REMOVAL OF COLORANTS FROM WASTEWATER: A REVIEW ON SOURCES AND TREATMENT STRATEGIES

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CERTIFICATE FROM THE SUPERVISOR

SaistaAlam is an obedient student of B. Sc. (H) Sem-VI. Under the course schedule he has performed the dissertation work titled **REMOVAL OF COLORANTS FROM WASTEWATER: A REVIEW ON SOURCES AND TREATMENT STRATEGIES.** During the study she had been provided all supports like Computers with internet access, books and review journal.This work will encourage her in her future studies.

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Abstract

Removal of dye containing wastewater from the industries are to be done in order to control the negativeimpact to our environment due to polluted water. In this review, different types of dyes, pigments and colorants materials responsible for coloration of water are described. Different recent technologies for theremoval of dyes from wastewater are discussed briefly. The technologies such as coagulation,membrane treatment, advanced oxidation process, biological treatment and adsorption, theirperformance, features, advantages and disadvantages have been highlighted. From the review, itis concluded that advanced oxidation process, biological treatment and adsorption are frequentlyused techniques for dye removal and large numbers of research were done in the field of adsorptionin recent years.

Keywords: .Toxic dyes; Environment; Treatment techniques; Dye removal; Adsorption

Introduction

Colorants substance are those substance which are capable of transmitting its color to the substrate. Colorants are used in the industries like, paints, clothes, plastics, photographs, prints and ceramics. Colorants are mainly used to make the product attractive and in food for appetizing. Colorants are divided into two categories namely, dyes and pigments. The mechanism of staining colours, chemical information are not provided to natural dyes as many natural dyes were obtained from plants in ancient days. Natural dyes are negatively as well as positively charged substance and anion usually gives the colour part of the molecule. Dyes are considered as organic compound or mixture that are used for sharing colour to a substrate like, cloth, paper, leather and other objects etc. A good dye should have suitable as well as attractive colour, property to bind itself to substrate, water soluble, affinity towards substrate. The properties, colours and uses of a dye also determined using chemical structures of a dye. Dyes are generally dissolved in aqueous solution to improve the fastness of the dye on substrate. In early days, the sources of colouring materials where from plants and insects but in recent time dyes are synthesized. They are soluble and go through an application process which, atleast temporarily, destroys any crystal structure by absorption, solution and mechanical retention or by ionic or covalent chemical bonds". Dyes are classified on the basis of structure and applications, they are, natural dye, synthetic dye, food dye and dyes used in leather, laser, paper industries etc., In modern world environmental pollution is the major problem. Industries such as dyestuff, pulp mills, distilleries, tanneries and textile are the producers of high coloured wastewater which contains dyes.

Different types of colorants materials are discussed below-

Natural dye andSynthetic dyes

Natural dye - Natural dye colorants are derived from plants, invertebrates or minerals. The dyes are majorly from vegetable sources i.e., from roots, berries, bark, leaves and wood and from other archeological sources such as fungi and lichens. Dyes which are derived from natural resources are termed as natural dyes.

Two categories of natural dyes are possible they are from animals - Cochineal insect (red) produced from cactus plants and from plants - cudbear Catechu (brown), Gamboge tree resin (dark mustard yellow).

Synthetic dyes - Derived from organic or inorganic compounds and it replaced natural dyes. They are used in wider range of industries for dying and printing. They are primarily made from aniline or chrome

They found to be stable to common oxidation and reduction process and very difficult to remove from industrial effluent

Classification of Pigments

Pigments and dyes are derived from same building blocks but differs with solubility factor where dye are soluble in the media in which it is incorporated and pigments are not.Pigments retain a crystal or particulate structure throughout the coloration process.

Organic Pigments

Based on carbon chains or carbon rings and it also contains metallic elements for stabilization of organic components. Used in the application of tinting strength and brilliant shades.

Inorganic Pigments

They are solutions of metallic salts precipitation and not based on carbon.Inorganic pigments are stable towards organic solvents .inorganic pigments areIron oxide , Cadmiumetc

Industries and Dyes

Cosmetic Industry

Cosmetic products are divided majorly into four components such as skin care, hair care, make-up products and other fragrance products.They are referred as non-essential products mainly bought to people in order to improve their appearance. The cosmetic products not only include mascara, lipstick, eyeliner and foundations, it also includes cleansing products required for hygiene, which are shampoos, soaps, toothpaste, shower gel, deodorants, shaving creams,

moisturizers etc.The chemicals like aluminum salts, petrochemical oils, formaldehyde, mercury and other heavy metals are found in cosmetic products.

Petroleum and Mineral Oil

Cosmetics mainly uses petroleum products in their products but the major drawback is that it clogs pores and causes dermatitis and acne. It was identified that petroleum products may contain polycyclic aromatic hydrocarbons (PAH) which is a cancer-causing agent

Hair Dyes

Hair represents attractiveness, masculinity, health and beauty of an individual. It covers whole mammal body and creates barrier between animal and environment.Hair plays major role in maintaining body image, hair texture, color, style and length are more important, its physical appearance can be modified without any surgeryHygiene refers to the removal of dirt, maintaining the hair style and protecting the cuticle, beautifying the air in terms of color and shape, correction refers to the medical or surgical treatmentsHair coloringis defined as the study of interaction between hair keratin and reactive organic dyes, oxidizing agents and conditioners. Hair dye includes minerals such as lead acetate, silver nitrate, salts of bismuth, copper, cobalt.Temporary and semi-permanent hair dyes are based on van der Waals force. Depends upon molecular weightPermanent hair colorconsists of hydrogen peroxide and ammonia.

Food Industry

For appealing and appetizing colorants are used in food. They enhance the existing colors which are lost during manufacturing or to increase the shelf life. Food colorants are majorly divided into two categories they are natural and synthetic colorants.

Chlorophyll

It's a natural pigment available in all green plants. From carbon dioxide and water chlorophyll synthesize carbohydrates with the help of sun light energy. This is named as photosynthesis and it is the evidence for life on earth. Mint flavored foods are sometimes flavored with chlorophyll

Turmeric

It's a natural additive color and when added with mustard it gives deep yellow color. They are found in the stem underground, particularly in India. In order to give yellow color mainly U.S food companies are using turmeric. It is also used as a basic as well as acid indicator. When turmeric blends with mustard it turns to red

Leather Industry

Due to socioeconomic activities of humankind our environment is worsening and leather industries play leading role in export as well as in environment.Depending upon the availability of sources in specific area the type of leather is chosen. The leather of goat, lamb, deer, ostrich, buffalo, yak, kangaroo and even leather of toxic animals such as snake, alligator, crocodile, and stingray are also chosen.Three main process such as beam house, tanning, finishing is involved in leather industry.In leather industry dying is considered as a key role as it gives desired color to the leather.

Synthetic leather tanning

Polymers like novalac, neradol and melamineare used for this type of tanning and they are identified by their creamy white color.

Vegetable tanning

Tree bark and naturally plant-derived sources are used for tanning. Soft leather was made when the leather is soaked into hot water. Brown leather are formed by vegetable tanning.

Textile Industry

Textile industries are one among the fast-growing industries. The raw materials such as fiber, fabric, dye stuff, chemicals and its auxiliaries are used in textile industries.Textile industries are classified into two categories one is dry fabric and another one is wet fabric.As per World Bank statement 17- 20% of industrial wastewater is contributed by textile industry.Three by fourth of dye products are utilized in textile industries.

Pharmaceutical industry

Wide range of colors are used in pharmaceutical industries. For easier medicine identification by the medical practioner and pharmacists mainly colors are used. In order to provide uniform, identifiable and attractive colors numerous coloring agents are used.More amount of dyes are not used in pharmaceutical industries when compared to other industries.

Health risk assessment on dyes

The term risk is defined as the combination of hazard and probability of hazard occurrence in specified area. The exposure of dye precursors leads to bladder cancer and the dermal exposure. Textile dyes are related with aromatic amines which are seen in textile dyeand damages the DNA in cells which leads to risk of cancer.The problem such as allergies, hyperactivity, irritability, aggressiveness and learning impairment are related with intake of food dye.Recurrent urticaria, angioedema, bronchoconstriction or dermatitis are the results of Ponceau and among 25 children aged between 1.5 and 12.5 years reported with allergic reactions after food intake.Oral provocation, skin irritation symptoms are generally seen.

The chromium used in leather industry act as lung irritant and carcinogen which affects the upper respiratory tract and increases the risk of lung and nasal cancer.

Various treatments method:

Coagulation

The synthetic coagulation is a regular (and a standout amongst the most famous) procedure utilized for the treatment of dyeing wastewaters. Coagulants are classified according to the characteristics and they are, inorganic coagulants and organic coagulants. Aluminum sulfate, aluminum chloride, ferric chloride, ferric sulfate, calcium oxide and magnesium oxide come under inorganic coagulants.

Human diseases like Alzheimer's and cancer are the drawbacks found in using chemicals as coagulants

Bio coagulants

Alternative coagulants other than chemicals are found to be ecofriendly and practically suitable for wastewater treatment. Plant based natural coagulants such as Moringaoleifera, stryconuspotatorum, Phaseolus vulgaris, prosopisjuliflora, Ipomoea dasysperma seed gum, Cactus species, and seeds of some plants due to its less processing time and sustainability during treatment.

Electro coagulation

Electro coagulation was found to be alternative technique for chemical coagulation which utilizes electrochemical treatment. Due to the electrolytic oxidation of anode the coagulant is produced. Low cost, minimal sludge, high efficiency is some of the advantages of electrocoagulation and other advantage during the process are non-generation of secondary pollutants.Many studies highlight the efficiency of electrocoagulation in removing the color from dye effluents and it also depends on the parameters like pH, dye concentration, current density and also reactor design.

Membrane Treatment

Due to its high efficiency, low cost comparing to advanced oxidation process and easy industrial scale-up membrane technologies are used. Nano filtration membranes due to its separation mechanism involving electrostatic repulsion, they are used for the removal of dyes.Membrane fouling was considered as great bane for this technology. It is defined as the accumulation of foulants on the or into the membranes and it degrades the selectivity as well as the permeability of the polymeric membranes. Two types of fouling are seen and they are, organic fouling and biological fouling.Natural substances like clay, zeolite, Kaolin, Perlite, Cordierite, calcium carbonate, dolomite is used as precursor's along with other chemicals for the preparation of membranes.

Advanced Oxidation Process (AOP)

For degrading the organic pollutants in water advanced oxidation process are widely used. It involves the production of oxidants and hydroxyl radicals for the degradation of pollutants. For the destruction of organic or inorganic contaminants in water as well as in wastewater AOPs are

used.Ozone are used for decolorization, detoxification. Disinfection, BOD/COD reduction and in sludge reduction.

Electrochemical Treatment

Due to removal of color, electrochemical treatment is paid more attention and this type of treatment are influenced by pH, temperature, electric voltage etc., and it has been found that adding some amount of NaCl and HCl results in additional removal of color and chemical oxygen demand.In many cases advanced oxidation process is combined with electrochemical treatment for efficiently removing dyes present in wastewater.H2O2 are produced on the cathode with continuous feed of oxygen and Fe2+ are electro-generated from Fe3+ at the surface of cathode.

Photocatalytic process

It is considered as potential and emerging technique over few decades. This process combines UV photon or low energy visible photon with semiconductor material. In order to generate hydroxyl radical (HO.), the semiconductor which act as a photo catalyst generates electron-hole pair after electron excitation.Solar Photo catalysis -Solar radiation are collected and distributed into the photo reactor that maximizes the photocatalytic efficiency. Two types of collectors are used generally and they are nonconcentrating collectors and concentrating collectors.Mainly TiO2, ZnO, CdS, ZrO2, WO3 are used as photo catalyst. TiO2 based photocatalytic oxidation process become popular because of these reasons, i) at ambient pressure and temperature the processes are carried out, ii) expensive oxidizing chemical are not consumed in this process, iii) the oxidants are strong resulting in complete mineralization. The parameters which affect photooxidation of dye molecule are i) initial dye concentration, ii) pH, iii) intensity of light, iv) electron scavenger, v) photo catalyst load.

Ozonation

Ozone are used mainly to decolorize wastewater. Based upon the pH the type of treatment, namely molecular ozone (i.e. direct reaction) or hydroxyl radicals (i.e. indirect reaction) or both can be carried out simultaneously during reaction process. In addition to it, ozone have high oxidation potential which allows it to degrade organic compounds in higher manner. Ozonation

moderately remove COD as well as TOC and degradation purely depends upon the ozone dosage .Ozone decolorize dye by attacking the double bonds which are associatedwith color. Apart from that it cleaves the unsaturated bonds in aromatic molecules in dyes and in pigments, finally color of the molecules is reduced. When ozone transferred into water, it reacts with organic and inorganic compound present in the wastewater. Ozone decomposes to oxygen by splitting the radicals such as hydroxyl radical (OH*), OH3, OH4 and super oxide (O2 *)

Plasma Treatment

Due to its high oxidation capacity, versatility and complexity the application of plasma-based oxidation methods for degradation of pollutants have been increased in recent years. Various methods namely, electrohydraulic discharge, corona discharge, dielectric barrier discharge (DBD), microwave discharge, radio frequency and other methods are seen. Among all technologies DBD technology was considered as efficient technology for various reactor types.It creates major effects on the surface of the materials, like cleaning, etching and functionalized effect and this effect modifies the surface without anychange in the bulk properties of the sample. Oxygen assisted plasma treatment are done for the degradation of dye. The dyes such as Acid Orange 7, Reactive Black 5, Reactive Blue 52, Reactive Yellow 125 and Reactive Green 15 are degraded using this treatment.

Biological Treatment

Biological treatment process is considered to be inexpensive, ecofriendly and economical solution for degrading the wastewater, especially containing dyes. Due to its genetic diversity and versatility it has become an alternative solution for treating dye water problem. The biological substance has the ability to convert pollutants into waster, carbon dioxide and salts which are inorganic in nature. The dye degradation are achieved using metabolic pathways or by adsorption which includes living as well as dead biomass like bacteria, fungi, yeasts, algae and plants.Fungal decolorization, microbial degradation, adsorption by living or dead biomass, bioremediation is commonly used biological treatments in industrial effluent treatment.Several species such as shewanella, bacillus, scheffersomyces, actinetobacter, cynobacteria are used for the treatment of dyes. Algae are considered to be primary producers and the functional groups such as hydroxyl, carboxylate, amino and phosphate are seenin the cell walls of algae which

plays major role in removing the pollutants from aqueous solution.Algae consist of alginate, carrageenan and polycolliod all together considered as polysaccharide.

Adsorption

Because of simplicity in operation, low cost in implementation, performance it can be used for wide range of treating effluents. Activated carbon is the basic material used in adsorption due to its textural properties, superior surface area, pore volume and pore structures and the textural properties depends upon the precursors used for preparing activated carbon. By means of physical as well as chemical activation, activated carbon are prepared. It's a combination of both separation and purification process which removes the pollution causing substance that are not biodegradable.

Biosorbents

It also utilizes solid waste like residual sludge for adsorbent production. Depending upon the influent of wastewater and the operating conditions the composition of activated sludge may vary from one system to another system. From industrial by-products alternative adsorbents are obtained due to its abundance and the sludge can be defined as the residue generated from effluent treatment process. The residue in primary treatment contains inorganic compounds and the biological process are involved in secondary treatment which consist of organic compounds and microorganisms in dead as well as in live condition and the characteristics of residue depends on the sludge origin, treatments and the additional agents applied. Microorganisms such as bacteria, protozoa are seen in activated sludge so they can be used in the form of sorbents, due to its negatively charged surface and membrane compositions.

Nanomaterials as adsorbents

The substance which are smaller than 100 nm are typically considered as nanomaterials. The novel size- dependent materials has some properties different from their bulk substance and they are related with its high specific surface area, dissolution in faster manner, high reactivity and some properties like superparamagnetic, quantum confinement effect, Plasmon resonance are seen and the degree of function depends upon the process and the reaction occurs on the time of degradation.

Carbon nanotubes

When comparing both Nanomaterials and activated carbon, both has high activated area, some of the nanomaterials are found to be advantageous than activated carbon: easy synthetization at low cost and minimum amount of usage for the removal of pollutants when comparing to activated carbon. Various types of heavy metal are treated using nanoparticles and minimum number of papers are available regarding adsorption of dyes based on nanomaterials. CNTs are known for its physicochemical stability, high selectivity and its structural diversity.

Combination and hybridization

The usage of combined treatments eliminates the drawbacks of single treatment with the outcome of excellent results. In recent times, combined as well as hybrid process attracted many researchers to work towards this area and it is also referred as synergism or integration. In combined process, more than two methods are carried out in sequential manner and in hybrid process, two or more methods are fused together. When comparing to combined process, hybrid process was found to be cost as well as time saving as multiple process are incorporated in single vessel. In a research the combined treatment of chemical as well as physical were done as the chemical treatment alone does not remove chemical oxygen demand and total organic carbon. The combined treatment of coagulation/flocculation and nano-filtration shows high concentration removal of dye water and low amount of sludge also produced.The combination of TiO2 and photocatalysis was used for treating Procion yellow H-EXL dye in both real as well as synthetic wastewater. Hai et al did some research on combination of chemical-chemical process such as combinations of AOPs which includes Fenron's reaction+ sonolysis, ozonation+UV radiation, electrolysis + sonolysis, photocatalysis + microwave radiation.Microwave assisted chlorine dioxide (ClO2) catalytic oxidation is another example for hybridization process. Enhancement with microwave irradiation provides good operating condition, wider pH range, reduced reaction time, lower in activation energy [196, 197]. The hybridization of membrane separation and photocatalysis termed as photocatalytic membrane reactors (PMR) comes under physical-chemical hybridization.

Objective of the study / Future prospective

The conventional treatment methods like, coagulation, membrane treatment, biological treatment, adsorption and the upcoming techniques such as advanced oxidation process which includes electrochemical treatment, photocatalytic process, ozonation, plasma treatment are discussed in detail. It is well understood from the summary of this review that advanced oxidation, adsorption and biological treatments are frequently investigated techniques in past few years. More than 80 percent removal efficiencies are achieved with these above techniques and in several cases 90 percent removal efficiencies are achieved with different combination of treatments. In coagulation, disposal of coagulant is the major problem and wide varieties of dye wastewater cannot be treated using coagulation alone and research were on process with combinations of coagulation for effective removal. Membrane process is found to be very complex and cleaning. Membrane fouling, concentrated sludge productions are some of the processes related problem identified in membrane process. Lot of research work on the production of low-cost membranes with high mechanical strength. In advanced oxidation process are found to be effective in discoloration and mineralization and energy consumption is found to be high in these type of advanced oxidation treatments. Biological treatment process was found to be environmental friendly and easy approach in dealing with wastewater related to dye. The parameters such aseffluent conditions, environmental impact, type of dye, operating conditions, costs and others. It is considered as time consuming process and many researchers should focus on reduction in degradation time. Wide ranges of adsorption materials are reviewed. Large numbers of papers are published continuously on adsorption using dyes but the regeneration of spent adsorbent is considered as a great issue. Adsorption was found to be efficient and beneficial technique in all aspect such as, cost, area, efficiency, flexibility etc. Many researchers focused on the spent adsorbent. The spent adsorbent used can be used for many times for the treatment without any degradation in its quality. The prepared adsorbent should be selective and specific to the type of the dye wastewater to be treated and also it should be of low cost. Many research works were carried out in recent years in treating the wastewater as water is the precious resource and abiotic component of our ecosystems. As treatment in safer manner and conservation of water is every person duty. In future, sophisticated technologies are developed in order to treat waste water with low cost and improved efficiency.

Conclusion

Dyes are under important pollutant class and it affects our ecosystem in drastic manner. The selection of appropriate colorants for the desired products plays an important role in manufacturing industries and the production of wastewater by these industries create negative impact to our environment and therefore before discharge, dye industry wastewater has to be treated. In this review paper, several dye removal technologies such as coagulation, membrane treatment, advanced oxidation process and adsorption were discussed and among them chemical oxidation, biological treatment and adsorption were found to be frequently used techniques in recent decades. The discussed techniques show more than 80-90% of dye removal efficiency. In recent decades, several methods on dye removal from water have been reported in faster rate as well as in lowcost. As water is found to be important and second precious abiotic component in our ecosystem. It is our duty to conserve and to treat the polluted water. In future, there is a hope in the development of sophisticated technologies both in industrial as well as in pilot level with low cost and in high efficiency.

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A Review on Aldol Reaction

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CERTIFICATE FROM THE SUPERVISOR

MD SHAHABUDDIN is an obedient student of B. Sc. (H) Sem-VI. Under the course schedule he has performed the dissertation work titled **A REVIEW ON ALDOL REACTION**. During the study he had been provided all supports like Computers with internet access, review article and journal. This work will encourage him in his future studies.

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Dr. Tapas Kumar Paira

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Md Shalabuddin

Signature of Student:

Abstract

Aldol condensation is an important synthetic method widely used in organic synthesis. Development of catalytic methods that avoids the production of stoichiometric by-products while maintaining high levels of control available from stoichiometric processes provides an atom economical alternative for these important transformations. Indeed, numerous catalysts for the aldol reaction have been reported in recent years, including enzymes, catalytic antibodies, organometallic, organocatalysed and small molecules. Direct aldol reaction is the most important reaction employed by synthetic chemists as well as by nature. Recently, various Lewis's acids have been examined as catalysts for aldol reactions. But aldol condensation in micellar medium has not been carried out in details so far. Due to stronger environmental concerns, organic reactions in green media, especially in water, have attracted more attention. It is believed that micelles act as nano reactors to enhance the reaction rates and give very good to excellent yields of end products.

Introduction

Over the last decade, organ catalysis has become an area of active interest to the scientific community working in the fields of synthesis and catalysis. The bona fide area of organic syntheses largely depends on carbon-carbon bond forming reactions. Though the topic has been much cultivated historically, steps relating to its justification, alternative easy routes, significant advances both in main-group and transition-metal mediated pathways giving rise to diverse degree of substrate-reagent interactions have kept the subject relevant even today. New reactions improvising catenation in organic reactions leading to ever wondering molecules like catenates, rotaxanes have opened up a new horizon to the conventional organic chemistry. Beside this story, there is another one which is one of the most important in this regard and constitutes a significant challenge in synthetic chemistry: the aldol and related reactions. These are some well documented organic reactions which take place by condensation of enolates and specific enol equivalents with carbonyls. The reaction products, β-hydroxy carbonyl compounds, are common in many natural products. In addition, the hydroxyl and/or carbonyl groups can be converted selectively to other functional groups. Under some circumstances, the aldol product dehydrates to give an α, β-unsaturated carbonyl compound. The traditional aldol reactions are generally performed using alkalis like NaOH and KOH in an organic solvent. The basic reagents are good catalysts for the aldol condensation as well as for the side reactions. Therefore, it is very important to modify the experimental conditions to avoid the competitive reactions. The efforts in making these bases reusable would be highly appreciated in order to have environmentally friendly alkali-based processes. The major drawback of alkalis as catalyst is their non-recyclability due to either their consumption in reaction (salt formation) or devastation in post reaction workup generating inorganic waste. The cross-aldol condensation, also known as Claisen Schmidt reaction, is another important class of organic reactions for the synthesis of α, β- unsaturated carbonyls (cross aldol products). Stereospecific and asymmetric aldol condensations yield enantiomeric β-hydroxy carbonyls which are precursors for antihypertensive drugs and calcium antagonists.15 Chiral β-hydroxy carbonyl compounds, which are the building blocks for antibiotics, pheromones and many biologically active compounds, can be readily converted to 1,3- syn-diols and anti-diols and amino alcohols.

scientists of modern generation seek to overcome its main drawbacks which are certainly true for all other organo-based synthetic approaches—it is the eco-abuse of such reactions regarding

their hazardous solvent selection, low atom economy, higher chemical consumption and obviously throwing out toxic and non-biodegradable waste materials into the environment. Chemical universe has reached far today and the divergent temperament of chemical community surely demands greener preparative courses to arrive at a billion-dollar word- 'sustainability'! The domain of green chemistry contemplates risk-free performance criteria while designing new age laboratory processes to explore alternative fresh routes to accomplish the desired chemical transformations with minimized waste as well as eliminating the use of conventional organic solvents, wherever possible.

The present write up is thus a sensible effort to summarize the attempts that have been made in the field of aldol and related reactions performed in micellar media till date and to give an insight of the greener prospect of the said topic.

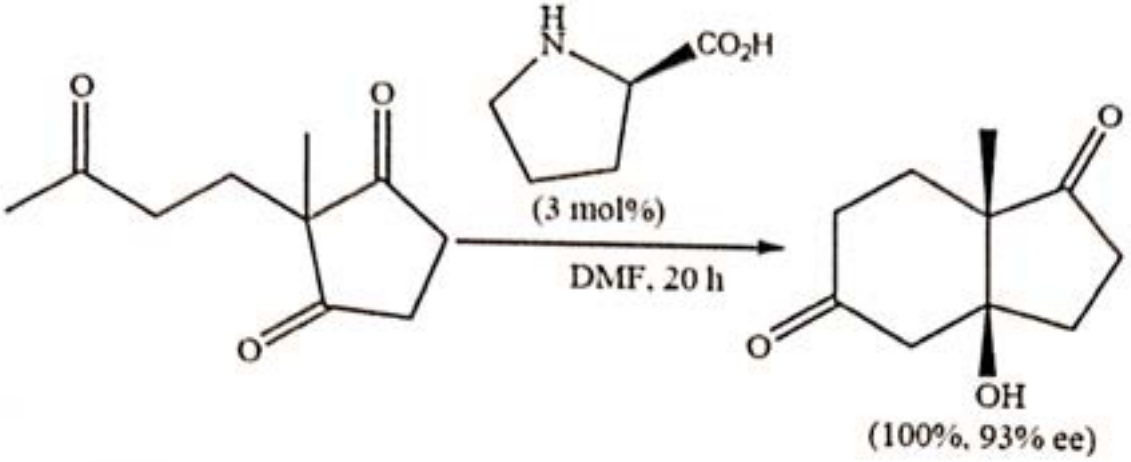
ROLE OF CATALYST IN ALDOL CONDENSATION

1.Proline in Aldol Condensation

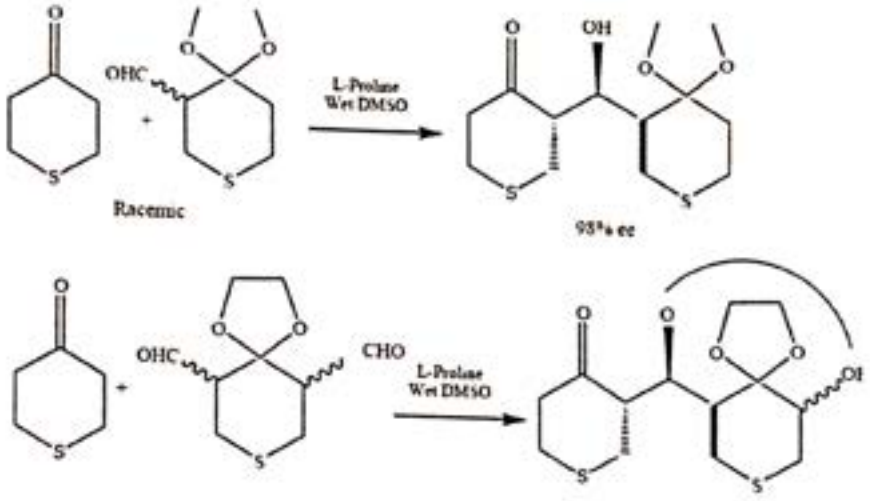
Proline, a simple enzyme, is the cornerstone in the field of organocatalysis due to the fact that it has been used as a catalyst in a wide range of asymmetric reactions with excellent results in many cases, its high efficiency being clearly demonstrated in the intramolecular and intermolecular aldol reactions.

2.Proline Catalysed Intramolecular Aldol Condensation

The first report of a direct asymmetric aldol reaction catalyzed by a small molecule was the Hajos-Parrish- Eder-Sauer-Wiechert cyclization, disclosed in 1971. This intramolecular aldol cyclization proceeded with only 3 mol% proline to give the cyclized product in excellent yield and enantioselectivity



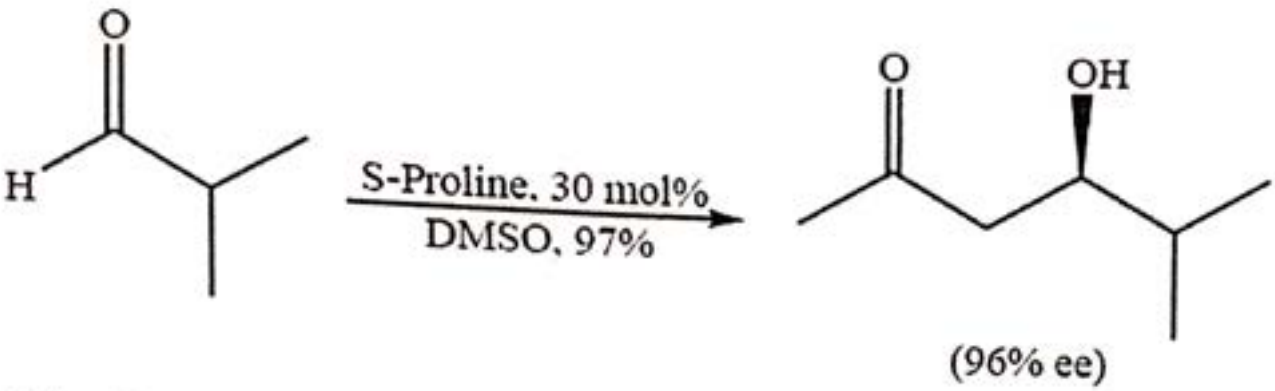
Proline catalysts are very important portion in the field of direct aldol condensations. Tetrahydro-4H-thiapyranone with racemic 1,4-dioxa-8-thia spiro decane-6-carboxaldehyde and with meso/dl 1,4-dioxa-8-thiaspiro decane-6,10- dicarboxaldehyde proceeded with dynamic kinetic resolution and gave single adducts when proline is acting as catalyst.



3.Proline Catalysed Intermolecular Aldol Condensation

The first intermolecular proline catalyzed aldol reaction was reported by List and co-workers By using 20-30 mol% L-Proline and a 4:1 solution of DMSO and acetone, the desired aldol adducts were obtained37. S-Proline is successfully used as catalyst in the field of intermolecular aldol reaction. Intermolecular aldol reaction between two carbonyl compounds is central to sugar metabolism. Class I aldolases catalyze this process by using an enamine mechanism39. Several early bio-organic studies appeared in which simple small molecule amines and amino acids served as aldolase models. Although, previously, it was shown that, proline reacts unproductively with aldehydes,

intermolecular reaction between a ketone and an aldehyde is possible if large ketone donor is used. For example, Acetone reacts with iso-butyl aldehyde in DMSO to give the aldol product in excellent amount



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4. Non –Enamine Organocatalysts Based Aldol Condensation

There has been various reports of use of tertiary amines and quaternary ammonium salts in aldol reactions. Few of the catalytic systems for the aldol reaction that use stoichiometric or even larger amounts of base, are therefore not direct aldol reactions. This includes phase-transfer catalysts that use hydroxide based aqueous phase. The substrate scope for these types of processes is typically much smaller than that available to enamine catalyzed processes due to mechanistic requirements Tertiary amines and quaternary ammonium salts are used successfully for a number of aldol reactions; though most of these types of processes require stoichiometric amounts of base. The syn selective hydroxy-acetone direct aldol reaction reported by Mlynarski does not require stoichiometric base. This procedure could prove useful if the enantioselectivity were improved with proline catalysis

5. BINOL Based Aldol Reaction

Various catalysts have been developed based on BINOL, which are developed by Shibaski. He reported the first direct intermolecular aldol of simple ketones using lanthanum-lithium-BINOL complex. Shibaski described a barium BINOL- derived catalyst for direct aldol reaction of acetophenone with alkyl aldehydes. The catalyst was used in 5 mol% and the reaction took 18-48 hours for completion. Here though the catalytic activity was improved but the enantioselectivity was not as high as the lanthanum-lithium-BINOL catalyst56. Shibaski reported the development of the lanthanum-lithium- BINOL derived catalyst for asymmetric aldol in 2001. In the year of 2003, Yao and Wang reported a Zirconium-BINOL catalyst for

the direct aldol reaction of diazo ester. In this case the adducts were found with 47-82% yield and in 53-87% ee. Use of diazo esters allows the extension of the substrate scope of BINOL-based catalysis to donors at the carboxylic acid oxidation state

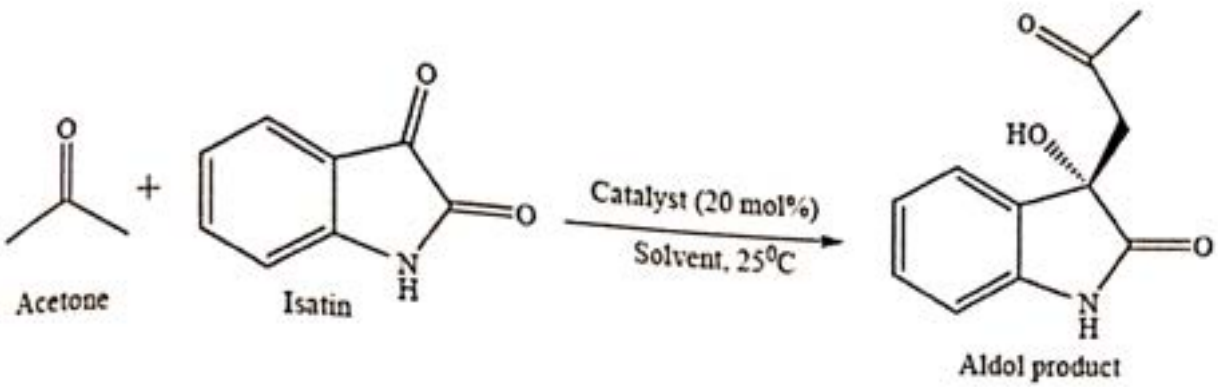
6.Miscellaneous Catalysts Based Aldol Reaction

A-branched aldehydes gave aldol adducts with 70-88% yield, while α-unbranched aldehydes gave poor enantioselectivity and very poor yield. Darbre et al. reported the asymmetric aldol reaction of acetone with aromatic aldehydes, using zinc-proline catalyst. Gathergood and Joregensen reported the utility of copper-BOX catalyst for direct aldol of α-keto ester. In 2009, Feng and co-workers reported the use of cinchonine, along with BINOL and titanium for direct catalytic aldol of diazo esters with several variety of aldehydes

SOLVENT SELECTION IN ALDOL KINETICS

The use of solvents, especially in organic synthesis, is one of the largest areas of research conducted within the field of green chemistry. In lot of cases, this research begins with the identification of an unusual solvent, often an ionic liquid, for which an application is developed as a means of demonstrating the prowess of that solvent. The art of dissolution captured the minds of even the earliest chemists, the alchemists. Even Aristotle had something to say on the subject, remarking "No coopora nisi fluida", or "No reaction occurs in the absence of solvent". Whether he was actually right or not has been a matter of debate now, with the emergence of 'solventless' reactions. In addition to solubility arguments, solvent melting and boiling points of solvents are often crucial to the chemistry they are applied to, along with other more application specific properties.

The above mentioned reaction proceeded very slowly using different type of polar and apolar solvents and even in water with low conversions and enantioselectivities being achieved. However, when the process was carried out under solvent-free conditions, the reaction rate increased tremendously.



UTILIZATION OF GREEN ALDOL CONDENSATION

Aldehydes and ketones are the starting materials in all procedures based on aldol reactions. Various hazards are associated with aldehydes and ketones. All low molecular weight aldehydes are toxic. Formaldehyde and acetaldehyde are irritating to eyes, skin and tracheal tract and, more importantly, they have been reported as carcinogens. Saturated ketones which are only moderately toxic, can cause depression of the central nervous system. One of the serious hazards associated with ketones is their ability to react with hydrogen peroxide to give dangerous explosive peroxides, a feature in connection with aldol reactions. It is now a great challenge for the chemists to run the aldol condensation in a greener way.

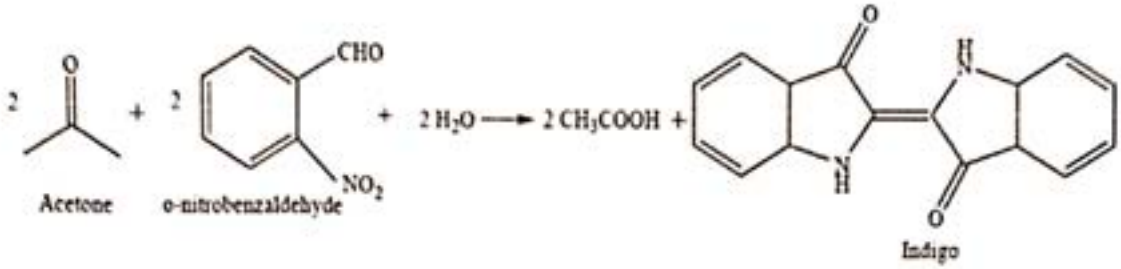
APPLICATIONS OF ALDOL CONDENSATION IN BIOORGANIC AND MEDICINAL CHEMISTRY

Aldol condensation in biological and medicinal area has attracted considerable interest over the years, as the aldol reaction is one of the most fundamental tools for the construction of new carbon-carbon bonds.

1.Indigo Preparation

An interesting example of an aldol condensation is the synthesis of indigo. Indigo is the dye used in blue jeans. In ancient times, indigo was isolated from plant sources, such as Indigo fer. In India, it was used to dye cloth and in Egypt, mummies were sometimes wrapped with indigo-dyed ribbons. It became known in Europe after the discovery of the sea route to India. The method to synthesize indigo was developed by Baeyer in the 1880s. While it is not the

procedure used commercially to synthesize indigo today, it works well to produce small quantities of indigo to be used to dye samples of cloth. The balanced reaction for the synthesis of indigo is



2.Medicinal Chemistry

Aldol reaction, a distinct area of chemical research, plays an important role in the chemistry in the pre-clinical and clinical studies for drug discovery research. It is associated with the isolation and purification of the chemical products, developed by using various methods in determination of chemical structure by NMR studies and identification of the pharmacological areas of the chemical product. Synthetic strategies and tactics are used in the field of organic chemistry by providing challenging targets so that the biological activity of the product reaches the targeted site

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