Global Journals Inc.
Global Journal of Science Frontier Research: C
Biological Science
Volume 15 Issue 2 Version 1.0 Year 2015
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Synthesis, Characterization and Biodegradation of Some Polymeric Azo Compound

By Rehab Abdeen
Kinh Khalid university, Saudi Arabia

Abstract- A diazinum salt of Benzidine was coupled with aniline to form 4, 4\-Bis (1"-azo-4"-aminobenzene) biphenyl. The resulted azo dye was polymerized with different diacid chloride to form azopolymers. Monomer azodye and its azopolymer were determined using elemental analysis , Infrared spectroscopy and HNMR. The microbial degradation constant and rat of azopolymer were quantitatively assessed against fungi *(Aspergillus flavus, Aspergillus fumigatus, Aspergillus niger, Aspergillus ochraceous and Fusarium oxysporum). Pleurotus ostreatus Hngary* (HAR17) *And Ganoderma resencium* mycelial hyphae, *Candida albicans* was used as yeast model. However, *Escherichia coli* was used as bacterial organisms, using different concentration from azopolymers.

Keywords: *azo dye, azo polymers, microbial degradation and azo reduction.*

GJSFR-C Classification : *FOR Code: 279999p*

SYNTHESISCHARACTERIZATIONANDBIODEGRADATIONOFSOMEPOLYMERICAZOCOMPOUND

Strictly as per the compliance and regulations of :

Open Association of Research Society, USA
Research | Diversity | Ethics

Synthesis, Characterization and Biodegradation of Some Polymeric Azo Compound

Rehab Abdeen

Abstract- A diazinum salt of Benzidine was coupled with aniline to form 4, 4\-Bis (1"-azo-4"-aminobenzene) biphenyl. The resulted azo dye was polymerized with different diacid chloride to form azopolymers. Monomer azodye and its azopolymer were determined using elemental analysis , Infrared spectroscopy and HNMR. The microbial degradation constant and rat of azopolymer were quantitatively assessed against fungi *(Aspergillus flavus, Aspergillus fumigatus, Aspergillus niger, Aspergillus ochraceous and Fusarium oxysporum). Pleurotus ostreatus Hngary* (HAR17) *And Ganoderma resencium* mycelial hyphae, *Candida albicans* was used as yeast model. However, *Escherichia coli* was used as bacterial organisms, using different concentration from azopolymers.

Keywords: azo dye, azo polymers, microbial degradation and azo reduction.

I. Intoduction

Azo dye has received great attention due to its environmental stability, ease of preparation and its optical and electrical properties. Much work has been done on the molecular design, synthesis, and assembly of structures with desired properties [1-5]. The discovery of diazo compounds occurred around the year 1858, which parallels the beginning of what is considered the starting point of modern organic chemistry [6,7].

An area of polymer research that presents great current interest, yet has received insufficient attention, is that of the development of polymers with antimicrobial activities, generally known as polymeric biocides. In the area of health care and hygienic applications, biocidal polymers may be incorporated into fibers, or possibly extruded into fibers themselves, and used for contact disinfectants in many biomedical applications such as sterile bandages and clothing. For example, antimicrobial surgical gowns and antifungal polymeric coatings on surfaces such as shower walls and many kinds of tubing minimize the problems of biofouling and the release of pathogenic microorganisms into streams of flowing fluids [8].

To overcome problems associated with the low molecular weight antimicrobial agents, antimicrobial functional groups can be introduced into polymer molecules. The use of antimicrobial polymers offers promise for enhancing the efficacy of some existing antimicrobial agents and minimizing the environmental problems accompanying conventional antimicrobial agents by reducing the residual toxicity of the agents, increasing their efficiency and selectivity, and prolonging the lifetime of the antimicrobial agents. . Also, polymeric antimicrobial agents have the advantage that they are nonvolatile and chemically stable and do not permeate through skin. Therefore, they can reduce losses associated with volatilization, photolytic decomposition, and transportation. In the field of biomedical polymers, infections associated with biomaterials represent a significant challenge to the more widespread application of medical implants [9–13]. Research concerning the development of antimicrobial polymers represents a great a challenge for both the academic world and industry [8]. Significant advances in the past three decades have been made in the synthesis and applications of polymers to prevent microbial attack and degradation for diverse end uses [15].

Basic Requirements for Antimicrobial Polymers. The ideal antimicrobial polymer should possess the following characteristics: (1) easily and inexpensively synthesized, (2) stable in long-term usage and storage at the temperature of its intended application, (3) not soluble in water for a waterdisinfection application, (4) does not decompose to and/or emit toxic products, (5) should not be toxic or irritating to those who are handling it, (6) can be regenerated upon loss of activity, and (7) biocidal to a broad spectrum of pathogenic microorganisms in brief times of contact [8]. The elucidation of degradation pathways is of special interest considering health and environmental priorities. Directly on incubation medium have been used for the first time to follow kinetics of sulfonated azo dye Orange II enzymatic degradation. Nine transformation products were identified using these complementary analyses performed ex situ without any prior treatment. Three types of cleavage are proposed for the degradation pathway: (i) a symmetrical splitting of the azo linkage that leads to the formation of 4-aminobenzenesulfonate (and 1-amino-2-naphthol, not detected); (ii) an asymmetrical cleavage on the naphthalene side that generates 1,2-naphthoquinone and 4-Diazoniumbenzenesulfonate as products, with the latter one being transformed into 4-hydroxybenzensulfonate; and (iii) a third degradation pathway that leads to 2-naphthol and 4-hydroxybenzenesulfonate [16].

Author: Health science program, Biology Department, Faculty of Science, King Khalid University, Women center Al-Samer, Abha, KSA. e-mail: Mohamed_abdin60@yahoo.com

The goal of this work is to prepare and investigate the production of polyamide containing azogroup, by the reaction of Benzedine with aniline and copolymerization with different diacide chlorideby different methode and discusses the mechanism of degradation of azopolymers.

II. Experimental

a) Materials

(*Benzidine*, aniline, Terephthaldehyde, PTHFdipropionic acid and Dithiodipropionic acid) was purchased from Aldrich, USA and was used as received without further purification. Succinic acid was purchased from El-Naser pharmaceutical chemicals, Egypt and was used as received. Adipic acid was used as received from El-Gomhouria chemicals Co., Egypt. Azealic acid was purchased from Aldrich and was used as received without further purification.

b) Microorganisms

The following microorganisms were chosen to evaluate its activity towards the reduction or (degradation) of the synthesized polymers Aspergillus flavus, Aspergillus fumigatus, Aspergillus niger, Aspergillus ochraceous and Fusarium oxysporum were isolated from the soil and identified. Pleurotus ostreatus *Hngary* (HAR17), was obtained from Agricultural research center, Cairo. Egypt*. And Ganoderma resencium* mycelial hyphae were isolated and purified from their fruiting bodies, *Candida albicans* was used as yeast model. However, *Escherichia coli was used as bacterial organisms.*

c) Media

Nutrient agar and Nutrient broth medium were used for growing *Escherichia coli* as bacterial cultures. However, *Sabouraud dextrose agar was used for growing of Candida albicans.* Additionally, Malt extract medium was used for growing *Pleurotus ostreatus, Ganoderma resencium, Aspergillus flavus, Aspergillus fumigatus, Aspergillus niger, Fusarium oxysporum, and Aspergillus ochraceous.*

d) Evaluation of the azo polymers microbial biodegradation.

For each tested organism a series of a test tube have been prepared to obtain active vegetative microbial growth before the process of biodegradation. Stock cultures were used to inoculate 5 ml of broth medium specific for organism in number of tested tubes. After incubation for ~24 h at specific temperature for each organism, the cells were harvested by centrifugation (4000 rpm) for 10 min, suspended in 0.5 ml of PBS buffer, pH 7.2 (2mM KH2PO4, 3mM Na2HPO4. H2O, 167 mM NaCl) containing 0.125 mM benzylviologen and 6.3 mM (D.glucose monohydrate). A certain volume has been over the proper solid medium, and the colony forming unit has been determined by spread plate technique.

Approximately 10^7 colony forming unit per ml of tested microorganisms were used to inoculate the proper medium contains 33 μM of tested azo polymers and 0.125 mM benzylviologen in test tube. Then the test tubes were closed with rubber stopper, and incubated at 37°C in a horizontal shaking water bath, set at 100 rpm/min. At regular time intervals, one tube was withdrawn from the water bath, opened and 0.5 ml of 30 % trichloroacetic acid aqueous solution was added to stop the reaction, the absorbance of the clear supernatant was measured at the maximum wavelength of absorbance (λ max=332 &228 for XXI and 320 &230 for XXVII) of the tested azo polymer. A calibration graph for each azo polymer was carried out by measuring the absorbance of PBS buffer solution pH 7.2, solution containing 3% (w/w) of trichloroacetic acid and known concentration of the azo polymer. From the calibration graph, the azo polymer concentration was determined and plotted against the time. The rate of azo polymer degradation (K, the slope of the linear part of the degradation curve) was calculated as micromoles of azo polymer degraded per hour and per ml of inoculum (μ mol/h/ml).

III. Instrumentation

FTIR spectra were recorded on a Perkin- Elmer 1430 Ratio Recording Infrared Spectrophotometer apparatus from KBr pellets.

UV spectra were taken on a Shimadzu UV-2101 Dc Spectrophotometer.

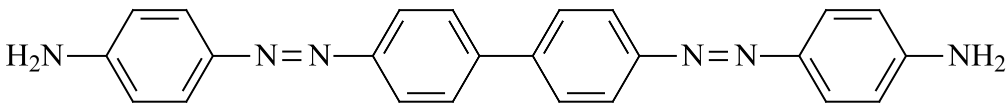
^{1}H NMR spectra were recorded using a Varian 300 M, Mercury-Oxford and a Jeol JNM-PM X90 SI NMR spectroscopy.

Tetramethylsilane (TMS) was employed as the internal standard. Melting points were determined on a Gallenkamp apparatus.

Global Journal of Science Frontier Research (C) Volume XV Issue II Version I Year 2015

IV. Preparation

a) Synthesis of 4, 4\-Bis (1"-azo-4"-aminobenzene) biphenyl (I)

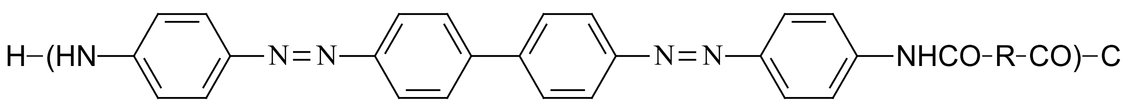


(I)

Benzedine, 1.9 g (10 mmol) was dissolved in 8 ml of conc. hydrochloric acid and 90 ml water. The solution was cooled to 2 °C, and then 5 ml of the sodium nitrite solution (1.5 g of sodium nitrite in 5 ml of water) was added dropwise, below 5 °C. The reaction mixture was stirred for another 1 h at 5 °C, and then was filtered. The filtrate was added dropwise to the aniline solution, (1.92 g, 20 mmol) aniline in 5 ml hydrochloric acid and 50 mL water. The solution was stirred for 1 h, and neutralized with a solution of sodium acetate, then kept overnight. The formed yellow azo product was filtered off, washed with water (3x), and then dried under vacuum at room temperature overnight. The product with molecular formula $C_{24}H_{20}N_6$ and molecular weight **(392.46)** was obtained in **90%** yield. It was characterized by ^{1}H NMR, elemental analysis and IR as shown in **Tables (1, 2, 3),** respectively.

b) Polymerization of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl (I) with various diacid chlorides

Polycondensation of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl **(I)** with various diacid chlorides were carried out by two methods as follows:-



(II-VIII)

c) Solution Polycondensation Method

Polycondensation of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl **(I)** with various diacid chlorides was achieved by the reaction of the components in dry ethanol free chloroform. The following procedure using succinyl diacid chloride is typical.

For a cooled solution of 1.55 g (10 mmol) of the succinyl diacid chloride in 15 ml of dry ethanol free chloroform, 18 mL of TEA was added in a 100 mL round bottomed flask. The reaction mixture was stirred in an ice bath at -10 °C for 15 min, then a solution of 3.92 g (10 mmol) of compound **(I),** in 25 ml dry ethanol free chloroform, was added dropwise with constant stirring. The reaction mixture was further stirred at -10 °C for 30 min then for 48 h at room temperature .The chloroform layer was extracted with 0.1 M HCl (3X), 0.1 M NaOH (3X) and finally with water. The chloroform layer was dried over anhydrous $MgSO_4$ overnight at room temperature. The $MgSO_4$ was then filtered and the chloroform was evaporated on rotary evaporator and the product **(II)** was further dried under vacuum at room temperature overnight. The product was characterized by elemental analysis as shown in **Table (2)** and IR spectra as shown in **Table (3).**

Other solution polycondensation were carried out similarly. **Scheme (2)** shows the outlines of the reaction**,** and **Table (4)** show the quantities of the reactants involved. Polymers **(III-VIII)** were characterized by elemental analysis as shown in **Table (2)** and IR spectra as shown in **Table (3).** Polymer **(VII)** was also characterized by ^{1}H NMR cf. **Table (1).**

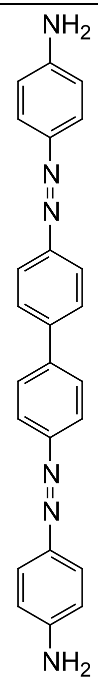
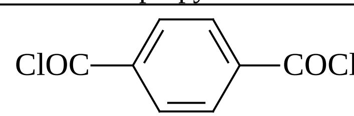
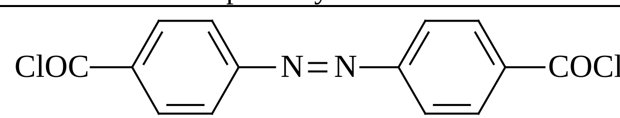
d) Interfacial polycondensation method

Interfacial polycondensation of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl **(I)** with various diacid chlorides was achieved by the reaction of the components in methylene chloride. The following procedure using succinyl diacid chloride is typical:

A solution of 3.92 g (10 mmol) of **(I)** in 45 mL water, 2 drops of pyridine and 13 mL dichloromethane was vigorously stirred. Then a solution of 2.31 g (10 mmol) of succinyl diacid chloride in 27 mL of dichloromethane was added with constant stirring for 10 min. Product **(II)** was collected by filtration using G4 sintered glass funnel, washed (3x) with dichloromethane, and dried under vacuum at room temperature overnight. Product **(II)** was characterized by elemental analysis as shown in **Table (2)** and IR spectra as shown in **Table (3).**

Other interfacial polycondensation were carried out similarly. **Scheme (2)** shows the outlines of the reaction and **Table (4)** shows the quantities of reactants involved. Polymers **(III-VIII)** were characterized by elemental analysis as shown in **Table (2)** and IR spectra as shown in **Table (3).**

Table 4 : Reactant quantities of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl with various diacid chlorides melting point

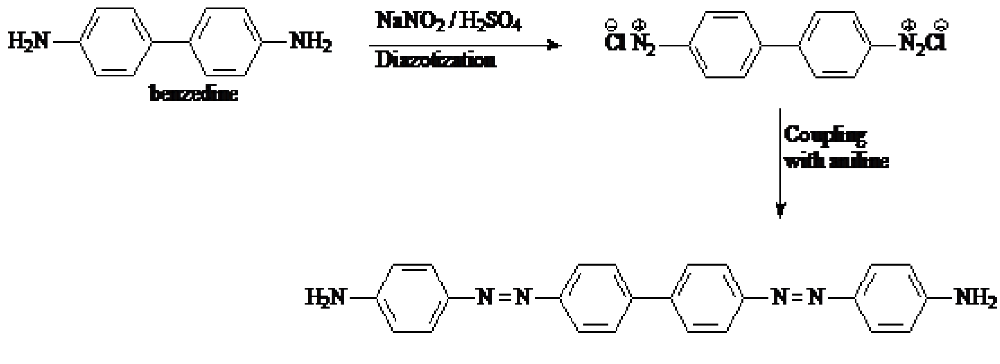
Monomer (mmol, g)	Diacid chloride COCl-R-COCl	Diamine (mmol, g)	Polymers		
			Code	m.p (° C)	Yield (%)
 (10 mmol,3.29 g)	$ClCO—(CH_2)_2—COCl$ Sucinnyl dichloride	(10 mmol, 1.55g)	**II**	175	72
	$ClCO—(CH_2)_4—COCl$ Adippyl dichloride	(10 mmol, 4.26 g)	**III**	160	75
	$ClCO(CH_2)_8COCl$ Azeil dichloride	(10 mmol, 1.8 g)	**IV**	195	77
	$ClCO—(CH_2)_3—S—S—(CH_2)_3COCl$ Dithiodipropyl dichloride	(10 mmol, 2.1 g)	**V**	___	Viscous 82
	$ClOC—(CH_2)_3—O—(CH_2CH_2CH_2CH_2O)_n—(CH_2)_3—COCl$ PTHF dipropyl dichloride	(10 mmol, 8.14 g)	**VI**	___	Viscous 80
	 Terephthaloyl dichloride	(10 mmol, 2.1g)	**VII**	Over 280	70
	 ABAC	(10 mmol, 3.71g)	**VIII**	240	74

V. Results and Discussion

a) Synthesis of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl (I)

A procedure using sodium nitrite and sulphuric acid, and coupling of the diazonium salt with aniline was done in moderately acidic medium at 0-5°C, to give a yellow dye of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl **(I)** as shown in **Scheme (1).** The azo dye **(I)** was in yield (90%), and its structure was conformed by elemental analysis. The data as given in **Table (2)**, it was in good agreement with the calculated values. IR spectrum of the dye **(I)** as in **Table (3)** showed the appearance of peak at 1517 cm^{-1}, 1453 cm^{-1} for (-N=N-), at 1614 cm^{-1} for (-NH_2) which confirmed the formation of the azo dye.

^{1}H NMR spectrum for dye **(I)** was recorded in (d_6-DMSO) and showed the following peaks: δ= 7.0-8.0 ppm (*m*, 12 H , ArH), and δ= 12.4 ppm (*s*, H, 2 NH_2) **cf. Table (1).**



Scheme (1) : Synthetic route of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl

b) Polymerization of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl with various diacid chlorides

The polymerization 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl was carried out by two methods, the first is solution polycondensation in ethanol free chloroform, with the use of triethylamine (TEA) as an acid acceptor, and the second is the interfacial polycondensation in dichloromethane with the use of pyridine as an acid acceptor.

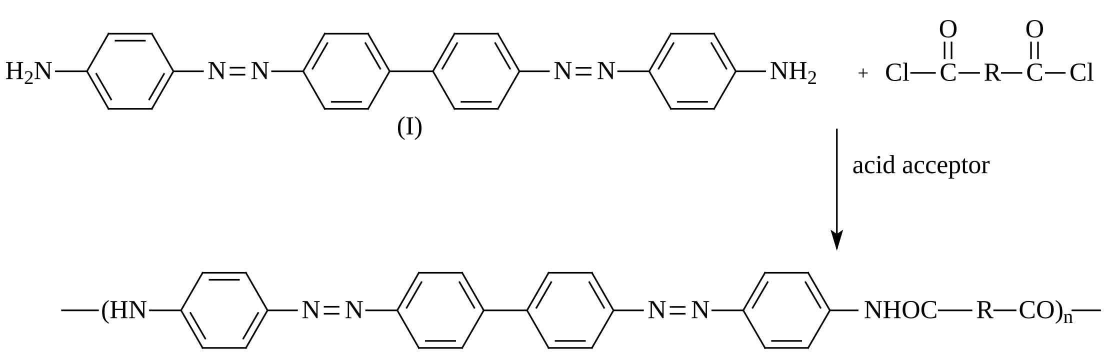
i. *Solution polycondensation*

Biodegradable azo-containing polyamides were prepared by solution polycondensation of azo monomer, 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl **(I)** with various diacid chlorides.

The solution polycondensation of the diacid chlorides was carried out using the quantities listed in **Table (4).** The amount of the diacid chloride was added to OH terminated azo monomer, 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl **(I)** in the presence of dry TEA as an acid acceptor to form the corresponding azopolyester. The reactions were conducted at low temperature then at room temperature under anhydrous condition as outlined in **Scheme (3).** Both polymer products were obtained in high yields.).

The elemental analyses of the synthesized azopolyamides are in a good agreement with the calculated values as shown in **Table (2).** The IR spectra of the azopolymers as in **Table (3)** showed appearance of peaks at1520-1526 cm^{-1} and 1630-1774 cm^{-1} for (C=O) in (CONH), at 3028-3052 cm^{-1} and 3314-3426 cm^{-1} for (N-H) in (CONH), and disappearance of peak at 701 cm^{-1} for (-C-Cl). The appearance of peak at 2924-2935 cm^{-1} for $(CH)_{alph}$ in samples **(II-VII)** confirmed the formation of azopolyamides.

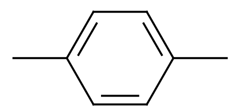
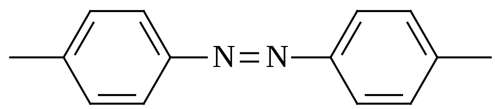
The ^{1}H NMR spectra for azo polyamide **(VIII)** was recorded in (d_6-DMSO) : δ= 7.0-8.0 ppm (m, 12 H, ArH), δ= 6.5 ppm (s, H, NH_2) and δ= 10.1 ppm (s, H, NH) cf. **Table** (1).



(II-VIII) Polyamide

Global Journal of Science Frontier Research (C) Volume XV Issue II Version I Year 2015

Scheme (2) : Synthetic route of copolymer of 4, 4\-bis (1"-azo-4"-aminobenzene) biphenyl with various diacid chlorides

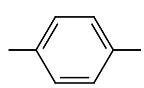
Azo polymer	Diacid chloride	-R-
II	Succinyl dichloride	$—(CH_2)_2—$
III	Adipyl dichloride	$—(CH_2)_4—$
IV	Azeil dichloride	$—(CH_2)_8—$
V	Dithiodipropyl dichloride	$—(CH_2)_3—S—S—(CH_3)_3—$
VI	PTHF dipropyl dichloride	$—(CH_2)_3—O—(CH_2CH_2CH_2CH_2O)_n—(CH_2)_3—$
VII	Terephthaloyl chloride	
VIII	ABAC	

ii. *Interfacial polycondensation*

Interfacial polycondensation of 4\-bis (1"-azo-4"-aminobenzene) biphenyl **(I)** with various diamines were carried out by A solution of the diacid chloride in dry methylene chloride according to the quantities of the reactants used listed in **Table (4)** was added to 4\-bis (1"-azo-4"-aminobenzene) biphenyl **(I)** in (water-methylene chloride) mixture in the presence of pyridine as acid acceptor as shown in **Scheme (2).** This method is faster than solution polycondensation, but with low yield as a result of hydrolysis apart of azobenzene diacid chloride. The quantities of the reactants used are as listed in **Table (4)** and the reaction scheme is as outlined in **Scheme (3).**

The elemental analysis and the IR spectra of the synthesized azopolyamides from interfacial polycondensation were similar to the azopolyamides synthesized from solution polycondensation.

Table 1 : ^{1}H NMR. shifts in ppm for azo dye **(I)** and polymers **(VIII)**

Groups Compound		NH	NH_2
1	6.5-8 (m)		6.2 (s)
VIII	7-8 (m)	10.1 (s)	6.5 (s)

* *s. singlet m: multiplet*

* *Appear of two peaks at δ= 2.4 for DMSO and δ=3.5 for water*

Table 2 : Elemental analyses of azodyes and its copolymers

Polymer	C%		H%		N%	
	Calc.	Found	Calc.	Found	Calc.	Found
I	73.46	72.92	5.13	4.57	21.40	21.30
II	66.01	62.33	5.10	4.45	11.80	11.10
III	71.70	63.74	5.20	5.39	16.70	14.44
IV	72.66	67.92	6.05	6.35	15.40	13.70

V	63.56	59.98	4.20	3.95	16.09	15.11
VI	68.87	62.90	5.10	5.38	16.19	12.65
VII	75.60	70.39	5.70	4.74	10.50	8.70

Table 3 : I. R. analysis of azodyes and its copolymers

Polymer	$-NH_2$	1,4 Disubstitued benzene	$-N=N-$	O=C−NH		$(CH)_{alph}$	N=CH
				C=O	-N-H		
I	1614	697	1453, 1517	–	—	—	—
II	—	821	1443, 1553	1630, 1520	3052, 3423	2928	—
III	—	759	1452, 1592	1664, 1520	3088, 3402	2933	—
IV	—	758	1406, 1595	1664, 1526	3040, 3314	2929	—
*V	—	808	1434, 1565	1727, 1520	3424	2924	—
*VI	–	756	1408, 1486	1732, 1519	3028, 34444	2935	—
VII	—	759	1441, 1596	1774, 1520	3421	–	—
VIII	–	761	1489, 1599	1677, 1520	3037, 3426	—	—

* *measured in solution state in chloroform.*

iii. *Microbial degradation of the azo polymers*

The degradation of azopolyamide by tested fungal species as *Aspergillus*, *Candida albicans*, *Escherichia coli, Pleurotus ostreatus* and *Ganoderma resencium* vs the incubation time was study. It can be seen that, after an initial latency phase, the concentration of azo compounds decreases linearly as a function of the incubation time, indicating that the azo reduction is a zero-order phenomenon [16].

Moreover, the linearity of the degradation was confirmed by studying the influence of the dye concentration on the degradation rate (data not shown). No change of the degradation rate could be observed when the initial concentration of azo polymer was doubled.

To our knowledge, almost little or no work has been done concerning the biodegradation of azo dyes by fungi. Present study revealed that all tested microorganisms could degrade poly azo benzene diamin-*co*-PTHF dipropyl dichloride as indicated by measuring the absorbance at wave length 328 nm. The maximum biodegradation percentage was obtained by *A. fumigatus* (97%), and the minmum was achieved with *E. coli* (91%) at wave length 328 nm. However, *A. flavus* was degraded 89% of used poly azo benzene diamin-*co*-PTHF dipropyl dichloride as indicated with measuring absorbtion at 230 nm. Furthermore, *A. flavus* was also performed the highest degradation percentage for poly azo benzene diamin-*co*-Azelic dichloride (96%) at both measured wave length (332 and 228 nm). *E. coli* didn't produced any absorbance change at either at 332 nm in case of poly azo benzene diamin-*co*-PTHF dipropyl dichloride or at 228 nm in case of poly azo benzene diamin-*co*-Azelic dichloride indicating that the degradation of these polymers might with a mechanism different from that of fungi. Actually, the process of azo polymers degradation isn't easy. Bacteria or fungi are unable to oxidized azo dyes readily due to the azo linkage which doesn't occur in nature [17]. On the other hand, it has been found that aerobic bacteria can degrade aromatic amines. Therefore, non-enzymatic reduction of azo dyes to amines could facilitate further degradation by bacteria. It has been demonstrated that two *pseudomonas* strains completely degrade 6-aminonaphthalene-2-sulfonic acid [18].

Degradation of poly azo benzene diamin-*co*-PTHF dipropyl dichloride and poly azo benzene diamin-*co*-Azelic dichloride as azopolymer by microorganisms has demonstrated that *Aspergillus* fungi have produced the highest value, followed with yeast (*C. albicans*,), and then *E. coli* as bacterial organism. However, *G. resencium* and *P. ostreatus* as a model organism of basidiomycetic fungi came in the last rank.

There is extensive informations available on biodegradation of polymers by hydrolysis; although little is known about azo polymers. There is no reliable evidence to suggest that the insoluble azopolymers degradable through azo reduction by biological systems. In spite of the ability of many bacteria and mammalin cells to cleave the azo bonds in low molecular weight azo compound and water soluble high-moleculare weight polymeric derivatives of certain azo dyes has been demonstrated.[19]

Current data indicated that the degradation of poly azo benzene diamin-*co*-PTHF dipropyl dichloride and poly azo benzene diamin-*co*-Azelic dichloride, with different tested microorganisms produced different values of degradation rate constant (Azo Reductase Activity), which varied from organism to other. The highest rate constant of poly azo benzene diamin-*co*-Azelic dichloride degradtion was obtained by *A. niger* which produced 5.5±0.115 μmol/ml/h at 230 nm, however *A. ochraceous* performed 0.84±0.12 μmol/ml/h. degradation constant increase of poly azo benzene diamin-*co*-PTHF dipropyl dichloride at 328 nm. The highest poly azo benzene diamin-*co*-Azelic dichloride degradation rate constant (μmol/ml/h) was obtained by *A. fumigatus* which preformed 5.71±0.23 μmol/ml/h at 228 nm; however *A. ochraceous* produced the lowest poly azo benzene diamond- *co*- Azelic dichloride degradation rate constant of 0.94±0.72 μmol/ml/h at 332 nm.

We anticipate that the azo polymers degradation process occurs exactly if the azo reductase was able to distinguish between the azodyes present concurrently in the medium according to their redox potential as also listed by [19]. Surprisingly, *P. ostreatus* and *G. resencium* have preformed the hightest rate constant for degradation of poly azo benzene diamin-*co*-Azelic dichloride which produced 10.43±0.21 and 8.55±0.16 μmol/ml/h at 330 nm and *Pleurotus ostreatus* (edible mushroom) was preformed a high rate of degradation constant more than *Ganoderma resencium* with two synthesized polymers as shown.

Since the discovery of the activation mechanism of sulphasalazin into 5-amino salicylic acid by the intestinal microflora. Until now, there is insufficient understanding of azo reduction mechanism and the difficulty in obtaining successful colonic delivery system to protect a drug from mouth to caecum and to afford its site- specificity are obstacles[19]. From results it appears that no relationship could be established between the structure of azopolymers and degradation rate constant value (K). The degradation process occurs exactly as if the azo reductase were able to distinguish between the azopolymers present in the medium.

We believe that adding one of the safe microorganisms used in this study to the drug coated or supplied or supplied with the azopolymer will performed hydrolysis or degradation to the polymer and hence liberate the drug.

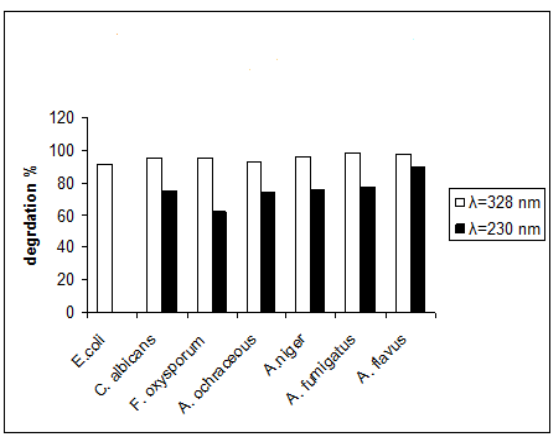


Figure 1: Degradation percent for poly azo benzene diamin-*co*-PTHF dipropyl dichloride (VI) against different microorganisms

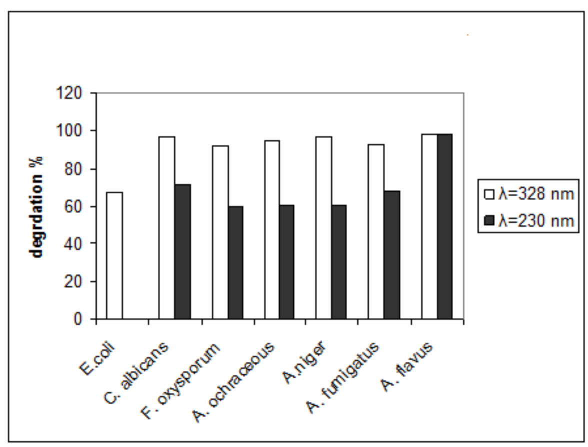


Figure 2 : Degradation percent for poly azo benzene diamin-*co*-Azelic chloride (IV) against different microorganisms

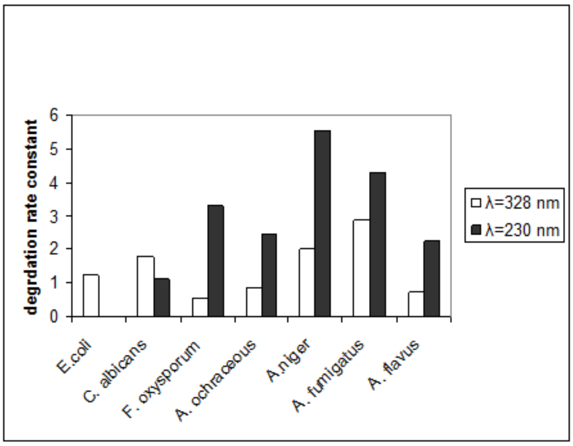


Figure 3 : Degradation rate constant for poly azo benzene diamin-*co*-PTHF dipropyl dichloride (VI) against different microorganisms

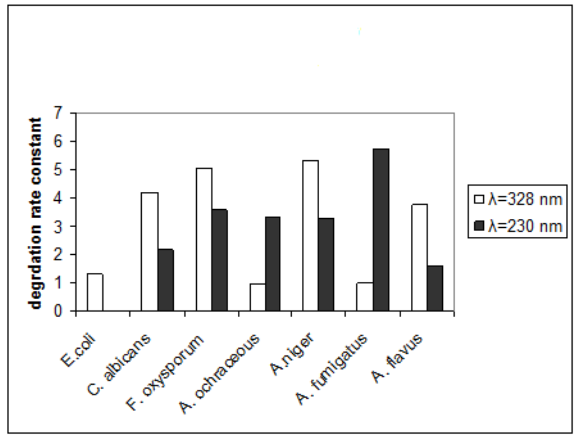


Figure 4 : Degradation rate constant for poly azo benzene diamin-*co*-Azelic chloride (IV) against different microorganisms

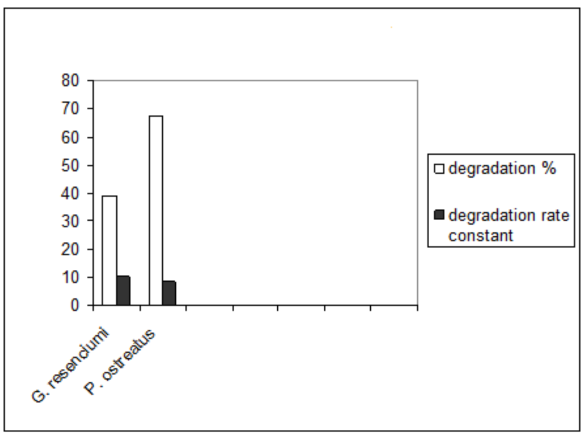


Figure 5 : poly azo benzene diamin-*co*-PTHF dipropyl dichloride (VI) against different microorganisms

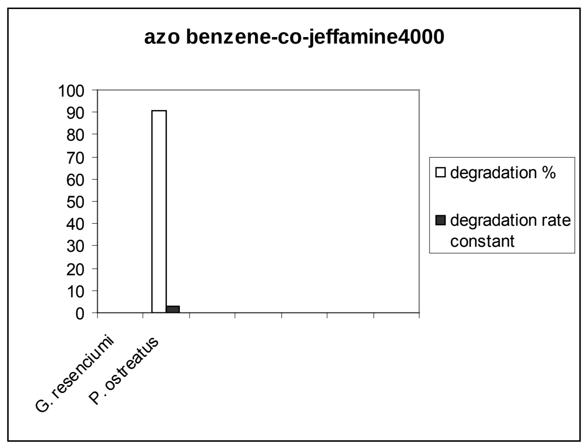


Figure 6 : poly azo benzene diamin-*co*-Azelic chloride (IV) against different microorganisms

VI. Conclusion

Azo dye polymer compounds have been synthesized from 4, 4\-Bis (1"-azo-4"-aminobenzene) biphenyl with diacid chloride. The azo dyes were investigated by elemental analysis, infrared spectroscopic, H^1NMR spectroscopic and absorption spectrum are used to prove the structure of azodye and its polymers. The UV-visible spectroscopic studies shows that the novel azo dye polymer compound has high degradation rate by treatment with different organisms.

References Références Referencias

1. Ho M S,Barrett C, Paterson J,E steghamation M , Natansohn A and Rochon P, Macromolecules, 199629,4613.
2. Yin S, Xu H, shi W ,Gao y, Song Y and Wing J, Polymer, 2005,46,7670.
3. Nabeshima Y, Shishido A, Kanazawa A, Shiono T, Ikeda t and Hiyama T, Chem Mater1997 ,9, 1480.
4. Hallas G and Towns A D , Dyes pigments, 1997,33,319.
5. Towns A D , Dyes pigments,1999, 42,3.
6. T. Mandel., and Y. Inber., Chem. Phys. Lett. 2004, 165, 387.
7. Hasanain A S. A Majeed, Alaa Yassin Al-Ahmad and Kawkab Ali Hussain, The Preparation, Characterization and the Study of the Linear Optical Properties of a New Azo Compound, Journal of Basrah Researches ((Sciences)) 2011,Vol.37.No. 2 .
8. Worley, S. D.; Sun, G. Trends Polym. Sci. 1996, 4 , 364-370.
9. Woo, G. L. Y.; Yang, M. L.; Yin, H. Q.; Jaffer, F.; Mittelman, M. W.; Santerre, J. P. J. Biomed. Mater. Res. 2002, 59, 35-45.
10. Acharya, V.; Prabha, C. R.; Narayanamurthy, C. Biomaterials 2004, 25, 4555-4562.
11. Jiang, H.; Manolache, S.; Lee Wong, A. C.; Denes, F. S. J. Appl. Polym. Sci. 2004, 93, 1411-1422.
12. Hume, E. B. H.; Baveja, J.; Muir, B.; Schubert, T. L.; Kumar, N.; Kjelleberg, S.; Griesser, H. J.; Thissen,

H.; Read, R.; Poole-Warren, L. A.; Schindhelm, K.; Willcoxy, M. D. P. Biomaterials 2004, 25, 5023-5030.
13. Baveja, J. K.; Li, G.; Nordon, R. E.; Hume, E. B. H.; Kumar, N.; Willcox, M. D. P.; Poole-Warren, L. A. Biomaterials 2004, 25, 5013-5021.
14. E. Kenawy,S. D. Worley and Roy Broughton, The Chemistry and Applications of Antimicrobial Polymers: A State-of-the-Art Review, Biomacromolecules, Vol. 8, No. 5, 2007.
15. Vigo, T. L. In Biotechnol. Bioact. Polym. [Proc. Am. Chem. Soc.Symp.]; Gebelein, C., Carraher, C., Eds.; Plenum Press: New York,1994; pp 225-237.
16. Walker R, Ryan AJ (1971), Some moleculae parameter influencing rate of reduction of azo compound bu intestinal folar. Xenobiotica 1: 483-486.
17. Nam, s and Renganathan, V,(2000), Non enzymatic reductionof azodye by NADH. Chemosphere, 40:351-357.
18. Brown D, Hamburger B (1987), the degradation of dyestus.: part III-Investigation of their ultimate degradability. Chemosphere 16: 1539-1553.
19. Semde R, Pierre D, Geuskens G, Devleeschovwer M, Moes AJ (1998) Study of some important factor involved in azo derivatives reduction bu Clostridium Perfringens, Int J Pharm 161:P 45-54.