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Schiff bases of chitosan

An overview

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Abstract

Chitosan is a polysaccharide that has amino and hydroxyl groups and other functional groups that enable functionalization. Schiff bases, which can be identified using ^{1}H NMR, FTIR spectrometry and thermal analysis, can be created when the C2-NH2 group reacts with primary amines.

Keywords: chitosan, Schiff base, spectral methods, thermal analysis

1. INTRODUCTION

Chitosan is a biopolymer comprised of N-acetylated glucosamine and glucosamine units connected by β-(1–4) glycosidic bonds (Scheme 1). It is obtained by the deacetylation of chitin. Chitin can be found in the shells of crustaceans, insects, and various other organisms such as fungi, algae, and yeast [1].

Chitosan molecules contain several functional groups, including C_3–OH, C_6–OH, C_2–NH$_2$, and acetyl amino and glycoside bonds. The acetylamino and glycosidic bonds are equally stable and not easily

broken. The C_3–OH group is a secondary hydroxyl group that cannot rotate freely and has significant steric hindrance, making it difficult to react. On the other hand, the C_6–OH and C_2–NH$_2$ groups are more active chemically, and their presence in chitosan allows for the introduction of other functional groups through various molecular design strategies. They can participate in metal coordination, chemical coupling, chemical crosslinking, graft copolymerization or alkylation reactions. The C_6–OH group can be esterified and carboxymethylated, too. The C_2–NH$_2$ groups can be acylated and Schiff bases are formed. Glycosidic bonds can be cleavaged by degradation [2].

     This review article centres on the examination of chitosan's Schiff bases, along with their characterization and diverse applications.

1.Schiff bases of chitosan characterization

     Schiff base compounds which have an imine group (–RC=N–) can be produced by the reaction of a primary amine with an active carbonyl. Chitosan, a polymer containing amino groups in its chain, is susceptible to various chemical modifications, such as the creation of Schiff bases via the reaction with aldehydes and ketones (Scheme 1).
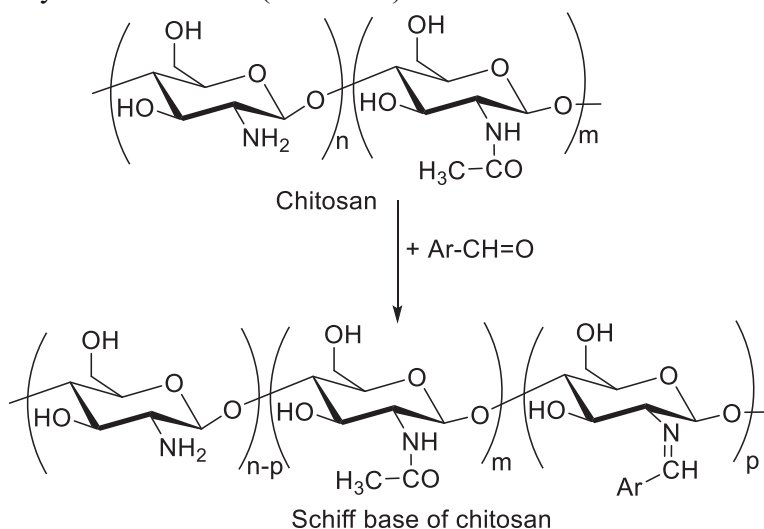
Scheme 1. Synthesis of Schiff bases of chitosan

     Characterization techniques FTIR and ^{1}H NMR spectroscopy were used to characterize the biopolymeric Schiff bases of chitosan.

Chitosan and Schiff bases of chitosan show an intense band in the region of 3400 cm^{-1} assigned to the stretching vibrations of the -OH and –NH$_2$ groups of their structure. A band between 3000 and 2880 cm^{-1} was assigned to symmetrical and asymmetric C-H stretch. Other characteristic bands of chitosan are shown at 1690-1630 cm^{-1}, 1600-1560 cm^{-1}, 1430-1380 cm^{-1} and 1200-1000 cm^{-1} which were attributed to C=O stretching of the acetamide group (amide band I), N-H stretching of acetamide group (amide band II), C-N deformation of amino group (amide group III) and O-C-O stretching of the glycopyranoside ring, respectively. The spectra of chitosan-Schiff bases derivatives show a new band at 1650-1560 cm^{-1} due C=N vibrations. The bands ranging from 1400 to 1500 cm^{-1} are due to the C-C stretching vibrations of the aromatic ring. The absence of the characteristic band of aldehyde in the region 1660–1730 cm^{-1} indicates that there is no traceable residue of free aldehydes [1-9].

A significant change in the spectra was observed when comparing the Schiff bases to chitosan, with distinct ^{1}H NMR signals characterizing each [5-6, 8-9]. The chitosan spectra and the Schiff base spectra exhibited a singlet between 1.23 and 1.87 ppm, attributed to the acetyl proton, and a singlet between 1.91 and 2.98 ppm, corresponding to the (H-2) proton of the pyranose ring. On the other hand, the Schiff bases demonstrated a sharp singlet between 8.78 and 9.79 ppm due to the imine group's proton (–N=CH–), and different signals between 6.0 and 10.2 ppm, mainly resulting from the aromatic rings present in the Schiff bases.

Chitosan-Schiff bases were characterized by thermogravimetric analysis [1-5, 6-8]. Thermogravimetry of Schiff bases derived from chitosan shows that they have nearly the same decomposition temperature as the chitosan, indicating that Schiff bases are thermally stable. The studied Schiff base of chitosan has water elimination up to 120°C. The second degradation step is observed around 200°C-300°C, due to the decomposition of the polymeric chains followed by the thermal degradation of a new material formed by the residual of the second stage of the degradation process.

Table 1.Spectral and thermal data of Schiff bases of chitosan

No	Schiff base of chitosan	Main IR absorption bands (cm⁻¹)									¹H NMR peaks (δ/ppm)				TGA analysis	Ref
		VNH2	VOH	VC-H	VC=O	VNH	VC-N	Vglyc	VC=N	VC=C	H-amide	H-2	H-imine	H-Ar	Temp. (°C)	
1	Schiff base of chitosan with 4-chlorobenzaldehyde	3200-3600	3200-3600	2919 2879	1650	1575	1380	1150	-	-	-	-	-	-	~100°C 220-350°C t>350°C	[1]
2	Schiff base of chitosan with benzophenone	3200-3600	3200-3600	2919 2879	1650	1575	1380	1150	-	-	-	-	-	-	~100°C 220-350°C t>350°C	[1]
3	Schiff base of chitosan with -ndole-3-carboxaldehyde	3200-3400	3200-3400	2960 1933	1645	1565	1370	1000-1200	-	-	-	-	-	-	ambient-~100°C 140-200°C	[3]
4	Schiff base of chitosan with 1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde	3374	3374	2877	1660	1596	1381	1157 1099 1032	1565	1503 1475	-	-	-	-	29-87°C 208-404°C 404-694°C	[4]
5	Schiff base of chitosan with 1-Phenyl-1H-pyrazolo[3,4-b] quinoxaline-3-carbaldehyde	3374	3374	2877	1660	1596	1381	1157 1099 1032	1568	1505 1476	-	-	-	-	28-98°C 207-434°C 434-695°C	[4]
6	Schiff base of chitosan with -1-phenyl-3-(thiophene-2-yl)-1H-pyrazole-4-carbaldehyde	3439	3439	2900-2800	1644	-	1426	1057	1634	1400-1500	1.23	1.91	8.78	8.38 7.87 7.70–7.08	~92°C ~294°C ~530°C	[5]
7	Schiff base of chitosan with 1- phenyl-3-(furan-2-yl)-1H-pyrazole -4-carbaldehyde	3439	3439	2900-2800	1636	-	1426	1157	1634	1400-1500	1.23	1.91	9.72	10.17, 9.41 8.0, 7.5	~35°C ~295°C ~530°C	[5]
8	Schiff base of chitosan with 1-phenyl-3-(pyridine-3-yl)-1H-pyrazole-4-carbaldehyde	3439	3439	2900-2800	1644	-	1426	1057	1634	1400-1500	1.24	1.91	9.11	9.99, 9.39 8.67, 8.33 8.0, 7.5	~70°C ~304°C ~530°C	[5]

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Table 1. Spectral and thermal data of Schiff bases of chitosan (Continuation)

No	Schiff base of chitosan	Main IR absorption bands (cm^{-1})									^1H NMR peaks (δ/ppm)				TGA analysis	Ref
		V_{NH_2}	V_{OH}	V_{C-H}	$V_{C=O}$	V_{NH}	V_{C-N}	V_{glyc}	$V_{C=N}$	$V_{C=C}$	H_{amide}	H-2	H_{imine}	H_{Ar}	Temp. (°C)	
9	Schiff base of chitosan with benzaldehyde	-	3416	2916	-	-	-	1111	1647	1475	1.77	2.88	9.63	7.3-7.6	-	[6]
10	Schiff base of chitosan with 4-(dimethylamino)benzaldehyde	-	3423	2874	-	-	-	1057	1598	1475	1.34	2.45	9.23	7-7.3		[6]
11	Schiff base of chitosan with 4-hydroxy-3-methoxybenzaldehyde	-	3425	2870	-	-	-	1022	1646	1507	1.68	2.78	9.26	6.6-7	-	[6]
12	Schiff base of chitosan with 5-Chloro-3-methyl-1-phenyl-1H-pyrazole-4- carbaldehyde	3400	3400	2984	1690	1600	-	1160	1646	1466	-	-	-	-	55-100°C 260-428°C t>430°C	[7]
13	Schiff base of chitosan with 1-phenyl-3-methyl-5-p-nitro phenyl-1H-pyrazole-4-carbaldehyde	3400	3400	2991	1680	1600	-	1160	1646	-	-	-	-	-	-	[7]
14	Schiff base of chitosan with vanillin	-	-	-	-	1589	-	1026	1636	1520 1458	1.87	2.97	9.47	7.2-7.3 6.8	55-230°C 230-320°C 320-600°C	[8]
15	Schiff base of chitosan with ethylvanilin	-	-	-	-	1589	-	1026	1640	1520 1458	1.87	2.97	9.45	7.2 6.8	55-230°C 230-320°C 320-630°C	[8]
16	Schiff base of chitosan with veratraldehyde	-	-	-	-	1589	-	1026	1641	1512 1458	1.86	2.98	9.53	7.4 7.2 6.9	55-230°C 230-325°C 325-625°C	[8]
17	Schiff base of chitosan with 2,4,6-trimethoxy benzaldehyde	-	-	-	-	1589	-	1026	1610	1520 1458	1.85	2.95	9.79	6	55-220°C 220-330°C 330-625°C	[8]
18	Schiff base of chitosan with 4-ethoxy 3-hydroxy benzaldehyde	-	-	-	-	1589	-	1026	1640	1512 1458	1.87	2.97	9.48	7.3 7.1 6.9	55-225°C 225-325°C 325-625°C	[8]
19	Schiff base of chitosan with salicylaldehyde	3368	3368	2880	1655	1598	-	-	1631	1498	-	3.1	9.78	6.8-7.6	-	[9]

2.Schiff bases of chitosan with antimicrobial activity

The antimicrobial activities of chitosan and its Schiff bases were tested against *Staphylococcus aureus, Bacillus cereus, Bacillus subtilis* as Gram-positive bacteria and *Escherichia coli, Pseudomonas aeruginosa, Salmonella sp, Klebsiella pneumonia as* Gram-negative bacteria. Antifungal activity was tested on *Candida albicans* and *Aspergillus niger*. The antimicrobial activities of the chitosan derivatives were compared with those of chitosan. The antimicrobial activities of the Schiff bases of chitosan were stronger than those of chitosan in most microorganisms.

The Schiff bases of chitosan with vanillin, ethyl vanillin, veratraldehyde, 2,4,6 trimethoxy benzaldehyde and 4-ethoxy-3-hydroxy benzaldehyde showed better antimicrobial activities against *Staphylococcus aureus, Bacillus subtilis, Escherichia coli* and *Aspergillus niger* than chitosan. Among all the above-mentioned chitosan derivatives, the Schiff base with vanillin was most effective against *Staphylococcus aureus* and *Bacillus subtilis.* Also, the Schiff bases of chitosan with vanillin and 4-ethoxy-3-hydroxy benzaldehyde showed the best antifungal activity against *Aspergillus niger* [8].

The chitosan Schiff bases prepared via coupling of chitosan with 4-chloro benzaldehyde and benzophenone [1], respectively, were more effective against Gram-negative bacteria than Gram-positive. Chitosan-4-chloro benzaldehyde Schiff base showed the highest activity against *Candida albicans, Pseudomonas aeruginosa* and *Bacillus cereus*. The activity of chitosan-benzophenone Schiff base against *Staphylococcus aureus, Bacillus cereus, Escherichia coli* and *Salmonella sp* was stronger than those of chitosan.

From the study of antimicrobial activity of the chitosan Schiff bases obtained by coupling of chitosan with indole-3-carboxaldehyde and 4-dimethylamino benzaldehyde, respectively, was observed the highest activity for the Schiff base of chitosan with indole-3-carboxaldehyde [3]. However, the chitosan Schiff base with 4-dimethylaminobenzaldehyde was more effective against *Staphylococcus aureus* and *Bacillus cereus* Gram-positive bacteria.

The inhibitory effect of chitosan Shiff bases resulted from the reaction of chitosan with 5-chloro-3-methyl-1-phenyl-1H-pyrazole-4-

carbaldehyde, 1-phenyl-3-methyl-5-o-cresyloxy-1Hpyrazole-4-carbaldehyde, 1-phenyl-3-methyl-5(-2-chloro phenyl)-1H-pyrazole-4-carbaldehyde, 1-phenyl-3-methyl-5(-p-Nitro phenyl)-1H-pyrazole-4-carbaldehyde and 3-methyl-1-phenyl-5-(piperidin-1-yl)-1H-pyrazole-4-carbaldehyde, respectively, against *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* was higher than those of chitosan. From the above-mentioned derivatives, 5-chloro-3- methyl-1-phenyl-1H-pyrazole-4-carbaldehyde showed better antibacterial and antifungal activity (against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Candida albicans*) [7].

3.Pollutants removal with Schiff bases of chitosan

The Schiff bases of chitosan with 1*H*-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde and 1-phenyl-1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde, respectively were evaluated for the removal of hexavalent chromium from synthetic samples [4]. The optimum pH value for the absorption process of Cr(VI) was 6. The two Schiff bases of chitosan showed high removal efficiency. The best removal efficiency for 1*H*-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde was 96.78 % at the optimum dose of 150 mg/L. In case of 1-phenyl-1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde, the best removal efficiency was 98.85 % at the dose of 250 mg/L. From the study of the effect of chromium initial concentration it was observed that the removal efficiency decreased when the initial concentration of Cr(VI) increased.

The salicylaldehyde-chitosan Schiff base was used as an electropositive adsorbent in order to study the electrostatic adsorption behavior of dyes like methylorange, anionic xylenol orange, methylene blue and cationic basic fuchsin, respectively [9]. The results showed that the anionic dyes exhibited a much better adsorption performance than cationic dyes. The color of methylorange and xylenol orange (the anionic dyes) disappeared after 40 min while basic fuchsin and methylene blue (the cationic dyes) exhibited an insignificant adsorption performance.

4. CONCLUSION

Some chitosan's Schiff bases obtained by the reaction of C_2-NH_2 group with primary amines were characterized using FTIR and ^{1}H NMR spectroscopy and thermal analysis.

The antimicrobial activities of chitosan and its Schiff bases were studied against *Staphylococcus aureus*, *Bacillus cereus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella sp*, *Klebsiella pneumonia*. Antifungal activity was tested on *Candida albicans* and *Aspergillus niger*.

The Schiff bases of chitosan with 1*H*-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde and 1-phenyl-1H-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde were studied for the removal of hexavalent chromium from synthetic samples and it was observed the best removal efficiency for 1*H*-pyrazolo[3,4-b]quinoxaline-3-carbaldehyde.

The Schiff base of chitosan with salicylaldehyde was used as an adsorbent in order to study the electrostatic adsorption behaviour of some dyes.

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Degradation of some azo dyes by Fenton process

An overview

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Abstract

Dyes are used in various industries as colouring agents. Synthetic dyes released in wastewater pose a threat to environmental safety. Several methods have been used for the removal of dyes from water bodies. The advanced oxidation processes (AOPs) have been proven to be effective technologies for dyes degradation. In this review, different types of Fenton processes such as electro-Fenton, photo-Fenton and sono-Fenton were chosen to study the degradation of some azo dyes.

Keywords: azo dyes, electro-Fenton, photo-Fenton, sono-Fenton

1. INTRODUCTION

Textile wastewater causes serious environmental problems because of its toxicity and persistence. As the most common synthetic dyes released into the environment, azo dyes pose a serious threat. Their chemical structure is characterized by one or more azo groups (-N=N-) [1]. These dyes and their biodegradation products, exhibit toxicity to

aquatic organisms and are mutagenic and carcinogenic to humans. Consequently, it is crucial to remove these dyes from wastewaters before their discharge into the environment [2].

Several methods have been applied for the elimination of organic pollutants from wastewaters, including biological treatment, coagulation, chemical oxidation, electrochemical treatment, ozonation, adsorption, etc. [3]. The oxidation by Fenton's reagent has shown great effectiveness in eliminating a wide range of organic pollutants present in wastewater [4].

Different variants of Fenton processes are available for utilization, including electro-Fenton, photo-Fenton, photo-electro Fenton, sono-Fenton, sono-electro Fenton, and sono-photo Fenton processes [5].

This review describes the degradation of some azo dyes such as Acid Orange 7, Ponceau S, Sunset Yellow FCF, Reactive Brilliant Orange X-GN, Direct Red 81, Amaranth, Acid Red 1, Chocolate Brown HT, Eriochrome Black by Fenton process such as: electro-Fenton, photo-Fenton, sono-Fenton [1-4, 6-9] (figure 1).

a. Electro-Fenton Process

In a study conducted by T. X. H. Le et al., the Electro-Fenton process was investigated for the degradation of Acid Orange 7 azo dye in an acidic medium with a pH of 3 [1]. The carbon-felt cathode was employed in this study. The optimal operating conditions for achieving maximum degradation were determined as -8.3 mA cm^{-2} for the applied current density and 0.2 mM for the catalyst concentration. Under these conditions, the mineralization of 200 mL of Acid Orange 7 reached 96.2 % after 8 hours of treatment (Table 1).

H. S. El-Desoky et al. studied the oxidation of Ponceau S azo-dye in aqueous solutions using electro-generated Fenton's reagent [2]. The experiments were performed at a pH of 2.5, using a reactor equipped with a reticulated vitreous carbon (RVC) cathode and a platinum gauze anode. The results demonstrated that complete colour removal of 0.05, 0.1, and 0.3 mM Ponceau S could be achieved by electro-Fenton oxidation within 30, 60, and 90 minutes, respectively (Table 1).

M. M. Ghoneim et al. investigated the oxidation of Sunset Yellow FCF azo dye [3]. The experiments were carried out at room temperature using an undivided electrochemical reactor with an RVC cathode and a platinum gauze anode. Optimizing operational parameters (by using a 0.05 M Na_2SO_4 aqueous solution with a pH = 3, containing 0.1 mM $FeSO_4$, and controlling the applied potential of the RVC cathode at -1.0 V vs. SCE), the researchers achieved complete decolourization (100 %) of Sunset Yellow FCF azo dye through electro-Fenton oxidation. The treatment duration required to achieve this complete decolourization was 120 minutes (Table 1).

In a study published by M. O. A. Pacheco-Alvarez et al., they investigated the electrochemical degradation of various azo dyes, including Chocolate Brown HT and Eriochrome Black [9]. The Boron-doped Diamond electrode was used as cathode. The researchers conducted electrolysis with a current density of 20 mA cm^{-2}, treating a solution containing 150 mg/L of each dye at a pH range of 2.8–3.0. Under these conditions, the decolourization efficiency for Chocolate Brown HT dye, after 60 minutes, was 92 %. On the other hand, the use of Eriochrome Black dye led to nearly complete decolourization, approaching 100 % within the same timeframe (Table 1).

b. *Photo-Fenton Process*

Q. Chen et al. conducted a study where they prepared a heterogeneous photo-Fenton catalyst using iron pillared vermiculite (Fe-VT) [4]. In their experiment, they used a solution containing 100 mg/L of Reactive Brilliant Orange X-GN dye. A pH value of 3 and a hydrogen peroxide concentration of 3.92 mM were used. Additionally, a dosage of 0.5 g/L of Fe-VT catalyst was employed. With a UV irradiation time of 75 minutes, the results demonstrated that the system achieved an impressive decolouration efficiency of 98.7 % (Table 1).

In a study conducted by L. Wang et al., a Z-scheme heterogeneous system comprising flower-like Fe_2O_3 and nanosheet-like g-C_3N_4 was used for the photo-Fenton degradation of Amaranth dye [7]. By optimizing the experimental parameters such as pH value, H_2O_2 dosage, Fe_2O_3 loaded amount, the authors found that an 8 % Fe_2O_3/g-C_3N_4 catalyst exhibited excellent photocatalytic degradation activity

towards Amaranth dye. Remarkably, within 10 minutes of reaction time, the system achieved an impressive degradation efficiency of 97.6 % (as shown in Table 1).

C.-E. Tan et al. developed a mixed organic ligand composed of 2-methylimidazole and fumaric acid to enhance the photo-Fenton decomposition of Acid Red 1 azo dye [8]. The researchers demonstrated that the prepared catalysts exhibited remarkable adsorption capacity and photocatalytic efficiency. Specifically, in the presence of trace amounts of hydrogen peroxide, a 100 % removal of Acid Red 1 dye was achieved after only 45 minutes of irradiation. This impressive performance is highlighted in Table 1.

c. *Sono-Fenton Process*

G. Harichandran et al. conducted a study on the degradation of a reactive azo dye, Direct Red 81, using the Fenton process and in combination with sonolysis (Sono-Fenton) [6]. Through their investigation, they identified the following optimum conditions for decolourization: a pH value of 3.0, a ferrous ion concentration ($[Fe^{2+}]$) of 0.2 g/L, a hydrogen peroxide concentration ($[H_2O_2]$) of 5.1×10^{-3} mol/L, and ultrasonic parameters including a frequency of 120 kHz and a power of 60 W.

Under these optimized conditions, the system achieved an impressive decolourization rate of 99 % for Direct Red 81 within a total treatment time of 75 minutes [6]. The obtained results are summarized in Table 1.
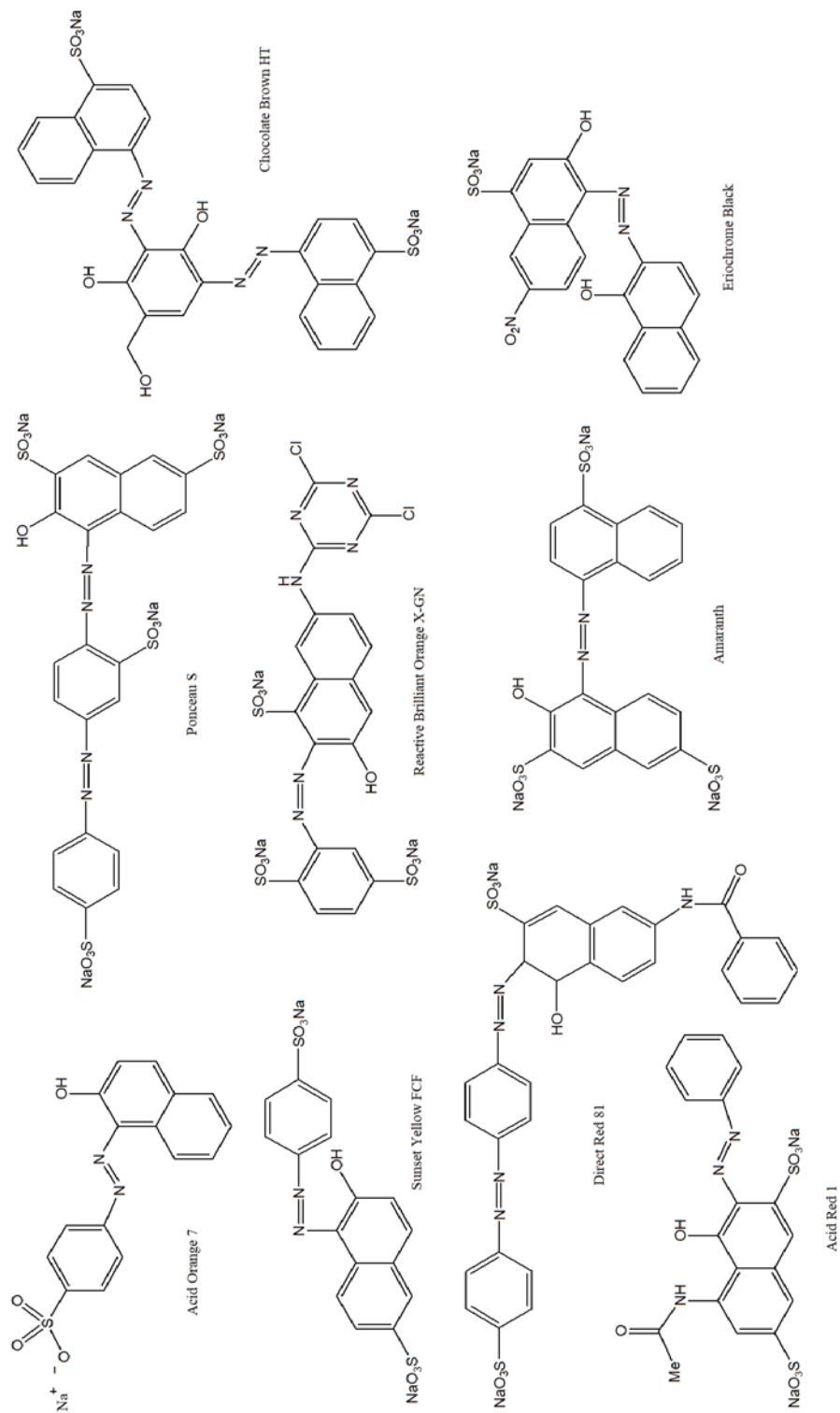
Figure 1 Chemical structures of studied azo

Table 2. Discoloration of various azo dyes by Fenton reagent

No	Name of dye	Degradation method	Λ_{max} (nm)	pH	Azo dye concentration	Discoloration time (min)	Discoloration (%)	Ref
1	Acid Orange 7	Electro-Fenton	485	3	0.1 mM	120	90	[1]
2	Ponceau S	Electro-Fenton	515	2.5	0.1 mM	180	100	[2]
3	Sunset Yellow FCF	Electro-Fenton	480	3	0.2 mM	120	100	[3]
4	Reactive Brilliant Orange X-GN	Photo-Fenton	479	3	100 mg/L	75	98.7	[4]
5	Direct Red 81	Sono-Fenton	523	3	50 mg/L	75	99	[6]
6	Amaranth	Photo-Fenton	522	3	0.03 mM	10	97.6	[7]
7	Acid Red 1	Photo-Fenton	532	-	100 mg/L	45	100	[8
8	Chocolate Brown HT	Electro-Fenton	424	3	150 mg/L	60	92	[9
9	Eriochrome Black	Electro-Fenton	580	3	150 mg/L	60	100	[10]

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4. CONCLUSION

This study describes the degradation of some azo dyes by electro-Fenton, photo-Fenton and sono-Fenton processes, respectively. Under the optimized conditions, the decolourization rates were ≥ 90 % for Acid Orange 7, Ponceau S, Sunset Yellow FCF, Reactive Brilliant Orange X-GN, Direct Red 81, Amaranth, Acid Red 1, Chocolate Brown HT and Eriochrome Black after 120 min (for Acid Orange 7 and Sunset Yellow FCF), 180 min (for Ponceau S), 75 min (for Reactive Brilliant Orange X-GN and Direct Red 81), 10 min (for Amaranth), 45 min (for Acid Red 1) and 60 min, respectively of treatment (for Chocolate Brown HT and Eriochrome Black).

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