2.1 REVIEW OF LITERATURE

That benzene sulphonamides have been reported to an non carcinogenic and used as intermediates in the synthesis of azo dyes [1-12]. It have been reported that 4-amino-N-(4-aminophenyl) benzene sulphonamide compounds and 1,2-bis-sulphanilylamino-ethane[13] were substituted for benzidine to synthesize azo dyes.

Data’s in the literature firmly shows that the established of crystal formation by single crystal X-ray crystallography that only one of the two azo-nitrogen is coordinated to the central metal atom in the commercially tridentate diarylazo dye complexes, and that a different coordinating nitrogen affects the colouring properties, several attempts have been made to find methods for assignment of the legating azo nitrogen in unsymmetrically substituted o-dihydroxydiarylazo-complexes (Na-Nb-isomerism), and to describe the factors determining this type of isomerism. Very few unambiguous coordinating nitrogen assignments have been made, which should be compared to the large number of complexes reported [14 - 16]. In order to overcome the solubility problem and facilitate the full assignment [17] of the C¹³ – spectra by heteronuclear NMR correlation technique, a number of soluble square planne, a number of soluble square planner platinum complexer platinum complexes have been designed and synthesized. Mono anionic octahedral chromium (III) – and cobalt (III) complexes with two o- dihydroxy-diarylazo ligands would be expected to exist in
six different isomers, one meridional and five facial [18]. It has been found that
the type of isomer formed is determined by the resulting angular strain of the
chelate rings. It is generally stated that tridentate diarylazo ligands, which form
one five membered and one six membered chelate ring with the central metal
atom, coordinate in the meridional mode, while tridentate diaryl azo ligands
forming two annelated six –membred chelate rings form facially coordinated
complexes. The evidence for this assumption is largely the number of isomers
formed and separated by chromatography [19-21].

In major literature the azo compounds constitute the largest and the most
diverse group of synthetic dyes with application not only as textile colourants but
in many other industrial fields for colouring different substrates, biological
medical studies, in the field of non linear optics and optical data storage [22-24].
A systematic approach to the design of new dyes [25-27]. Structure information
obtained from single crystal X-ray diffraction analysis including confirmation,
stereochemistry, intra and inter molecular interactions are in relation with optical
properties as well as with technical properties of azo dyes and pigments [28].

It has been reported that arylazopyridones have excellent colouration
properties [29-31]. Very few investigations have been published with respect to
the metal complexes of azopyridone dyes. Wang et al. reported the synthesis of
some Cr(III) complexes of o,o’- dihydroxyazo pyridine dyes [32] but the Cu(II)
complexes of azopyridone compounds have not been developed.

A perusal of the literature have been suggested novel alkali azo disperse
dyes containing a sulfonyl fluoride group. Azo disperse dyes containing a fluoro
sulfonly group are hydrolyzed under alkaline condition by SN2 mechanism, and pseudo first order kinetics were determined by analysis of the dye hydrolysis under alkaline conditions using HPLC. And also it has been reported that the synthesis of some diazo components and the subsequent mono azo disperse dyes containing a fluorosulfonyl group, 4-(N,N-diethylamino)-4-fluorosulfonylazobenzene derivatives [33-37] as well as the spectral properties of the various dyes prepared.

Dickey,j.B.et al., has been investigated that monoazo dyes based on 2-amino-5-nitrothiazole 4 and 5-acetyl-2-amino-3-nitrothiophene-1 has a colourants and it is commercially desirable showing bathochromism. However, whereas the marketing of thiazolylazo dyes followed, the use of the thienylazo derivatives was not viable industrially owing to the unfavourable economics of available chemistry,3,5 which involved the amonolysis of the activated halothiophenes. It appaers that nitrothiophene derived dyes were not manufactured until the early 1970s when ICI developed an economic Gewald–based synthesis of 2-amino-3,5-dinitrothiophene .6,7 much patent activity ensued,especially concerning dyes derived from the dinitro component, and interest in 5-acyl-3-nitrothienylazo dye were revived by the disclosure of a new route to the diazo component[38-43].

Squarylium dyes has been attracted much attention because of their potential application in photoconductor photoreceptor [44], optical recording media [45], organic solar cells[46] and non linear optics [47]. Structural modification of dyes in an active area of research for obtaining good properties. This class of cyanine exhibits a sharp absorption with high coefficients in solution
in the visible and near-infrared region. A novel class of symmetrical squarylium dye based on 2,6-di-t-butylpyrylium[48] but the synthesis of asymmetrical squarylium dyes based on 2,6-di-t-butylpyrylium have never been reported. The majority of a wide range of squarylium dyes belong to the class of symmetrical cyanine dyes.

De Giorgi et al., has been reported that the disperse azo dyes derived from thiadiazole are of interest because they are suitable for dyeing various fibres [49,50]. The fastness properties of a series of thidiazolyl azo dyes, applied as disperse dyes on polyester fibres, have been explored previously by a chemometric approach with the aim of establishing quantitative structure and activity relationships(QSAR)[51,52]. This approach has shown to be an valid strategy for selecting the most informative structures in various series of dyes.[53].

The universal textbook from Klages today still provides a very readable introduction and compendium on organic dyes[54]. The development of colour theory up until 1984 has been outlined by Griffiths, who goes in to the PPP method[55]. Herbst and Hunger et al., have been developed modern monograph on this theme comes from[56]. “Phthalocyanins”. [57] Ullmanns encyclopedia are also of great value. The most modern view points of higher performance pigments (HPPs) are to be found in smith[58]. Desiraju put particular emphasis of the chemistry of organic solids (crystals) since 1983[59]. The contrast intramolecular and intermolecular is put in to perspective for organic crystals one could even particularly say “leveled” are places them along inorganic crystals.
In major literature of the azo and several series of C.I Disperse Yellow, Red, Orange, Purple, Blue, Green, Brown and black are commercially available. The 2-hydroxyl-6-pyridone form and the pyridine-2,6-dione form. On considering numerous publications which have focused on the industrial applications such as dye fixing, pasting and dispersing, printing and so on, the structural characterizations on the intermolecular and intramolecular interactions in supramolecular level and the computational studies on confirmation originated from the isomerization/tautomerism or the stereochemistry of molecules are rarely involved\[60-69]\.

The great interest in the synthesis of more environmentally safe1:2 Fe complexed dyes \[70, 71\]. A key objective of this study is to compare the light stability of some 1:2 chromium, cobalt and iron complexed azo dyes. Although metalized dyes are a commercially very important class of colourants, there are relatively few studies concerning their photolytic behavior. Graves et al \[72\].studied the effect of metallization of azo dyes (mostly 1:1 metal complexes) under aerobic conditions and they found that the dyes with metal ions having low lying exited states suppress single oxygen formation completely. Recently the photodegradation of some 1:2 metal complexed formation dyes\[73\] was investigated and the quantum yield of process was also measured.

First choi JH,Hong SH et al.\[74\] have been introduced for the discharged printing of polyester and exhaust dyeing of polyester alone or blended with cotton in 1976 by ICI\[75\].these dyes were designed by Lead better PW,leaver AT to rupture under the action of alkaline after treatment to produce colourless or
only slightly tined decomposition products[76]. Koh JS, Kim JP et al., have discussed phthalamide based alkali clearable dyes[77,78]. These dyes, containing phthalamide moiety undergo ring opening and convert to water soluble products under relatively mild alkaline conditions. One advantage of the dye is the lack of azo bond reduction, which can lead to harmful primary aromatic –amine compounds.

Gewald J.B et al., in the 1960s of the versatile synthetic method for 2-minothiophenes, as part of his research in to the preparation of heterocycles from active methylene nitriles, sparked renewed commercial interest in these compounds as diazo compounds and again Dickey et al., have been established the potential of thienylazo disperse dyes, although their use was fructurated by unfavourable economics of the available chemistry. The promise of Gewald’s discovery signaled a burst of patent activity, which was followed by a steady stream of application concerning thiophene based azo dispersive dyes over the next 20 years. The original version of Gewald synthesis involved the reaction of ccarbonylthiols with nitriles processing an active methylene group, in the presence of catalytic amount of base.[79-89].

Fabrin J, Nakazumi H, Matsuoka M et al are investigated the squaryline dyes are 1,3 disubstituted derivatives of squaric acid (3,4 –dihydroxy-1-2-dioxocyclobut-3-ene) was first synthesized 40 years ago. Emmelius M Pawlowski G Vollman HW et al are studied photochemical stability high photo conductivity and sharp and intense absorption in the red and infrared(NIR) regions [90-94]. Particularly in the last two decades, squarylium dyes have found extensive
application in the domain of photonics, mainly as substrates for optical recording media, xerographic photoreceptors and organic solar cells[95]. Akkaya EU,Turkyilmaz S .Tetrahedron Lett et al .are interest in the class of dyes as sensor for determination of metals ,sensitizers for photodynamic therapy (PDT) and noncovalent lables for biomolecules .the cyanin type have holding comparatively much less attention .especialy in what concerns the development of new sensitzcers for (PDT ) ,cationic squryiyum cyanine dyes are of great interest once cationic cyanins started to be regarding as promising sensitizers agent.[96-106].

Melntosh,S.a.,Freeman ,H.S and Singh ,p et al are reported findings from x-ray studies designed to enhance our understanding of experimental results obtained when a group of ortho substituted monoazo disperse dyes 1(X=H,Me,OMe,CN,Br,NO2) was irradiated with UV light [104].X-ray data proved particularly useful in explaining the differences in the photostability of the cyano and nitro substituted dyes .subsequently , we have extended our work in the area to pair of di azo disperse dyes, namely C.I.Disperse Yellow 23(2) and C.I.Disperse orange 29 (3)[107-109].

Some of the authors like G.McMullan, Meehan, A.Connely, N.Kirby, T.Robinson P.Nigam, I.M Banant,R.marchant,W.F.Smyth are analysed general data about 100,000 dyes have been synthesized worldwide ,and more than 700,000 tonnes are produced annually .More than 10,000 dyes are commercially available but over 5 % is discharged in to aquatic environments by plants and users.[110].
Some dyes are usually stable in acidic and alkaline media and resistant to
temperature, heat, light and microbes. Most dyes are toxic, carcinogenic and
mutagenic causing allergies, dermatitis, skin irritation, cancer and mutation in
humans destructive treatments, including electrolytes, oxidation and reduction.
Some of them have proved effective, but they often have serious limitations, for
instance, activated carbon is the most effective and popular absorbent, so it is
often used to treat variable wastewater.

Chemical and thermal regeneration of spent carbon are both expensive and
impractical on a large scale; also they produce additional effluent and result in
considerable absorbent loss. Natural substances have also been used as sorbents,
e.g. wood dust, bentonite and waste solids adsorption rate and difficult
reproduction restrict the extensive use of most sorbents. An important statement
for membrane filtration is slow and entails a high cost of use, while flocculation
entails several problems, including colour reservation of treated water and
disposal of sludge with high water content; and destructive treatments with high
cost often cause secondary pollution[116-120].

Thoughtfully, the “using waste to treat waste” paradigm in the treatment
of waste water is often adopted because waste reuse is an optimal solution. Some
wastes have been reused and applied in the treatment of dyes waste water, such as
fly ash, deoiled soya wheat husk and so on, which do significant contributions to
the pollution control and resource reuse partly. There has been a great deal of
interest in the design and synthesis of inorganic / organic complex materials to
achieve specific properties. Various synthesis techniques developed during the
last few years have given us access to functional materials with characteristics such as surface modification, inorganic / organic hybridization and functional ligand-loading [121-136].

R.T. Buwalda, J.M.Jonker, J. B.F. N. Engberts, Aggregation of azo dyes and these materials have been widely applied in various fields such as films, catalysts and pharmaceutical products. A dye with a functional group that absorbs visible light is often used to prepare hybrid materials for application to solar cells and sensors. However, these synthesis methods often require complicated products, strict conditions and high purity reagents. Adsorptive precipitation was discovered during the mid 20th century and applied most in analytical chemistry. The classical co-precipitation method has been extensively applied to the enrichment of metal ions and the synthesis of functionalized materials. As conventional dyes, weak acidic pin red B(APRB) shown good electrophilicity and hydrophobicity, due to containing two negative sulfonic acid groups and a long hydrophobic alkyl chain[137-139].

The binding to polymers or proteins has been of great importance for it provides an insight in to general bio-macromolecular interaction in biochemistry. Changes in absorption spectra of dyes upon binding indicate the aggregation of neighboring bound dye molecules on the polymer chain. H- or J- aggregations are founded when azo dyes interact with charged or nonionic water-soluble polymers.

Azo dyes are well known to form dimmers or higher order aggregates in aqueous solution depending on the dye structure and media properties, and/or the presence of template molecules such as polymers, proteins and surfactants. The
aggregation of dyes is accompanied by the changes in the absorption or fluorescence spectrum compared to the individual monomeric molecules. According to kasha exciton theory, J- or H-aggregates can be formed depending on the angle (a) between the transition dipoles and the molecular axis of the aggregate. J-aggregates of dyes are very important for photophysical and nonlinear applications[140,141].

Rana K S Raizada S et al, have been discussed very toxic and resistant to physicochemical treatments and not easily biodegradable. The colour of dyes result from conjugated chains or rings that can absorb UV light to different wavelengths. The chromophores of dyes are usually composed of C=C, N=N,C=N, and aromatic and heterocyclic rings containing oxygen, nitrogen or sulphur. Some chemical such as hypochlorite, ozone, and hydrogen peroxide, in the absence and in the presence of UV light and hydrogen peroxide with ferrous ions, have been used for free treatment of dye bearing wastewater[142-148].

Ozone is very effective in decolourizing dye wastewater because it attacks conjugated double bonds that are often associated with colour. Ozone reacts with aqueous compounds in two paths: a direct path corresponding to the action of molecular ozone and an indirect path resulting from the decomposition of ozone to radicals. Decomposition favored by basic PH is initiated by hydroxyl ions (oh). But few studies have been carried out on the comparative research on the decolourization efficiency of different dyes by ozone and the residues of dye aqueous solutions[149,150].
2.2 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

Marine dyes are important class of compounds that are used in the protection of objects and structures that are employed under ocean. Since the need for such corrosion resistant materials is on very high rise, development of such material is a need of an hour. Hence the present investigations have been envisaged based on the following objectives.

To characterize the marine dyes using sophisticated analytical techniques in order to ensure the purity and quality.

To obtain metal complexes using the dye compounds as ligand moieties to check the complexation ability.

To characterize the complexes of dye substance using the state of the art analytical tools.

To assess the behavior of dyes in the presence of ultrasonic waves using the ultrasonic’s technique.

To envisage the photodegradation of textile dyes in order to assess the stability of dyes.

To understand the crystal parameter of indole derivative by single crystal X-ray diffraction analysis.

The methods adopted to achieve the objectives adhere to the standard procedure and protocols that would shed further light on the protective behavior of the dye substances in marine protection. Moreover the details of the results that were obtained out this study would further brighten the prospects of research done
in this area. Real time experiments that involve the application and performance of these dyes for protection in marine environments is yet to be carried out.
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