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Preparation and Studing of Photodegradation of Some MonoAzo in Presence and Absence of Titanium Dioxide (Anatase)

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Abstract

The work consists of two parts.The first deals with preparation of some mono azo dyes.There are:4-(2-adenine azo)-phenol(AAP),4-(2-adenine azo)-salicylic acid (AASA),4-(2-benzoic acid azo)-catechol(BAAC),and 4-(1,2-naphthol-4-sulphonic acid azo)-catechol(NSAAC).The prepared compounds have been identified by FT-IR spectroscopy.UV-visible absorption and fluorescence spectra also recorded.some of physical and chemical properties have been listed.

The second part consist of photodegradation of the azo compounds mentioned above at lab temp. in presence and absence of titanium dioxide(anatase)suspension by exposure of aquepus solution of dyes using light of middle pressure mercury lamp and quartz cell with continuous stirring of solution or suspension for 90 min.

Generally,it has been found that the rates of photodegradation of four dyes were higher in presence of TiO_2suspention.The work involved the studing of interaction between dyes and surface of $TiO_2$by x-rays diffraction spectra(XRD).

Introduction

Azo dyes occupied a considerable attention over a period of many years in many of studies(1-4). Those compounds are charactarized by the virtue of formation in a greate variance of chemical structure and colours, and acceptable solubility into low cost solvents.

The behaviur of some azo dyes toward the light has been studied in absence of titanium dioxide suspension(5-7), and in presence of it(8,9).Titanium dioxide have an important use in heterogeneouse catalysis as a result of its stability toward heat and photocorrosion. The mechanism of photocatalytic initiate by exciting of TiO_2

particles using light with energy equal or greater than its band gap energy which lead to generation of conducion band electrons(e-)and valence band holes(h^+). The e^- and h^+ can be used to drive many of desirable redox reactions on TiO_2surface. The generation of e^- and h^+ competite with back reaction between both. So, the increasing of activity of TiO_2 and other semiconductors is needs to sufficient separation between e^- and h^+which can be supported by existing of reactions on TiO_2 surface.in this state the photohelse h^+ enhance the photooxidation of adsorbed molecules on the surface and electrones(e)$^-$are used to performe the reduction reactions.

The rates of photooxidation depend on important factors such:quantity of TiO_2,concentration of adsobatese and temperature(10-12). X-rays diffraction technique was used to study the intraction of adsorbed molecules on TiO_2 surface(8,13,14).the main factors which limited the adsorption of molecules on the surface are chemical-nature of surface layer of semiconductor and chemical structure of adsorbate and temperature(15,16).The purpose of the present work is the preparation and studying of photooxidation reaction of some mono azo dyes in presence and absence of anatase suspension.

Experimental

Materials:all chemicals used in this work were reagent grade: 1-amino-2-napthol -4- sulphonic acid,sodium nitrite. catechol and phenol were obtained from Riedel de Haen. Hydrochloric acid. adenine. salicylic acid,acetic acid and ethnol were supplied by BDH. Ortho amino benzoic acid titanium dioxide (anatase) were received from Aldrich and Degussa respecively.

Preparation of dyes

All dyes were synthesized by general coupling reaction method using equimolar quantities,the dye product was filterated and washed with cold distilled water for several times and recrystallized from ethanol,then dried at 80 C for three hours and weighed. The purity of dyes was checked using thin layer chromatography. The Rf values of dyes were measured using the eluent (acetic acid: ethanol: water) 2: 4:4 respectively and silica gel supported on glass plate.

Preparation of samples for x-ray diffraction spectra

The samples for x-ray diffraction spectra were prepared according to impregnation method mentioned previously(12)by adding TiO2(5%)to the aqeous solution of dye(1x10m^{-4},then the suspension was stirring at 25C for 48 hours and separated by centerfuge and washed with hot distilled water until the color disappeared from washing.The samples dried at 120C for 4 hours and invistigated by x-rays diffractimeter and use CuKa radiation at 1.541.

Spectroscopic Measurements

FT-IRspectra of prepared dyes were recorded on Perkin Elmer FT-IR spectrophotometer using KBr disk in the range 500-4000 cm^{-1}.UV-visible spectra absorption spectra aqueous solution of dyes(1x10^{-4}$_{M}$)were obtained by Shemadzu UV-160 sectrophotometer. Fluorescence spectra of same compounds were measured using Jenwam model 6200 Fluorimeter.

Photodegradation Experiment

The photodegradation of dyes was performed by irradiating the aqueous solution of certain dye in quartz cell with light of middle pressure mercury lamp for 90 min at lab temperature. Sample for kinetic study were taken from reactor by syringe through the reaction. The quantity of degraded dye was estimated in the λ_{max} of dye using shemadzu UV 160 spectrophotometer.

The same photodegradation experiments were performed in the presence of TiO2 suspension (0.4gm/l) by stirring the suspension continuously.

Results and Discussion

The hazardous of casting of industrial azo solution into waters.sometimes occuring from stability of such compounds toward the natural degradation which attributes to their resistance against the environmental conditions. The scope of the present research a bout the preparation and investigating the stability of some azo dyes toward photodegradation process. table (1)shows the chemical and physical data of prepared dyes. figures (1)-(4)shows the FT-IR spectra of dyes. It is clear from these data,that the prepared dyes have an acceptable absorbance in visible region of spectrum which may lead to use of these compounds in photosensitization processes.but this point depends on the stability of dyes toward heat and high intensity of light. Scheme (1)shows the structural formula of dyes.

Generally, the overall dyes characterize with low quantum yield as a result of limiting the absorbance band of these dyes in visible region of spectrum. i.e. low fraction of visible light can be collected or harvested by solutions of dyes because the exciting of dye molecules competites by fast back reaction of oxidized species of dye with other neighburs species in solution.

Degradation of dyes

Azo dyes are main type of synthesized organic compounds which having carcinogenic hazardous(6)as a result of using such dyes in industrial fields such textile dying, coloring of gasoline, foodstuff, estimating the traces, so the pollution by solutions of those dyes is possible. Many of synthesized dyes resist the degradation, but some of dyes undergo to natural anaerobic reductive degradation(6,17).

The decolorization of azo dyes witnessed an important attention especially when semiconductors such TiO_2,ZnO,CdS,SnO_2…etc,are used in this process which called "photosensitization" which involves exciting the colored and adsorbed azo dye molecules on the semiconductor surface,then the electronic charge injectes into conduction band of semiconductor which can be used to reduce other adsorbates materials,so the neutral dye molecales are converted to oxidized species. This process depends on the chemical nature of semiconductor surface and concentration of dye solution.Fig.(5)-(8)show the x-rays diffraction spectra of adsorbed dyes on TiO_2 surface.When a comparison between these spectra and spectra of naked TiO_2(12)was made,it has been found as table (2)shows that the adsorption of dyes modifies the nature of surface layer of TiO_2 particles,i.e. chemisorption may be formed and new peaks are formed in XRD spectra of adsorbed dyes onto TiO_2 surface. Table (3)lists the rates of photodegradation reactions, when the conc. of dye $1x10^{-4}{}_{M}$.table(4)shows the rates when the quantity of anatase was used in conc.(0.4dm/l).It is clear that the rates in absence of TiO_2 are lower comparision with existing of TiO_2 particles as a result of the adsorbed molecules of colored dye onto TiO_2 surface after injecting their electrons into conduction band of TiO_2 become oxidize to cation species and these species are very reactive which may be susceptibleto another reactions or react with the injected electrons in solution in back reaction specially when TiO_2 is absence,so this statement may explain the lowering of quantum yield of photodegradation in absence of TiO_2 .The dye molecules in solution in presence of light may be converted to another species such as formation of dimers (18) or dye aggregates (19) which causes the reduce of absorbed species.

The result(table 4)indicate that the use of TiO_2 is an important factor affecting.The increasing of TiO_2 ratio causes linear increasing of dye photodegradation rate which due that in low concentration snspensions,the number of particles of TiO_2 is less than high number photenes.so the necessary absorbed,however,are low,most of remained photones are trans through the suspension which lead to decreasing the degradative quantity from dye. Table (4) illustres the photodegradation of dyes in presence of TiO_2 suspension,it is clear that the TiO_2 is an important factor in photodegradation process which due to adsorbing of dyes onto TiO2 particles and the photodegradation is driven by injection of electrons from excited state of dye into conduction band of TiO2 particles which lead to the oxidation of dye molecules caused by exciting the molecules using visible light,beside the electrons of conduction band caused by moving the electrons from valence band and these electrons may be used to drive another photoreactions of dye molecules in different routs causing the changing of absorbance of certain dye.The results of photodegradation of all dyes illustrate that the rate of degradation process independs on conc of dye.

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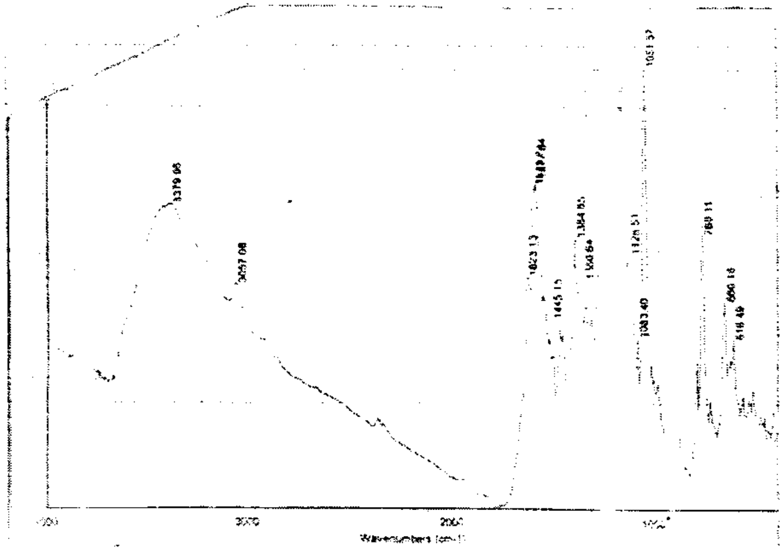
Table(1):Physical and *chemical* preperties of dyes.

	Molecular formula	M.wt g.mol-1	Rf	Color of crystals	Yield %	λMax,nm Absopti	λMax,nm Emission	ϵl.mol-1. cm-1	N=N Stretching cm-1
AAP	C11H9N601	351	0.840	Brown	84	390	400	5200	1430
AASA	C11H9N603	383	0.697	Brown	76	460	490	2150	1445
BAAC	C13H10N203	258	0.795	Brown	81	420	485	2000	1440
NSAAC	C16H12N206	360	0.874	Black-Brown	85	415	500	4500	1444

Table(2):Effect of adsorved dyes on the nature of TiO2 surface(relation of hkl with daccording to Braggs, equation)

hkl	101	103	004	112	200	105	211	213	204	116	220	215
Intensity of Beak Dye Adsorbed On TiO2 surface	vst	vw	st	vw	st	m	m	w	m	vm	Vm	m
TiO2	3.518	2.434	2.378	2.337	1.894	1.700	1.668	1.493	1.480	1.365	1.338	1.265
AASA/TiO2	3.516	2.437	2.376	2.337	1.891	1.690	1.665	1.492	1.485	1.364	1.334	1.264
AAP/TiO2	3.519	2.435	2.377	2.338	1.892	1.685	1.664	1.491	1.493	1.364	1.336	1.264
BAAC/TiO2	3.518	2.436	2.376	2.336	1.890	1.692	1.665	1.490	1.481	1.363	1.336	1.262
NSAAC/TiO2	3.516	2.436	2.374	2.337	1.892	1.699	1.666	1.493	1.483	1.363	1.336	1.265

*Values are obtained according to reference no.12.



Fig(1): FT-IR spectrum of AASA dye

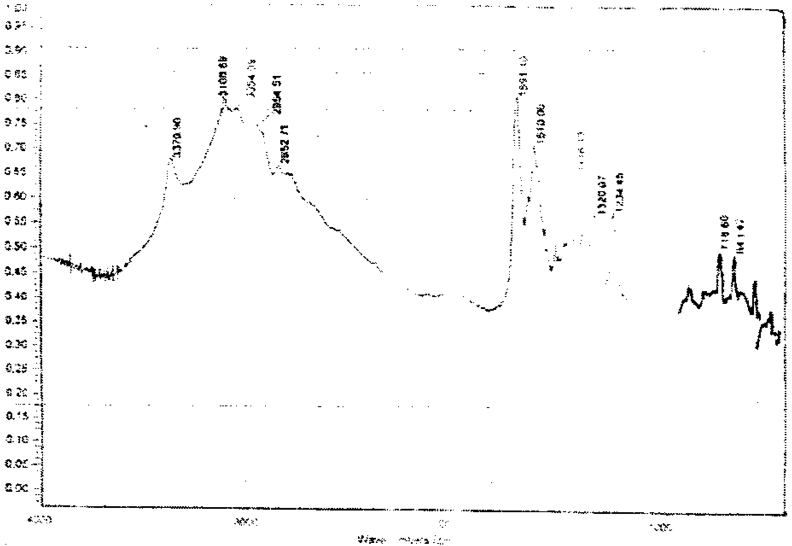
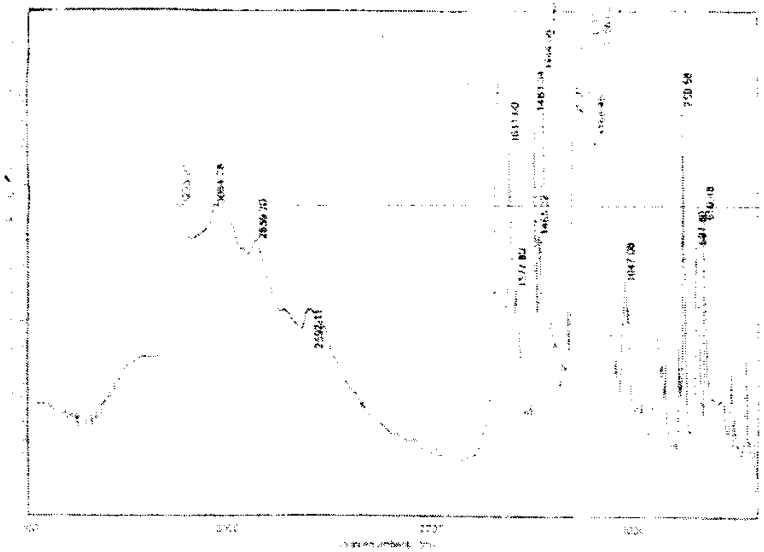


Fig.(2)-FT-IRspectrum of AAP dye.



Fig(3): FT-IR spectrum of [illegible]

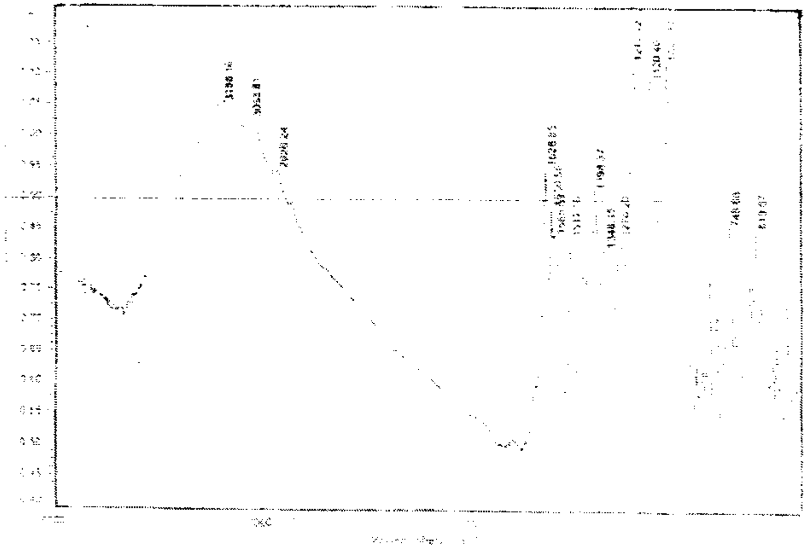


Fig.(4)-FT-IR spectrum of [illegible]

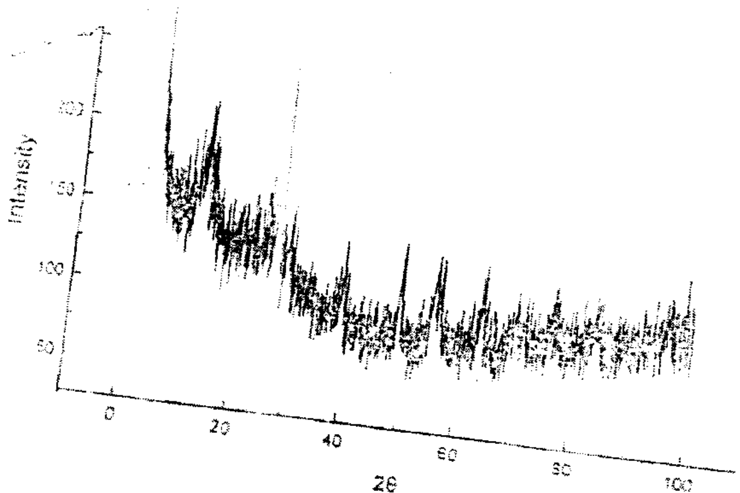


Fig.(5) [illegible] rays diffraction spectrum of AASA type (T[illegible])

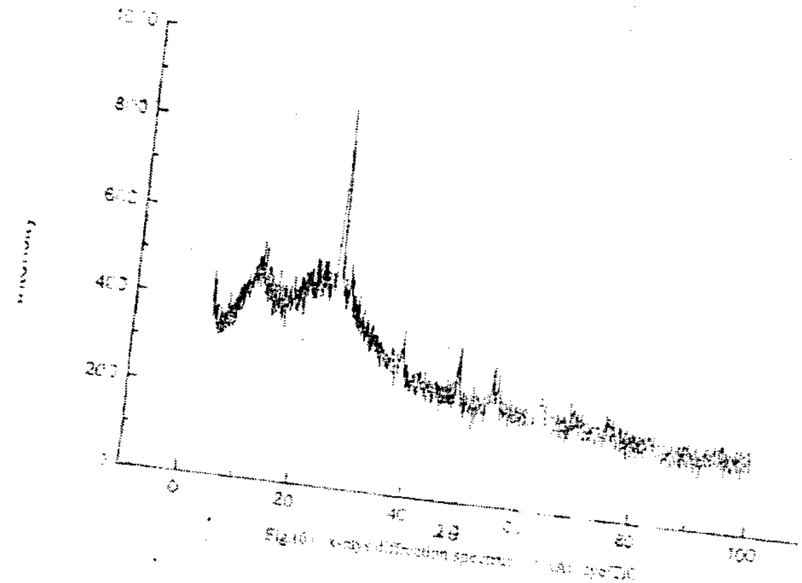


Fig.(6) X-rays diffraction spectrum [illegible]

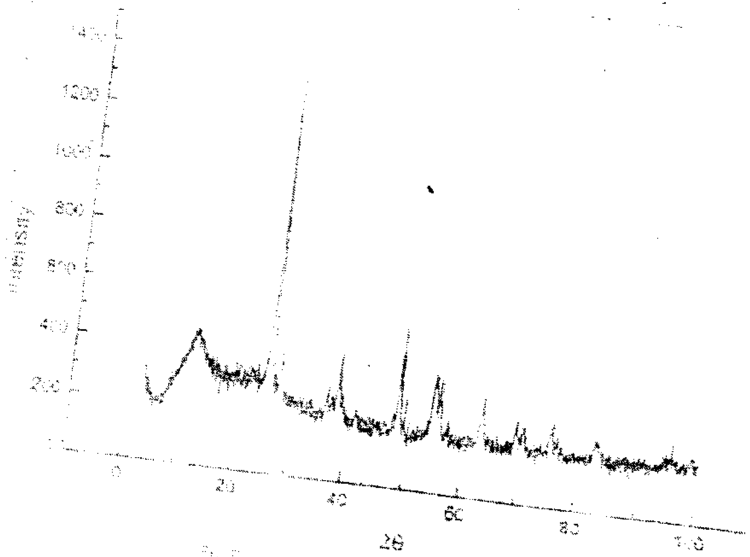


Fig.(7) [illegible] diffraction spectrum [illegible] BAA [illegible]

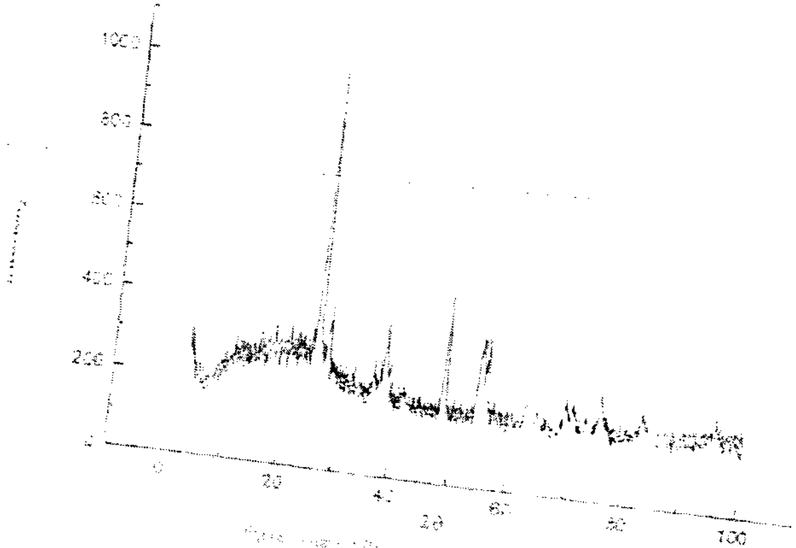
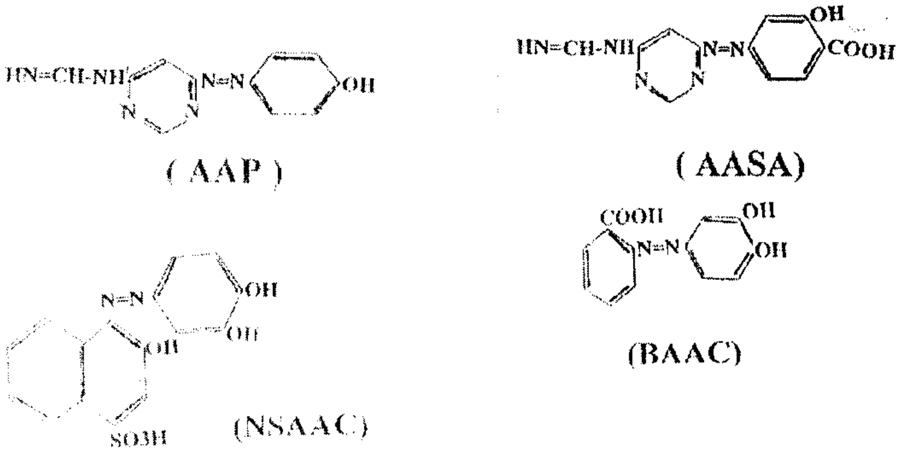


Fig.(8) [illegible] diffraction spectrum [illegible]



Scheme (1): Structural formula of dyes.

Table(3):Rates(x10^{5}mol.l^{-1}.sec^{-1})of photodegradation of dyes at different conc.in absence of TiO$_2$.

Conc. / Dye	1X10^{-4M}	7.5X10^{-5M}	5.0X10^{-5M}	2.5X10^{-5M}	1X10^{-5M}
AAP	4.620	4.891	4.723	4.062	4.122
AASA	9.252	9.155	8.729	8.833	8.12
BAAC	8.402	8.153	7.609	7.154	8.72
NSAAC	5.211	5.701	5.983	5.292	5.731

Table(4):Rates(x104mol.-1.sec-1.)of photodegradation of dyes at different conc.in presence of TiO$_2$(0.4gmLl)

Conc. / Dye	1X10^{-4}M	7.5X10^{-5M}	5.0X10^{-5M}	2.5X10^{-5M}	1X10^{-5M}
AAP	1.155	1.73	1.184	1.141	1.176
AASA	1.666	1.510	1.685	1.630	1.534
BAAC	1.764	1.824	1.792	1.763	1.703
NSAA	1.563	1.612	1.673	1.574	1.592

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تحضير ودراسة التحطم الضوئي لبعض أصباغ الازو الاحادية بوجود وغياب عالق ثاني اوكسيد التيتانيوم (الانتيز).

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الخلاصة

يشتمل البحث على جزئين، الاول يتضمن تحضير اربعة اصباغ ازو احادية(Mono Azo) وهي 4-(2ادنين ازو)- فينول و 4(-2ادنين ازو حامض السالسلك و 4-(2حامض البتروبك ازو)كاتكول و 4-(1-2 نفثول -4-حامض السلفونك ازو)كاتكول. تم تشخيص الاصباغ المحضرة بوساطة مطيافية FT-IR سجلت كذلك للاصباغ المحضرة اطياف امتصاص الاشعة المرئية وفوق البنفسجية واطياف انبعاث الفلورة، وتم دراسة بعض الخواص الفيزيائية والكيميائية.

ويتضمن الجزء الثاني من البحث دراسة التحطم الضوئي(Photodegradation) للاصباغ المحضرة في درجة حرارة المختبر بوجود وغياب ثاني اوكسيد التيتانيوم(Anatase) بوساطة تشعيع المحلول المائي للصبغة المعنية باستخدام خلية كوارتز ومصباح زئبقي متوسط الضغط(Middle Pressure Mercury Lamp) لمدة 90 دقيقة مع التحريك المستمر، ووجد بصورة عامة ان سرع الاكسدة الضوئية بوجود TiO_2 اعلى منها في حالة غيابه لجميع الاصباغ. تضمن البحث ايضا دراسة تداخل الاصباغ مع سطح TiO_2 بوساطة مطيافية انحراف الاشعة السينية(XRD).