants, there are many examples of modified TiO_2 surfaces (Villareal T. et al., 2004; Iesce M. et al., 2003; Magalhães F and Lago RM, 2009) and supported onto insoluble materials such as activated carbon (AC) (Ao C. and Lee S., 2004; Crap O. et al, 2004; Andriantsiferanaa C. et al., 2013).



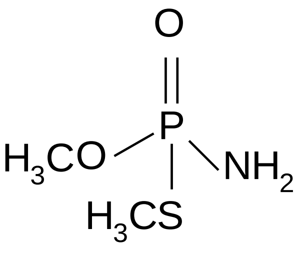
Naked TiO_2 catalysis

Dye-sensitized TiO_2 catalysis

Figure (2) A: TiO2 as a naked semiconductor B: TiO2 surface can modified by using low bap dyes, such as 2,4,6-triphenylpyrylium hydrogen sulfate (TPPHS)

Methamidophos (Scheme I) is a widely used insecticide, with trade names of Monitor, Tamaron, Filitox, Tamanox, Tarn, Patrole, Metamidofos Estrella; Methamidophos 60 WSC: Methedrin 60; Morithion; Red Star AlloranB (IPCS, 1993) .

The CAS and IUPAC name is O, S-dimethyl phosphoramidothioat. It was first prepared by W. Lorenz for Bayer in 1965 and called Methamidophos, and by P. Magee for Chevron in 1967 and called Monitor (The Merck Index, 2000). Pure methamidophos is a colorless crystalline solid with a melting point of 44.5 °C. Technical methamidophos, which is about 73% pure, is in the form of yellowish to colorless crystals. Methamidophos, which is readily soluble in water (>2 kg/liter), alcohols, ketones, and aliphatic chlorinated hydrocarbons, is sparingly soluble in ether and practically insoluble in petroleum ether. This insecticide is stable at ambient temperatures. Methamidophos decomposes before its boiling point is reached (at approximately 150°C) (Fest C. and Schmidt K.-J., 1973).



(Scheme I): Methamidophos

Methamidophos is effective against a broad range of insect pests (sucking, biting, and mining insects) on such crops as brassica, cotton, tobacco, sugar beet, head lettuce, and potatoes. Methamidophos is hazardous for humans when incorrectly handled. On overexposure, typical signs and symptoms organophosphorus poisoning may occur rapidly. It is readily absorbed via skin, ingestion, and inhalation; may cause organophosphate poisoning: weakness, headache, vomiting, excessive sweating and salivation, pinpoint pupils; in severe cases: convulsions, unconsciousness, and death due to respiratory paralysis (Burruel V., et al., 2000). The final degradation of methamidophos product is usually phosphoric acid. Same product has been observed when methamidophos is applied to crops (Sanjuán A., et al., 2000). Photo-electrochemical degradation using naked and/or sensitized TiO2 was used to degrade such insecticides (Geit G., and Braun A., 1997; Baolin Xing, et al., 2016).

In this work the catalytic activities of naked TiO2, TPPHS solution, TiO2/TPPHS, was compared to catalytic activity of AC/TiO2/ TPPHS system in photo-degradation of Methamidophos in water, using both UV and visible regions, besides that the catalytic activity of TiO2/MnP system was also tested for Methamidophos degradation .

EXPERIMENTAL:

Chemicals:

Methamidophos (600) was purchased from Bayer, dimethyl sulfoxide (DMSO) (679) was obtained from Carlo, in pure forms, anatase TiO2 (13463-67-7), 2,4,6-triphenylpyrylium hydrogen sulfate, H2TPyP, activated carbon (AC), manganese (II)-sulfate, and KBr were purchased from Aldrich. Organic solvents (methanol, DMF, and chloroform) were obtained from Reidel- DeHaën in a pure form.

Equipment:

The Methamidophos concentrations were calculated by measuring its electronic absorption spectra on a Shimadzu UV-1601 spectrophotometer and GCMS-QP 5000.The GC was equipped with an auto-injector (AOC-17), a Class 5000 software and a 30 m J&W SCIENTIFIC long and 0.25 mm I.D. capillary column DB-SMS (5% -phenyl) Methylopolysiloxane 0.25 μm thick film. The injector was set up at 250oC, GC-MS interface at 280oC, helium carrier gas at a flow rate of 0.8 mL/min at 25oC. The sample (2 μm) was injected in the splitless injection mode. The oven temperature was programmed starting at 100oC for 1 min, raised to 320oC (5oC/min), and held at 320oC for 10 min. Methamidophos was first extracted with organic solvents, and then the organic phase was injected for GC-MS analysis. FT-IR spectra were collected for TiO2, TiO2/TPPHS, AC/ TiO2/TPPHS as KBr pellets, on Shimadzu FTIR-8201PC. Illumination in the UV- range was carried out using a 500W Hg/Xe lamp (Oriel instruments, Universal Arc Lamp Housing, Model 66901) equipped with a fiber bundle inserted inside the reactor through a tube, the lamp was operated at 150W power, Model Oriel-66142.

Procedures:

Photo-degradation experiments:

To analyze for reaction products, the reaction mixture was taken after completion. The water was evaporated using a rotary evaporator. DMSO was used for extraction. The DMSO layer was then analyzed by GC-MS.

Concentration Measurements:

The reaction progress was followed by measuring remaining Methamidophos concentrations with electronic absorption spectrophotometry. A calibration curve was constructed for Methamidophos using the standard solutions in the range of (1×10-4 - 1×10-2) M throughout reaction course. The absorption spectra of standards and samples were measured on a Shimadzu UV-1601 spectrophotometer at wavelength 284nm.

RESULTS AND DISCUSSION :

Methamidophos degradation using AC/TiO2/TPPHS:

Control photolysis experiments were conducted without a TiO2/TPPHS catalyst in presence of light Figure (3) a, and with a TiO2/TPPHS without a light source. In these experiments, Methamidophos concentrations didn't significantly change after relatively prolonged times of two hours. TiO_2 and TPPHS were not catalytically active when used separately in Methamidophos photo-degradation.

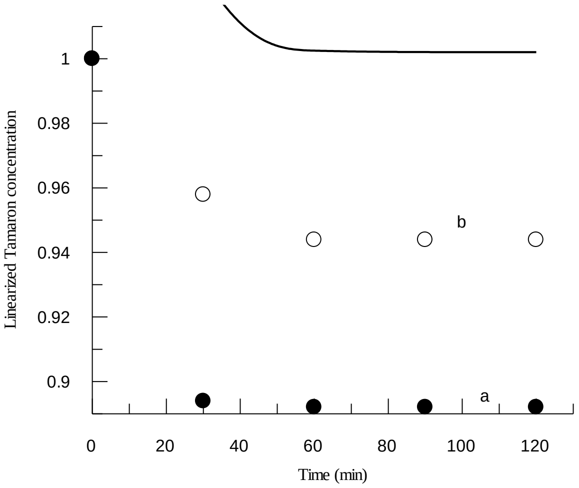


Figure (3): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments. (a) Using visible light but without TiO2/TPPHS, (b) TiO2/TPPHS without light.

Then in another experiment where TiO_2 and TPPHS were used separately to degrade Methamidophos with visible light, only little loss in Methamidophos concentrations occurred, **Figure (4).**

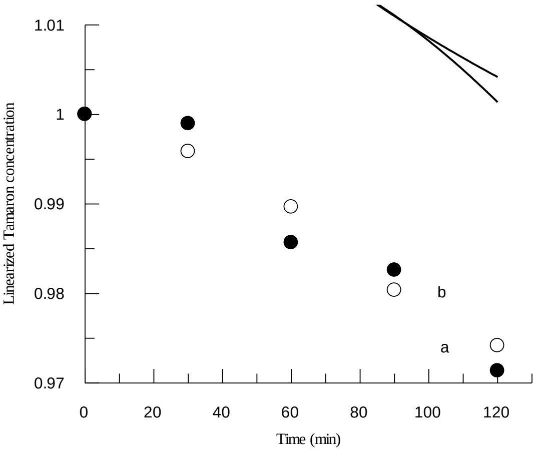


Figure (4): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments, using visible light. (a) Naked dye (b) Naked TiO_2. Experiments were conducted in the visible region at room temperature.

When TPPHS sensitized TiO_2 catalyst was used for Methamidophos degradation with visible light, there was a noticeable change in Methamidophos concentration in an open reactor using both visible light and UV light regions **Figure (5)**. The sensitizing activity of TPPHS is due to the excitation of the dye by the visible light (λmax ~435 nm, with ~2.8 eV), leading to formation of an electron (in the dye conduction band) and a hole (in the dye valence band). The electron, travels from the dye to the TiO_2 conduction band where it reduces oxygen molecules. The holes oxidize Methamidophos molecules, by traveling from the dye valence band. The sensitization process works in Methamidophos by the fact that Methamidophos is easy to oxidize as it has mild.

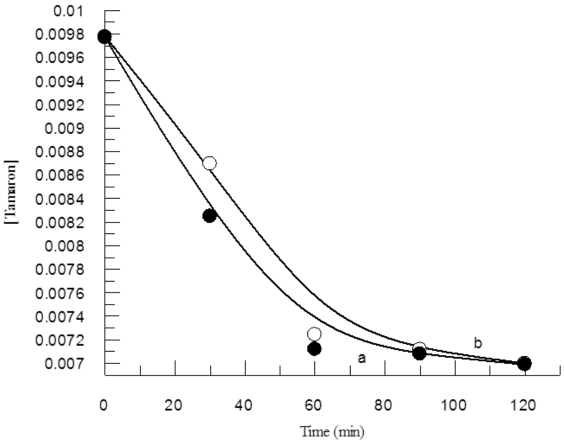


Figure (5): Plots of remaining Methamidophos concentration (M) vs. time using TiO_2 (0.5g), dye (0.005g, 1.23×10-5 mol) (a) UV region (b) visible region.

Different concentrations of TPPHS dye were examined for their activity of photodegradation of Methamidophos using a fixed amount of TiO2. In all cases the sensitized catalyst showed sound catalytic activity, reaching up to 33% completion in 120 min. Nominal dye concentrations did not affect the rate significantly **Figure (6).**

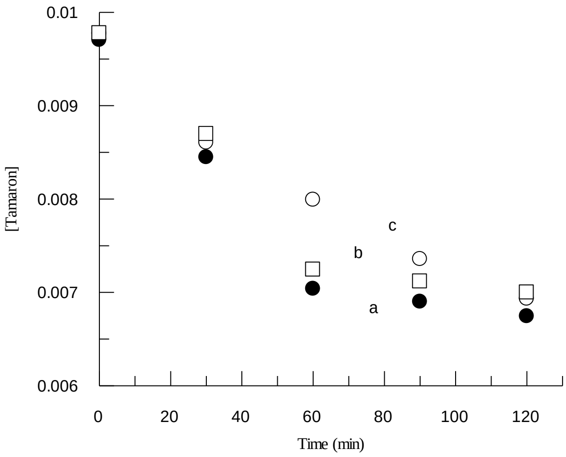


Figure (6): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments with fixed amount of TiO_2 (0.5g) (a), dye (0.005g, 1.23×10^{-5} mol), (b) dye

(0.003g, 0.738×10^{-5} mol), (c) dye (0.01g, 2.46×10^{-5} mol). All experiments were conducted using visible light, at room temperature

Among the reported processes for the treatment of the dye-containing wastewater, it has been shown that all kinds of TiO_2/AC composites are able to exhibit enhanced photocatalytic performance and increased removal efficiency compared to pure TiO_2 (Baolin Xing, et al., 2016). TiO_2/TPPHS supported onto AC surfaces was utilized in photodegradation of Methamidophos in the visible region comparing with TiO_2/TPPHS alone. All Methamidophos disappeared, within 2hr, when AC supported TiO_2/TPPHS catalyst was used under visible light **Figure (7).** It is assumed that AC does not affect TiO_2/TPPHS optical or electrical properties, but enhances its catalytic activity. AC adsorbs contaminant molecules, and brings them into close proximity to the TiO_2/TPPHS catalytic sites.

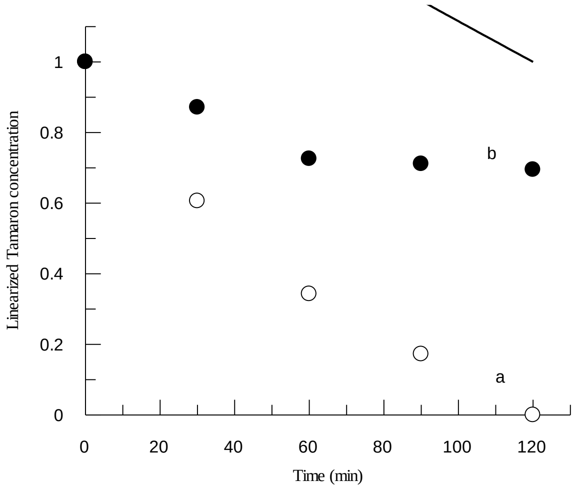


Figure (7): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments using TiO_2 (0.5g), dye (0.006g, 1.476×10^{-5} mol) (a) with AC (0.1g), (b) without AC. All experiments were conducted using visible light, at room temperature.

Changing the concentrations of TPPHS dye in AC supported TiO2/TPPHS catalyst has no influence in the photodegradation process of Methamidophos **Figure (8).**

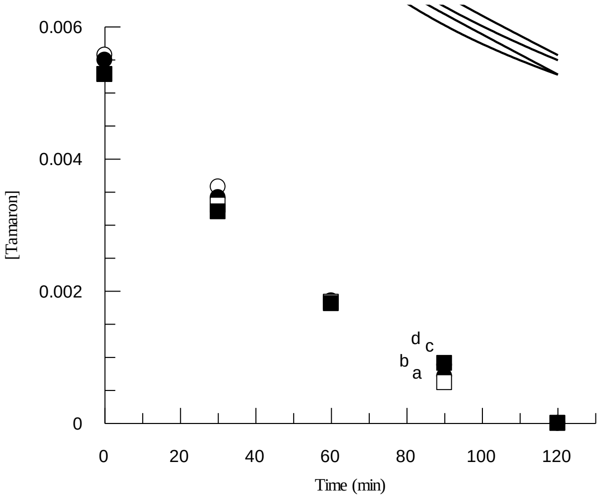


Figure (8): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments. TiO_2 (0.5g) AC (0.1g) (a) dye (0.006g, 1.476×10^{-5} mol), (b) dye (0.01g,

2.46×10^{-5} mol), (c) dye (0.012g, 20952×10^{-5} mol), (d) dye (0.003g, 0.738×10^{-5} mol). All experiments were conducted using visible light, at room temperature.

The effect of oxygen exposure, on Methamidophos degradation was also studied in the presence of visible light. Experiments were conducted using reactors that are open to air, closed to air or bubbled with air. **Figure (9)** shows that the reaction system, which was kept open to oxygen with no bubbling, was the fastest system. The reaction was hindered by air bubbling, compared to closed systems. This indicates that oxygen is needed by the reaction but may also inhibit it when used at higher concentrations. Therefore, unless otherwise stated, all degradation experiments were conducted in an open reactor with no air bubbling.

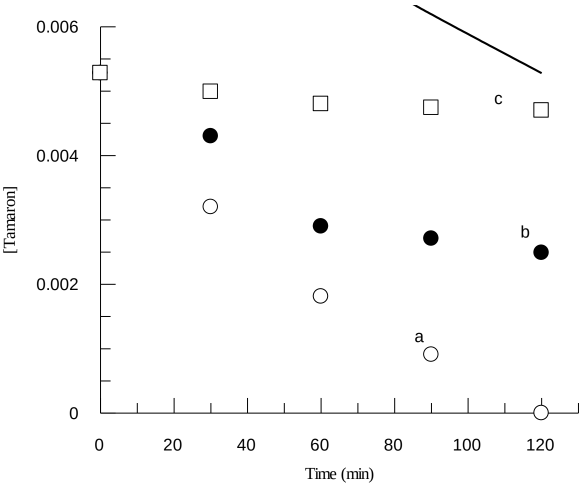


Figure (9): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments. TiO_2 (0.5g), dye (0.003g, 0.738×10^{-5} mol) AC (0.1g) (a) open reactor (b) closed reactor (c) bubbles of air. Experiments were conducted in the visible region at room temperature.

Oxygen was essential for semiconductor photocatalytic degradation of Methamidophos. Oxygen bubbling leads to a downturn of the reaction rate **Figure (9).** This behavior is consistent with reported results (Geit G. and Braun A., 1997).

Methamidophos degradation was studied using AC/TiO_2/TPPHS at different temperatures in the visible region. The rate of degradation was independent of temperature, and Methamidophos disappeared in all experiments after almost the same reaction time **Figure (10).**

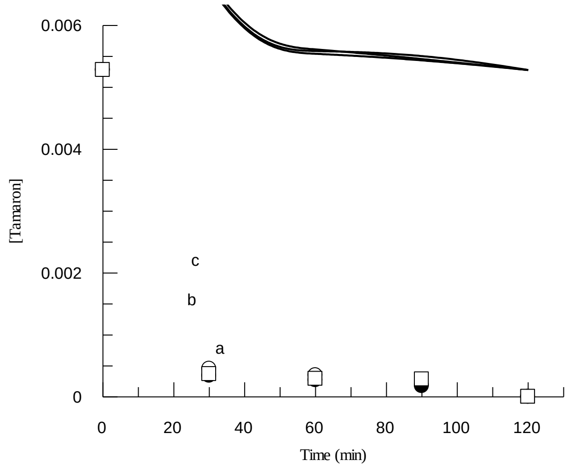


Figure (10): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments TiO_2 (0.5g), dye (0.006g, 1.476×10^{-5} mol), AC (0.1g) (a) 20°C (b) 30°C (c) 40°C. All experiments were conducted using visible light.

Methamidophos degradation using AC/TiO2/MnP:

TiO2 modification with tripyridylporhpyrinato manganese (II) enhanced its catalytic activity in Methamidophos degradation in both UV and visible regions. TiO_2 saturated with MnP were prepared, isolated and rinsed before use in an open reactor. **Figure (11)** shows that 20% Methamidophos degradation occurred in the visible region within 120 min using TiO_2/MnP compared to only 5% degradation using naked TiO_2.

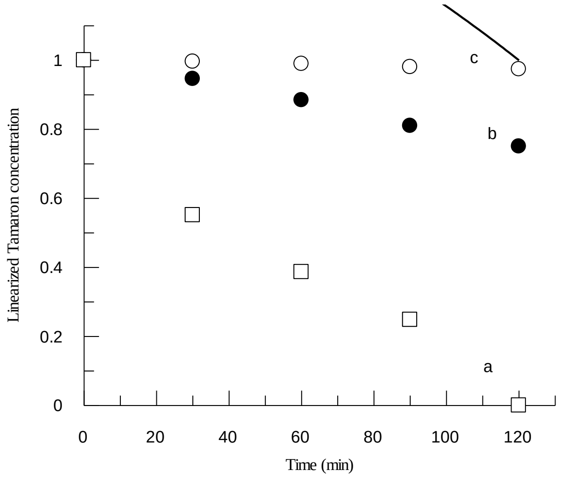


Figure (11): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments, (a) TiO_2 (2.0g), MnP (0.06 ml), AC (0.1g), (b) TiO_2 (2.0g), MnP (0.06 ml) (c) TiO_2 (2.0g). All experiments were conducted using visible light and at room temperature.

When TiO_2/MnP was supported onto AC, its activity was significantly enhanced. The AC/TiO2/MnP caused complete Methamidophos degradation in the visible region within 120 min. **Figure (11).**

The TiO_2/MnP system showed comparable catalytic activities, for Methamidophos degradation, in UV and visible, as shown in **Figure (12).** The Ac/TiO_2/MnP also showed comparable activities when used in the UV and visible regions **Figure (13)**, in either case, the AC supported system showed higher catalytic activity than the unsupported one.

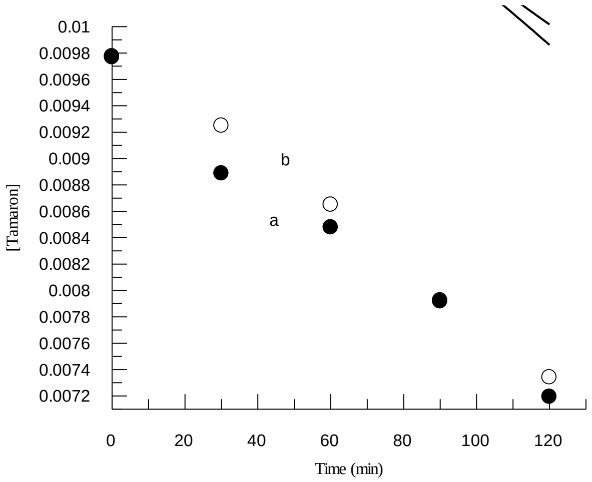


Figure (12): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments at room temperature using TiO_2 (2.0g), MnP (0.06 ml) (a) UV-light (b) visible light.

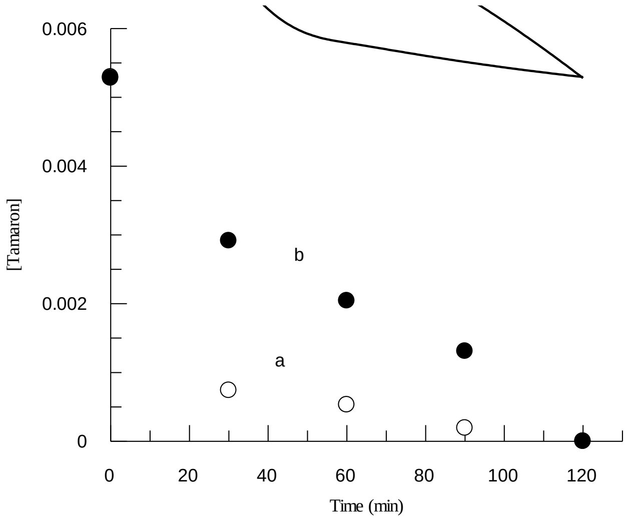


Figure (13): Plots of remaining Methamidophos concentration (M) vs. time for Methamidophos degradation experiments at room temperature using visible light and, TiO_2 (2.0g), MnP (0.06 ml), (a) supported on AC (0.1g) (b) not supported.

The TiO_2/MnP system was prepared and used to photo-degrade Tamaron. It was active in both UV and visible regions, as shown in Figure (5.12-5.13). TiO_2/MnP system was supported on AC and used to degrade Tamaron. The AC/TiO2/MnP system showed higher catalytic activity than the TiO_2/MnP, Figure (5.11). Discussion on effect of AC support on catalytic activity of TiO_2/TPPHS was presented earlier in Chapter (3), and need not be repeated here.

The efficiency of MnP to sensitize TiO2 for Tamaron degradation is understandable by the fact that it has band gap (2.68 eV, 463 nm) which is sufficient for Tamaron oxidation .

The efficiency of MnP to sensitize TiO2 for Methamidophos degradation is understandable by the fact that it has band gap (2.68 eV, 463 nm) which is sufficient for Methamidophos oxidation. **Table (1)** shows turnover number values of MnP in degrading Methamidophos.

Table (1): Values of turnover number for different catalytic systems in Tamaron degradation

Catalyst	TiO_2 amount g	TPPHS amount (mol)	Turnover number*
Naked TiO_2	0.5	0	16.9**
Dye only	0	0.006g (1.476×10^{-5})	19.0
TiO_2/TPPHS	0.5	0.01g ($2.46\times10\text{-}^{5}$)	384.3
	0.5	0.005g ($1.23\times10\text{-}^{5}$)	401.1
	0.5	0.003g (0.738×10^{-5})	376.7
AC/TiO_2/TPPHS	0.5	0.006g (1.476×10^{-5})	720.8
	0.5	0.012g (2.952×10^{-5})	718.4
	0.5	0.01g (2.46×10^{-5})	745.3
	0.5	0.003g (0.738×10^{-5})	714.7
TiO_2/MnP	2.0	0.06ml (2.4×10^{-5})	203.3
AC/TiO_2/MnP	2.0	0.06ml (2.4×10^{-5})	440

*Turnover number values, (reacted Tamaron moles/dye moles) were measured after 120 min reaction time

** Turnover number value was calculated assuming presence of TPPHS (0.006 g, $1.476X10^{-5}$).

CONCLUSION:

TiO_2 and TPPHS were not catalytically active separately in Methamidophos photo-degradation. The combined TiO_2/TPPHS system was active in the UV and visible regions. AC/TiO_2/TPPHS system showed higher catalytic activity than the TiO_2/TPPHS in Methamidophos degradation in UV and visible regions. This is attributed to the ability of AC to adsorb Methamidophos. There was no significant temperature

effect on catalyst efficiency in Methamidophos photo-degradation. Oxygen is essential for semiconductor photocatalytic degradation of Methamidophos, but higher oxygen concentrations lead to a downturn of the reaction rate. TiO_2/MnP system was catalytically active for Methamidophos degradation in both UV and visible regions. AC/TiO_2/MnP system showed higher catalytic activity than the unsupported TiO_2/MnP.

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