

GREEN SYNTHESIS OF AZO DYES USING POLYMERIC RESIN

PROJECT REPORT

*Submitted to Calicut University
in partial fulfillment of requirements for the degree of*

BACHELOR OF SCIENCE IN CHEMISTRY

By,

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N.S.S COLLEGE OTTAPALAM
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CERTIFICATE

This is to certify that the project report entitled **“Green Synthesis of Azodyes using polymeric resin”** submitted to Calicut University in partial fulfillment of the requirements for the award of the **Degree of BACHELOR OF SCIENCE IN CHEMISTRY**, is a record of the original work done by **RAHUL V NAIR (OTARSIC025), SOORAJ T S (OTARSIC026), SREELAKSHMI C B (OTARSIC027) SUBEESH P (OTARSIC028), PRIYANKA V S (OTARSIC031)** N.S.S College, Ottapalam under my supervision and guidance.

Date:

Dr.Sindhu Ramachandran

CERTIFICATE

This is to certify that the project entitled “**Green Synthesis of Azodyes using polymeric resin**” is an authentic record of the project work done by **RAHUL V NAIR (OTARSIC025), SOORAJ T S (OTARSIC026), SREELAKSHMI C B (OTARSIC027) SUBEESH P (OTARSIC028), PRIYANKA V S (OTARSIC031)** under the supervision and guidance of Smt. K. USHA, Associate Professor of Chemistry, NSS College, Ottapalam, in partial fulfillment of the requirements for the **Degree of BACHELOR OF SCIENCE IN CHEMISTRY**.

Place:

Date:

Signature of HOD

Submitted to viva-voce examination held on..... at
N.S.S College, Ottapalam.

Examiners:

DECLARATION

I hereby declare that the project report entitled **“Green Synthesis of Azodyes using polymeric resin”** submitted to the University of Calicut in partial fulfilment of the requirements for the award of the **degree of BACHELOR OF SCIENCE IN CHEMISTRY**, is a record of genuine work done by us under the supervision and guidance of **Dr.Sindhu Ramachandran.**, Department of Chemistry, NSS College, Ottapalam.

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No achievements blossom with the lone effort of a single person. It is true in the case of my project entitled “**Green Synthesis of Azodyes using polymeric resin**” There are many heads and hearts behind this work to bring to the final form within the stipulated period.

First and foremost I thank god almighty who gave the courage and strength for bestowing me with patience for successful completion of the work.

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ABSTRACT

This project describes the green approach for the synthesis of azo-dyes by a simple and efficient method for the diazotization and coupling of aromatic amines over polymeric nitrite resin and coupling agent at room temperature .This green methodology aims to overcome the limitations and drawbacks of the previously reported methods such as use of concentrated acids, alkalis ,toxic solvents, release of hazardous waste or by product. Other advantages of this methodology are the use of mild reaction conditions, avoiding toxic gases, short reaction time. This project suggests a green and eco-friendly method by use of new materials and methods, which can reduce hazards of some current methods.

INTRODUCTION

Human's love of color reaches back almost to prehistoric times, yet it is not actually until the modern era that the full range of the rainbow has been accessible to the majority of people in their clothes and other textiles. Ancient or medieval times have often been described as being quite splendid with their "Tyrian Purple" and medieval scarlet, but closer examination shows that some of these colours were quite dull by today's standards.

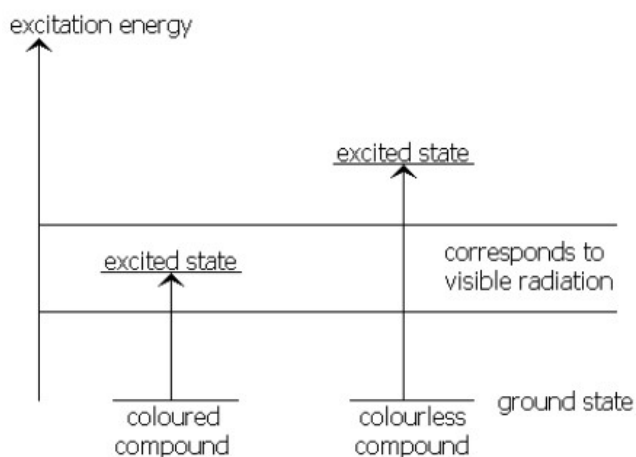
❖ DYES

Dyes are chemicals which bind to material and imparts color to that material. The color of a dye is due to the presence of chromophore group. They are widely used to color the substrate like textile fiber, paper, leather, hair, fur, plastic material, wax, a cosmetic base and food stuff. (Masitah Binti Hasan., 2008). Based on Chemical structure of chromophore there are 20-30 different groups of dyes. Azo (Monoazo, diazo, triazo, polyazo), anthraquinone, phthalocyanine and triarylmethane dyes are the most important groups (Safwat Mohammad., 2005). The majority of industrial important azo dyes belong to the following classes: Acid dyes, Basic dyes, Direct dyes, Disperse dyes, Mordant dyes, Reactive dyes and Solvent dyes. The Acid, Basic, Direct and Reactive azo dyes are ionic dyes (Anliker et.al., 1981). Dyes contain at least one nitrogen-nitrogen ($N=N$) double bond, however many different structures exist, For example, in the azo dyes, mono azo dyes have only one $N=N$ double bond, while diazo and triazo dyes contain two and three $N=N$ double bonds respectively. The azo groups are generally connected to benzene and naphthalene rings. These side groups are necessary for imparting the color of the dye, with many different shades and intensities being possible (Zollinger, 1991). These dyes have different absorption spectrum and associated with electronic transition between molecular orbital of synthetic dyes are produced annually worldwide. During dying process, a substantial amount of azo dye is lost in waste water (Ollgaard et al., 1998). Zollinger (1987) reported that about 10-15% of dyes were lost in effluent during dyeing process.

Chemistry of colour

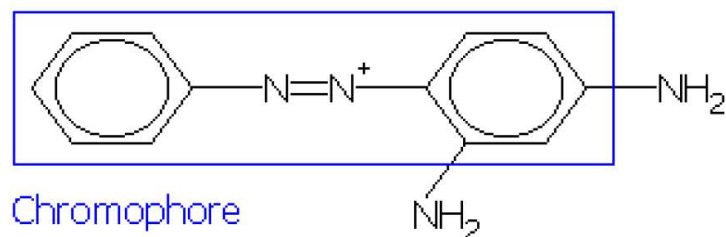
Coloured substances absorb radiation in the visible region of the spectrum. The energy absorbed causes changes in electronic energy. Electrons are promoted from a ground state to an excited state. The electrons excited in this case are the outer bonding electrons or lone pairs.

Not all electronic transitions are brought about by visible light as some require ultra-violet radiation. Those which absorb UV radiation appear colourless (unless they fluoresce). The energy needed to excite an electron in a coloured compound and in a colourless compound is shown below:



Coloured Organic Compounds

A dye molecule is built up from a group of atoms called a chromophore, which is largely responsible for its colour. Chromophores contain unsaturated groups such as $C=O$ and $-N=N$, which are often part of an extended delocalised electron system involving arene rings. Chrysoidine is a basic dye shown below:



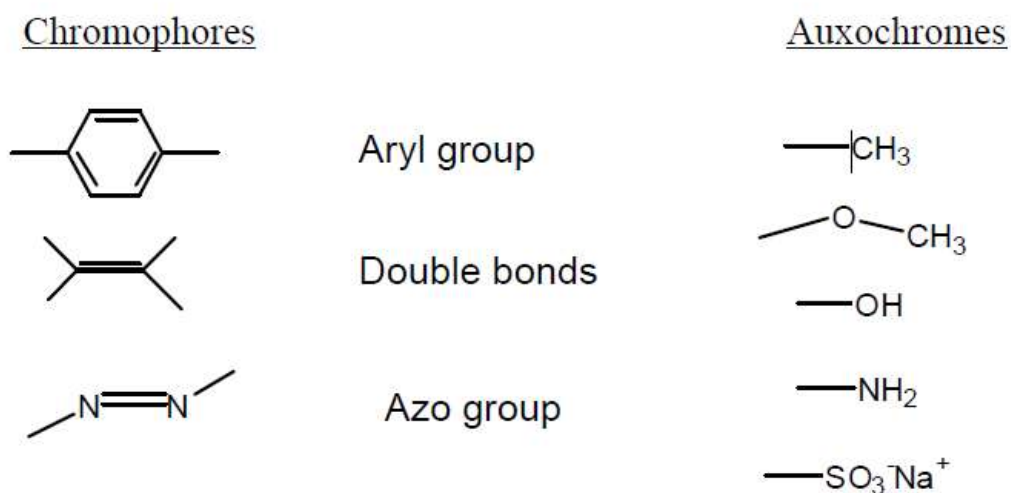
Azo dyes contain at least one nitrogen-nitrogen double bond ($\text{N}=\text{N}$); however many different structures are possible. Monoazo dyes have only one $\text{N}=\text{N}$ double bond, while diazo and triazo dyes contain two and three $\text{N}=\text{N}$ double bonds, respectively. The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups. These side groups are necessary for imparting the color of the dye, with many different shades and intensities being possible. When describing a dye molecule, nucleophiles are referred to as *auxochromes*, while the aromatic groups are called *chromophores*. Together, the dye molecule is often described as a *chromogen*. Dyes are organic molecules that selectively absorb wavelengths of light within the visible range of the electromagnetic spectrum (400-800 nm). The human eye responds to wavelengths within this range. The white light we receive from the sun contains all the wavelengths within the visible range. When an object absorbs a particular wavelength, we see the wavelengths that are left over, and the object appears colored. Filtering orange light out of “white” light, for example, results in blue-green (cyan) hue. The hue resulting from the removal of a color from white light is the latter’s complementary color.

Complementary Colors

Color absorbed	Wavelength absorbed (nm)	Color observed
Red	647-700	Green
Orange	585-647	Cyan (green-blue)
Yellow	570-585	Blue
Green	491-570	Red
Blue	424-491	Yellow
Violet	400-424	Yellow-green

So now what determines what wavelength is absorbed? The color in dyes is the consequence of the presence of a chromophore. Chromophores in dyes are generally large systems of conjugated double bonds (alternating double single bonds). It is this delocalized electron system that absorbs the energy from the light. For example, if the electrons in the dye require only a small amount of energy to be rearranged into new energy state, then the substance absorbs a low energy wavelength (λ). The longer the wavelength the lower the energy ($E = hc/\lambda$). If you look at the Table above you will see that the longest wavelength is associated with the absorption of red light. If the incident light is white and red light is absorbed, then the light reflected is perceived as green (the complementary color of red). If a lot of energy is required for the electrons promoted to a higher energy state, then it absorbs only a short wavelength light, since short wavelengths correspond to high energy. If it absorbs blue light, then the light it reflects is perceived as yellow. In general, the more conjugation (more double bonds) you have in a dye the less energy it takes to excite the electrons. But there is more to it than that. While the chromophore is the color-producing portion of the dye molecules there are other factors. Dyes also contain auxochromes, which are a group of atoms attached to a chromophore that modify the ability of that chromophore to absorb light. In general, auxochromes influence the intensity of the dye; but they can also provide a site by which the dye can chemically bond to the fabric.

Examples of chemical groups that are chromophores and auxochromes are shown below.



❖ EARLY HISTORY

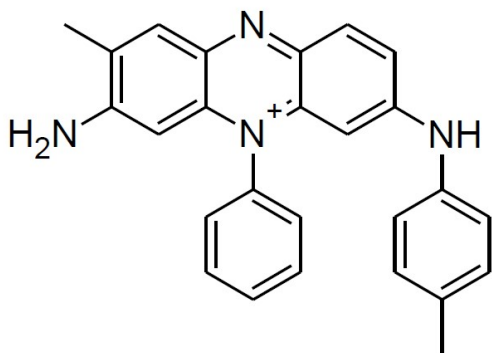
The history of dyeing can be divided into two great periods, the "pre-aniline," extending to 1856 and the "post-aniline" period. The former was characterized by a rather limited range of colors that were based on dye-producing animals and plants. The main vegetable dyes available were extracted from madder root (Asia and Europe), producing a brilliant red and leaves of the indigo plant (India), yielding the blue dye still used today in jeans. Among the most important animal based dyes is the famous and expensive "TyrianPurple" which was obtained from the small shellfish nurez. We have the ancients' word that this dye was unbelievably beautiful, but evidence taken from ancient samples prove that it ranges through a rather uninspiring series of reds and purples. After seeing it, we wish that Homer had written about some of today's inexpensive coal-tar purples and reds. A far more beautiful natural color was introduced to Europe from Mexico in 1518, the brilliant scarlet dye cochineal, which had been produced from tiny lice which infest certain types of cactus.

In 1856 William Henry Perkin accidentally discovered the world's first commercially successful synthetic dye. Ten thousand of new synthetic dyes have been developed and manufactured by the end of the 19th century (Ishikawa et al., 2000; Robinson et al., 2001). The synthetic dyes are defined as colored substances when applied to fibers and give them a permanent color which designed to resist fading upon exposure to sweat, light, water, and many chemicals including oxidizing agents and microbial attack (Rai et al., 2005). A well-flourished textile industrial development has originated increasing use of a wide variety of synthetic dyes and pollution by wastewater contaminated with dyestuff is becoming increasingly alarming worldwide (Pandey et al., 2007). The water consumption and the wastewater generation from a textile industry (dry processing mill and woven fabric finishing mills) depends upon the processing operations employed during the conversion of fiber to textile fabric (Dhanve et al., 2008). However, the textile industry is one of the greatest generators of liquid effluent pollutants, due to the high quantities of water used in the dyeing processes. Moreover, processing stages and types of synthetic dyes applied during this conversion determine the variable wastewater characteristics in terms of pH, dissolved oxygen, organic, and inorganic chemical content etc (Banat et al., 1996; Kalyani et al., 2008).

It is estimated that 280,000 tones of textile dyes are discharged in such industrial effluents every year worldwide (Jin et al., 2007).

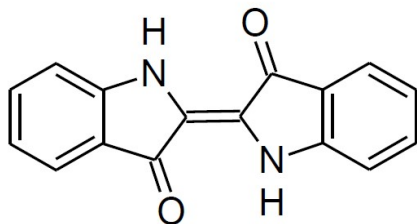
❖ MODERN HISTORY

Aniline ($C_6H_5-NH_2$) became available from coal tar in the 19th century and in 1856, William Henry Perkin at the age of 17 used it in the synthesis of Mauveine (a mixture of 4 compounds, one of which is shown below). The era of synthetic dyes was born



Structure of Mauveine A

Soon thereafter, the main component of the dye in the madder root, Alizarin, was isolated by Carl Graebe and Carl Liebermann, prepared in the lab and the process commercialized. Starting in 1865, recognizing the potential of synthetic dyes, Adolph von Baeyer researched the synthesis of indigo and determined its structure and first synthesis in 1870.



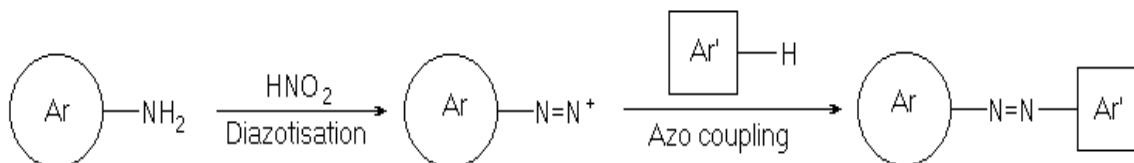
Structure of Indigo

In 1897 the large scale industrial synthesis of indigo started and rapidly reached 10,000 tons a year, completely replacing the agricultural production since prehistoric times, man has been dyeing cloth.

❖ SYNTHESIS OF AZO DYES

Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophiles. Amino- and hydroxy-groups are commonly used coupling components. Because of the diversity of dye components available for synthesis, a large number of structurally different azo dyes exist and are used in industry. Worldwide production of organic dyes is currently estimated at nearly 450,000 tons, with 50,000 tons being lost in effluents during application and manufacture. Azo dyes are prepared in a two step reaction, the first being the synthesis of an aromatic diazonium ion from an aniline derivative. The next step is coupling of the diazonium salt with an aromatic compound.

An overview of azo dye synthesis is shown below:



Stage 1- Diazotisation

This involves a primary aromatic amine, called the diazo component. It is treated in low temperature, acid conditions with sodium nitrite to form an unstable diazonium salt.

Stage 2- Azo coupling

The diazonium salt is reacted with a coupling component (for example a phenol or an aromatic amine). This forms the stable azodye. Together, the dye molecule is often described as a *chromogen*. Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophiles. Amino- and hydroxy- groups are commonly used coupling components. Because of the diversity of dye components available for synthesis, a large number of structurally different azo dyes exist and are used in industry. Worldwide production of organic dyes is currently estimated at nearly 450,000 tons, with 50,000 tons being lost in effluents during application and manufacture.

IMPACT OF AZO DYES

Azo dyes produce clear and strong colors. They are primarily used for colored cotton, leather, cosmetics, and food. Azo dyes belong to a group of organic compounds. The azo group of dyes binds to an aromatic ring. Through mineralization, these dye can be broken down into an aromatic amine, an arylamine that is suspected to be carcinogenic. Most of the azo dyes are water soluble and readily absorb through skin contact and in halation leading to the risk of cancer and allergic reactions, an irritant for the eyes and highly toxic, if inhaled or consumed (Nikulina, Deveikis and Pyshnov, 1995). For example, Para-phenylenediamine (PPD) also called 1,4-diaminobenzene or 1,4-phenylene diamine, is an aromatic amine, which is a major component of azo dyes. PPD-containing azo dyes are toxic and causes skin irritation, contact dermatitis, chemosis, lacrimation, exophthalmos, and permanent blindness. Ingestion of PPD products leads to the rapid development of oedema on face, neck, pharynx, tongue and larynx along with respiratory distress.

SAFETY AND REGULATION

Many azo pigments are non-toxic, although some, such as dinitroaniline orange, ortho-nitroaniline orange, or pigment orange 1, 2, and 5 have been found to be mutagenic. Likewise, several case studies have linked azo pigments with basal

cell carcinoma. Azo dyes derived from benzidine are carcinogens; exposure to them has classically been associated with bladder cancer. Accordingly, the production of benzidine azo dyes was discontinued in the 1980s "in the most important western industrialized countries". Avoid skin contact with all the chemicals, work under the hood, and wear gloves throughout the experiment.

- The nitroanilines and naphthols are highly toxic. Prevent skin contact.
- Sodium hydroxide and hydrochloric acid are corrosive.
- Sodium nitrite is a toxic oxidizer.
- Diazonium salts are explosive in the solid form. Keep them in solution and cold.
- Azo dyes are irritants.

❖ APPLICATIONS OF AZO-DYES

As a consequence of π -delocalization, aryl azo compounds have vivid colors, especially reds, oranges, and yellows. Therefore, they are used as dyes, and are commonly known as azo dyes, an example of which is Disperse Orange 1. Some azo compounds, e.g., methyl orange, are used as acid-base indicators due to the different colors of their acid and salt forms. Most DVD-R/+R and some CD-R discs use blue azo dye as the recording layer. The development of azo dyes was an important step in the development of the chemical industry.

Azo pigments consist of colorless particles (typically earths or clays) colored using an azo compound. Azo pigments are important in a variety of paints including artist's paints. They have excellent coloring properties, again mainly in the yellow to red range, as well as good light fastness. The light fastness depends not only on the properties of the organic azo compound, but also on the way they have been absorbed on the pigment carrier.

Azo dyes acquired wide interest in application to biological system and indicator in complexometric titration of analytical chemistry. Azo dyes are the most important group of synthetic colorants. They are generally considered as xenobiotic compounds that are very recalcitrant against biodegradative processes. Aromatic azo compounds especially are used as acid-base indicators, also used in biological strains and commercial colorants for clothing, plastics, cosmetics and food beverages. Color changes are caused by change in extent of delocalization of electrons. More delocalization shifts the

absorption max to longer wavelengths and makes the light absorbed redder, while less delocalization shifts the absorption max to shorter wavelengths.

In pharmaceutical, azo linkage was used to protect drug from undesirable reaction, such as prontosil was found to protect against, and cure streptococcal infections in mice. Interestingly prontosil was inactive on bacterial cultures. Prontosil is totally inactive in vitro but possesses excellent activity *in vivo*⁴. Due to the highly variable nature of biological treatment systems and especially textile effluents, there are a number of factors that may affect the biodegradation rate of azo dyes. Throughout the literature, researchers have discussed various problems associated with dye biodegradation that may or may not be anticipated or remedied. Non-dye related parameters such as temperature, pH, type and source of reduction equivalents, bacteria consortium, and cell permeability can all affect the biodegradation of azo dyes and textile effluents. Dye related parameters such as class and type of azo dye (*i.e.* reactive-monoazo), reduction metabolites, dye concentration, dye side-groups, and organic dye additives could also affect the biodegradability of azo dye wastewaters.

The azo dye structure can play a significant role in the dye biodegradation rate. Depending on the number and placement of the azo linkages, some dyes will biodegrade more rapidly than others. In general, the more azo linkages that must be broken will cause the reduction rate to be slower. While there are not a large number of studies that specifically address this factor, Brown and Laboureur observed that two poly-azo dyes showed only moderate to variable biodegradation as compared to four monoazo and six diazo dyes. The authors indicate that poly-azo dyes are less likely to be degraded than mono- or diazo dye types.

The azo dye sulfonamides antibacterial drugs were the first effective chemotherapeutic agents that could be used systemically for the cure of bacterial infection in humans. A series of azo dyes containing the sulfonamide functional group were synthesized as potential antimicrobial agents, sulfonamide was classified into three different types; antibacterials that are aniline-substituted sulfonamides, prodrug that react to generate active sulfanilamides and nonanilin sulfonamides. There are also other commonly used drugs that are azo dyes sulfonamides or sulfanilamides (the diuretic furosemide, the diuretic chlorthalidone and the oral hypoglycemic drug tolbutamide). Today, there are a few sulfonamides and especially sulfonamide-trimethoprim combination that are used extensively for opportunistic infection in the patients with AIDS.

GREEN PROCEDURE FOR SYNTHESIS OF AZO-DYES

Usually diazotization–coupling of aromatic amines is carried out in two steps by means of sodium nitrite in a strongly acidic medium (H_2SO_4 , HCl) at low temperature or by means of alkyl nitrites in organic solvents followed by reaction with coupling agent in presence of alkali. Both of these approaches to the diazotization step do not meet the requirements of green chemistry for the following reasons. First, the use of sodium nitrite as the diazotizing agent is almost always accompanied by the release of nitrogen oxides, an issue particularly with industrial-scale reactions. Second, the isolation of products from strongly acidic solution requires a neutralization stage, which generates large quantities of salts. In addition, a strongly acidic environment for the diazotization cannot be tolerated by amines containing acid-sensitive functional groups. The alternative reagents, alkyl nitrites, are not very suitable for diazotization on an industrial scale, since they are expensive, decompose during storage, and are corrosive. Moreover, alkyl nitrites generally can diazotize aromatic amines only in organic solvents (e.g., Et_2O , MeCN , THF), but not in water. It should also be taken into account that diazonium salts obtained under classical conditions are potentially explosive substances.

Little work on the diazotization of aromatic amines in a weakly acidic medium using nontoxic, nonflammable, and explosive-free conditions has been reported. Tundo et al. reported a diazotization–iodination with sodium nitrite and potassium iodide in a liquid carbon dioxide/water solvent system at 65 bar for a small number of anilines; however, in some of the cases, diazotization was accompanied by the formation of triazenes and biphenyls. A convenient and rapid method for the synthesis of iodoarenes in good yields has recently been developed; it involves the sequential diazotization–iodination of aromatic amines with sodium nitrite, solid silica sulfuric acid, and potassium iodide by grinding in a mortar.

This method proved to be applicable to various aromatic amines, but the grinding of the reaction components in a mortar cannot presently be implemented on a large scale, and the diazotization stage was accompanied by the release of nitrogen oxides, as is common with other diazotization conditions using sodium nitrite. A solvent-free, efficient and green approach for the synthesis of azo dyes has been developed by the diazo coupling

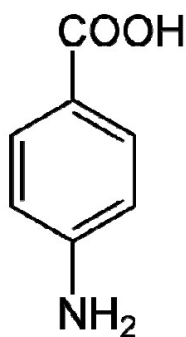
reactions of aromatic amines with β -naphthol in the presence of sulfonic acid functionalized magnetic Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$) by a grinding method at room temperature. This green methodology aims to overcome the limitations and drawbacks of the previously reported methods such as low temperature, use of acids, alkalis and toxic solvents, instability of diazonium salts at room temperature, modest yields, and long reaction times. Moreover, the attractive advantages of the process include mild conditions with excellent conversions, simple product isolation process, inexpensive procedure and recyclability of the magnetic catalyst.

A series of azo dyes were efficiently synthesized by mixing aromatic amines and NaNO_2 in the presence of nano silica supported boron trifluoride (nano $\text{BF}_3\cdot\text{SiO}_2$) and then diazo coupling with 1-naphthol under solvent-free conditions at room temperature. The present methodology has proven to be simple, rapid, environmentally benign, green, and cost-effective compared with previous synthetic methods. Also, by using this procedure, aryl diazonium salts supported on nano $\text{BF}_3\cdot\text{SiO}_2$ were very stable to be kept at room temperature for several months without any special conditions.

Recently we have shown that a sulfonic cation-exchange resin, p-toluenesulfonic acid (p-TsOH), or sodium hydrogensulfate are mildly acidic agents for the diazotization–halogenation of aromatic amines with sodium nitrite or tert-butyl nitrite in acetonitrile, water, or water pastes. However, the use of sodium nitrite or alkyl nitrite in these methods makes the release of gaseous nitrogen oxides difficult to avoid, and the above-mentioned problems with scaling up the process would still be an issue. Thus, the development of a new method to circumvent these problems is necessary. We have also recently shown that anion exchange resins saturated with nitrite ions from sodium nitrite are convenient and mild polymer-supported diazotization reagents. Until now, this reagent has not been used for the diazotization of aromatic amines in water or for one-pot diazotization–iodination reactions. We have found that simply stirring ‘Resin NO_2^- ’ with the aromatic amines in water in the presence of p-toluene sulfonic acid at room temperature for 20–30 minutes leads to complete conversion of the starting amines. The azo dyes possess antiseptic and antiprotozoal properties and also promote wound healing. The cationic dyes are more active in acidic medium and preferably attack on Gram positive bacteria as compared to anionic dyes. Most common azo dyes used as antiseptics are scarlet red & diamazon. The medicinal properties of azo compounds particularly synthesized from acetylsalicylic acid, thymol, aldimine and β -naphthol etc. have been frequently reported. However, paucity of

information could be traced on the synthesis of azo compound containing para-aminobenzoic acid.

Para-aminobenzoic acid is a naturally occurring compound, found in liver, kidney, wheat germ, bran, and yogurt. Furthermore, Para-aminobenzoic acid is involved in different biochemical reactions in living systems. Hence, we have opted Para-aminobenzoic acid for biomimetic growth of calcium carbonate. Since Para-aminobenzoic acid is consisting of both carboxylate and amino functionalities analogous to aromatic amino acids, a similar function is expected to control the nucleation and growth of calcium carbonate.



Structure of Para-amino benzoic acid

4-Aminobenzoic acid (also known as para-aminobenzoic acid or PABA because the number 4 carbon in the benzene ring is also known as the para position) is an organic compound with the formula $\text{H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$. Para-amino benzoic acid, a white-grey crystalline substance, is only slightly soluble in water. It consists of a benzene ring substituted with an amino group and a carboxyl group.

Para-amino benzoic acid finds use mainly in the biomedical sector. Other uses include its conversion to specialty azo dyes and crosslinking agents. In the past, Para-amino benzoic acid was widely used in sunscreens as a UV filter. It is a UVB absorber, meaning it can absorb wavelengths between 290 and 320 nm. Patented in 1943, Para-amino benzoic acid was one of the first active ingredients to be used in sunscreen.^[11] The first *in vivo* studies on mice showed that Para-amino benzoic acid reduced UV damage. In addition, it was shown to protect against skin tumors in rodents. Animal and *in vitro* studies in the early 1980s suggested Para-amino benzoic acid might increase the risk of cellular UV damage. On the basis of these studies, as well as problems with allergies and clothing discoloration, Para-

amino benzoic acid fell out of favor as a sunscreen. However, water-insoluble Para-amino benzoic acid derivatives such as aspadimate O are currently used in some products.

This project is about the concept of the environmentally friendly design of chemical products and processes.

Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances. Whereas environmental chemistry is the chemistry of the natural environment, and of pollutant chemicals in nature, green chemistry seeks to reduce the negative impact of chemistry on the environment by preventing pollution at its source and using fewer natural resources. The goal of green chemistry is the minimizing the hazards waste or byproduct, reagents are reused, toxicity eliminator, and maximizing the efficiency of any chemical choice.

Normally azo dyes were prepared in a two step reaction, the first step being the synthesis of an aromatic diazonium ion from an aniline derivatives. The next step is coupling of the diazonium salt with an aromatic compound. so in this preparation we use concentrated acids, alkali, toxic solvents. This cause harmful effect on both man and environment. And also toxic gases are evolved during the reactions by the use of concentrated acids and alkali. This toxic gases are harmful to human being. And also hazards waste are generated during the reaction this waste are discharged into environment cause environmental pollution. In industries large amount of azo dye prepared using normal method which cause large amount of waste and toxic gases. The green chemistry aims to overcome the limitation and drawbacks of the previously reported methods.

AIM AND OBJECTIVE

- To prepare series of azo-dyes from para-aminobenzoic acid in a green approach.
- This procedure describes simple and efficient method for the diazotization and coupling of aromatic amine over polymeric nitrite resin and coupling agent at room temperature.
- A dye is used to impart color to material of which it become an integral part of human life. Azodyes account for the major produced synthetic dyestuff because

they are extensively used in textile, leather, pharmaceutical and cosmetic industries, pose a threat for all life forms.

- Melting points were determined.
- The synthesized Dyes were characterized using IR spectroscopy.

MATERIALS AND METHODS

CHEMICALS

Standard reagents and chemicals of analytical grade were used. All the chemicals and solvents used for the study were purchased from MERCK.

1. Preparation Of Azodye From p-amino Benzoic Acid And Paracetamol (Normal Method)

a) Chemicals used

p-aminobenzoic acid, sodium nitrite, Dilute HCl, , sodium hydroxide

b) preparation of diazo compound

About 3.6459 moles of p-amino benzoic acid (500mg) taken in a 100ml beaker. Dissolve in 2N, 5ml dil.HCl and few drops of con.HCl. Then the beaker is placed in water bath contain ice. Then it is stirred using magnetic stirrer in 5min. About 400mg of sodium nitrite weighed and dissolved in minimum amount of water in test-tube, placed in ice. About 0.447g paracetamol weighed and it is dissolved in 10ml, 25% NaOH in 100ml beaker. After 5min the NaOH added slowly to the stirring acid, with wood stirring. After 20min the diazotization complete. The paracetamol in NaOH solution added. The reaction proceeds with stirring and solid precipitate formed. The precipitate are the crude azodye.

2. Preparation Of Azodye From P-Amino Benzoic Acid (Using Synthetic Resin)

a) Chemicals Used

Para amino benzoic acid, NaOH, HCl, NaNO_3 , resin.

b) Method

Preparation of polymer bound nitrite (occasionally this can be purchased, but is quite expensive).

Amberlyst A-26 strongly basic ion exchange resin was stirred over night at room temperature in 2M aqueous solution of sodium nitrite and stirred for 1hr. the polymer bound nitrite was isolated by filtration, washed with distilled water and allowed to air dry.

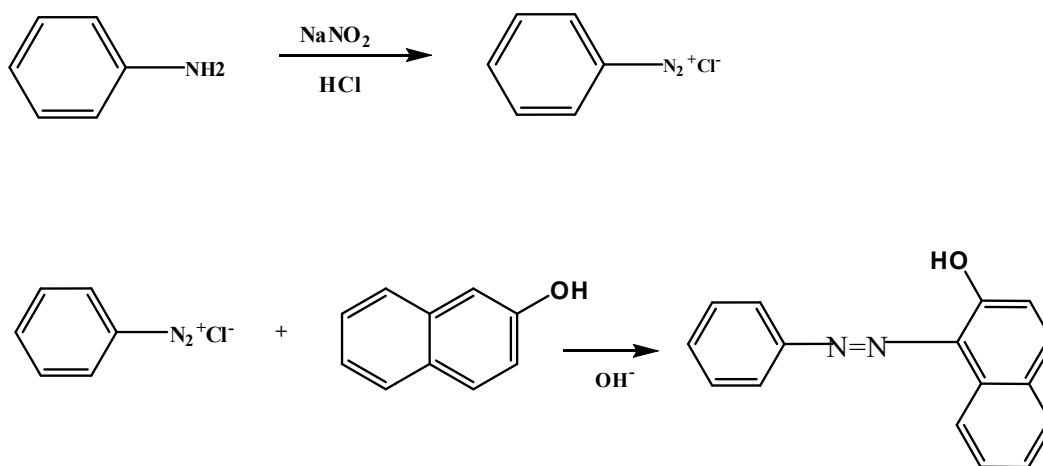
Preparation of diazo compound

- About 100mg para amino benzoic acid taken in a 100ml beaker. Dissolved in 4ml, 37% dil.HCl . Then the beaker is placed in water bath containing ice. About 701g of polymeric nitrite ion prepared above is weighed and it is added to the above solution. Then it is stirred using magnetic stirrer in 5min. After 5min, the solution is filtered to 100mg of coupling agents (paracetamol, 1-Naphthol, 2-Naphthol, Phenol, Methyl salycilate, Salycilic acid) dissolved in 8ml NaOH solution in a beaker. Then it is stirred for 20min. After 20min the solid precipitate formed. The precipitate are the crude azodye.

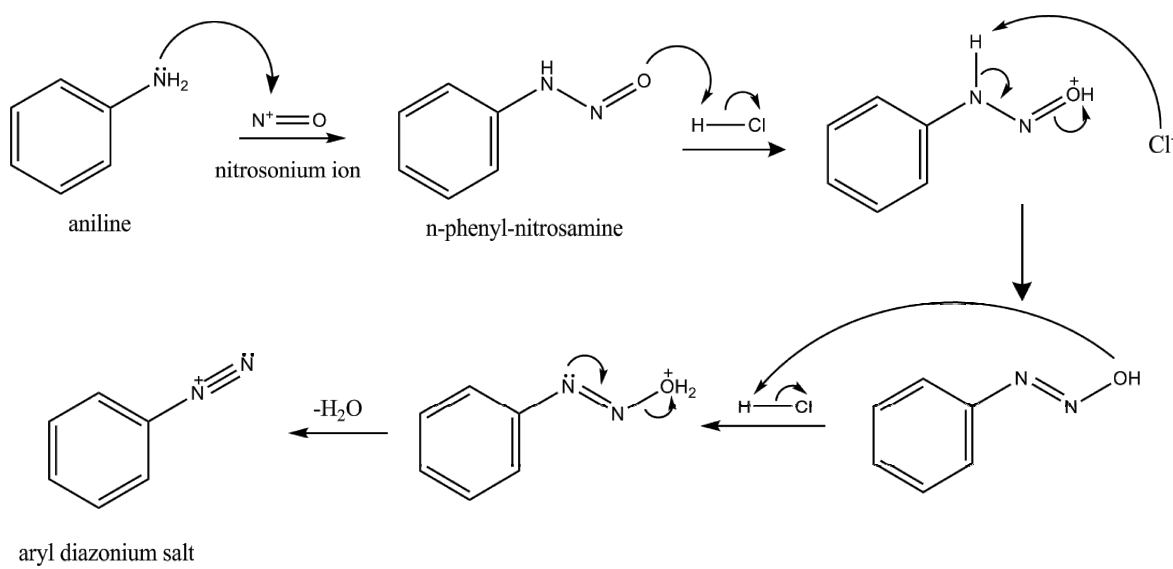
RESULTS AND DISCUSSION

The synthesis of an azo dye requires two organic compounds- a diazonium salt and a coupling component. The general synthesis of azo dyes is shown below:

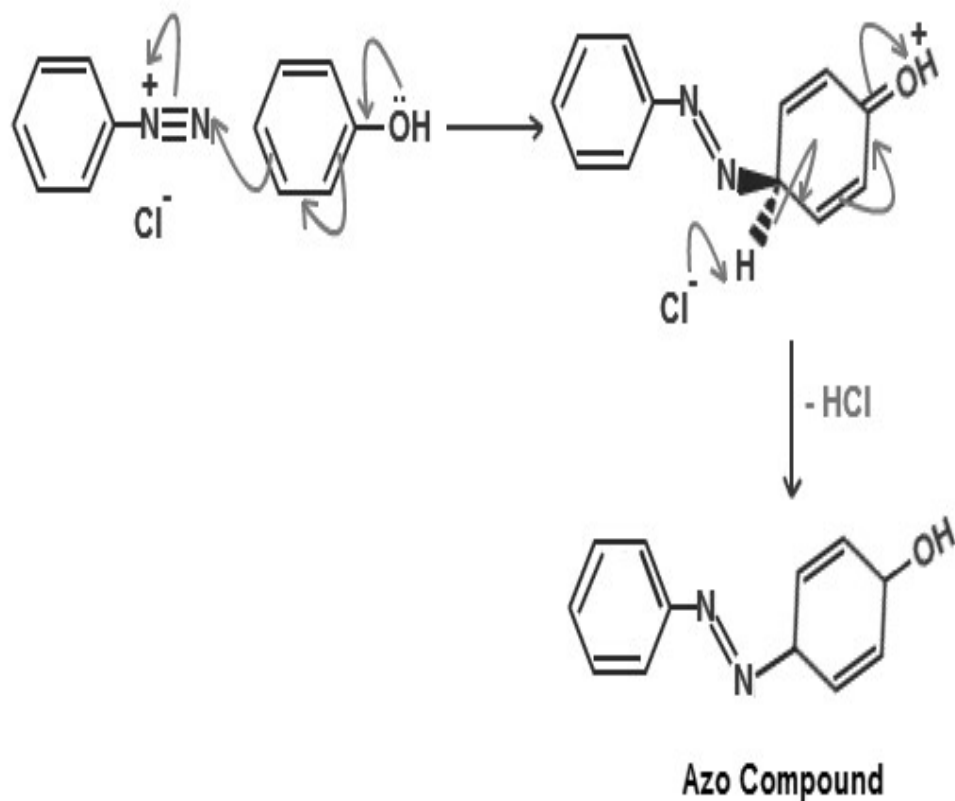
Synthesis of a dye



Mechanism of diazotisation



Coupling Reaction-Mechanism



The diazonium salt reacts as an electrophile with an electron-rich coupling component, like a β -naphthol, phenol and naphthalene derivative through an electrophilic aromatic substitution mechanism. The hydroxyl group (such as β -naphthol) direct the aryl diazonium ion to the para site unless that position is occupied, in which case the ion attaches ortho. (7. Kucharski S and Janik R, *New J Chem.*, 1999, **23**, 765).

The prepared products as azo dye were characterized by various available techniques. The infrared spectroscopy is one of the efficient techniques used in the characterization of organic compounds. FTIR was used in the present study to confirm the presence of functional groups. IR spectra of all seven series of acid azo dyes contain aromatic nuclei, azo group carbonyl and hydroxyl group. The strong band in the region 1712-1730 shows the carbonyl

group of p-aminobenzoic acid. The strong band at 1460-1483 cm^{-1} appeared in the spectra confirms the presence of azo ($-\text{N}=\text{N}-$) group. The broad band around 3445-3540 shows the presence of hydroxyl group. The weak bands observed 2890- and 2950 cm^{-1} which is attributed to the $-\text{C}-\text{H}$ stretching vibration. A polymer-supported reagent has been used to generate arenediazonium chlorides in aqueous hydrogen chloride. 'Resin NO_2- ' is readily obtained and is stable to storage at room temperature in a moist state for at least one month. In these reactions, the release of nitrogen oxides or other gaseous substances was never observed. After filtration of the resin, a pure and stable aqueous solution of the corresponding arenediazonium salt was obtained. The filtered diazonium salt will couple with alkaline solution of coupling agents to give dyes. Here we are using p-aminobenzoic acid for diazotization and the diazotized compound is coupled with alkaline coupling agent solutions. The NO_2 resin after diazotization can be reused which is another advantage of the method.

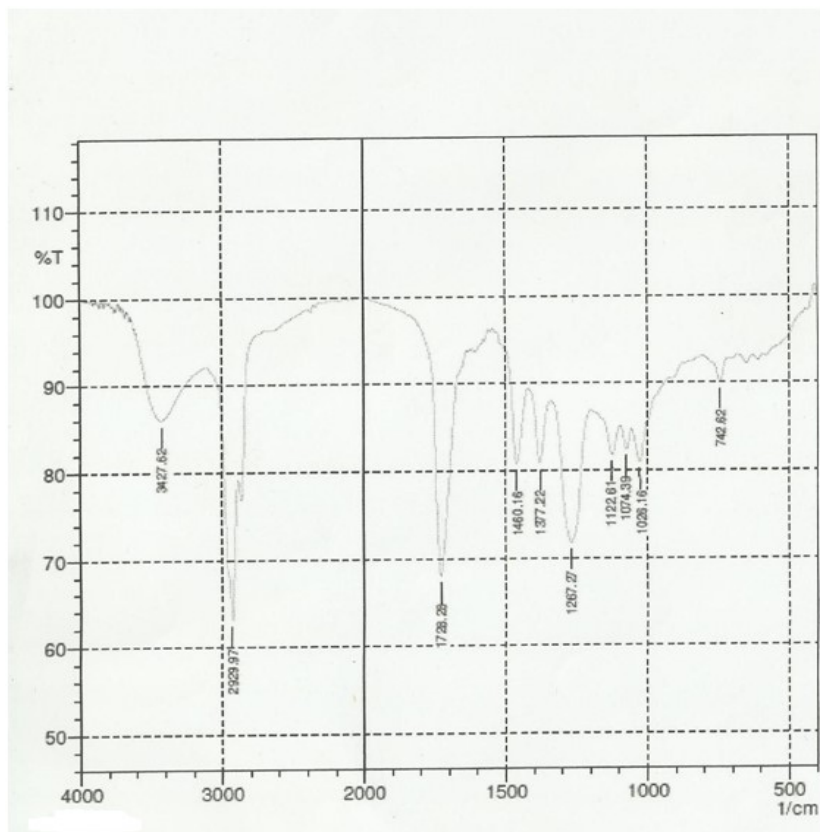
The visible absorption spectroscopic properties of the all dyes were recorded in DMF. The absorption maximum (λ_{max}) of all the dyes falls in the range 418-516 nm in DMF.

Table I ; Physical properties of azo dyes and characteristic IR bands

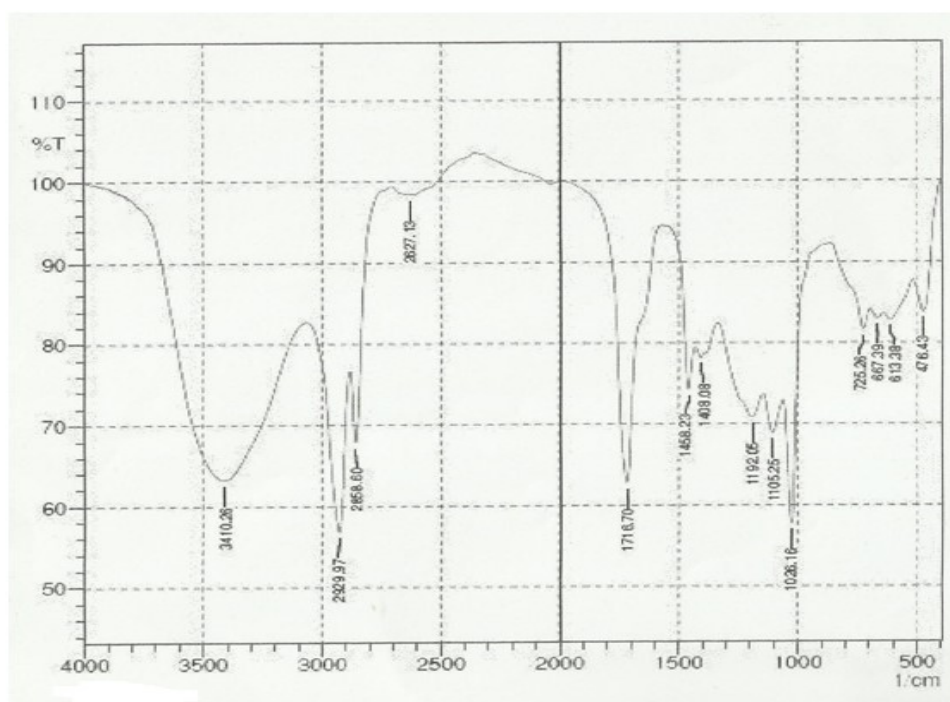
Coupling agent	Colour	Yield	M.p	Characteristic IR bands(cm-1)			
				ν OH	ν C-H	ν C=O	ν N=N
2-Naphthol	Red	66%	>240	3427	2929	1728	1460
1-Naphthol	Deep Brown	65%	>240	3410	2929	1716	1458
Aniline	Golden yellow	58%	150	3443	2928	1681	1454
Methyl Salicylate	Orange Red	63%	>250	3443	2930	1730,1651	1462

IR STUDIES

- IR Spectra of Compound a; Azo dye of p-aminobenzoic acid and 2-naphthol



IR Spectra of Compound b; Azo dye of p-aminobenzoic acid and 1-naphthol



CONCLUSIONS

The green approach for the synthesis of azo-dyes has been developed by the diazo coupling reactions of aromatic amines with coupling agents in the presence of synthetic resin. This green methodology aims to overcome the limitations and drawbacks of the previously reported method such as the

- use of concentrated acids, alkalis and toxic solvents.
- Release of hazardous or toxic gases
- NO₂ resin can be reused
- Normal conditions of reaction and moderate high yield

So this environment friendly method can be used for large scale preparation of azodyes .

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