Chapter-1

General Introduction

1.1 Motivation

Phenolic resin representing a mature, versatile and classical polymer family has attracted considerable attention throughout the world because of its many desirable characteristics including heat, chemical and flame resistance, dimensional stability and potential for chemical modification1[1.1-1.3]. Depending on conditions used in the synthesis there are two types of phenolic resins, the resole resin and the novolac resin. This resin has been studied for over a century and flexibility of its properties is employed to produce a broad variety of products that bring technological advances, and numerous other societal benefits. In fact, the versatility of the macromolecular chemistry is still a matter of great interest. This chemistry facilitates the tailoring of polymer physico-chemical properties to fulfill different applications. Despite numerous applications, there remains a host of new opportunities to develop phenolic resin-based materials for health care applications. However, phenolic resin-based materials for water purification and antibacterial applications are still being sought.

The use of synthetic dyes, in particular azo-dyes is a very mature practice creating color characteristics in different products such as textiles, foodstuffs, cosmetics, house products, paints, and inks etc. Their extensive use generates voluminous colored wastewaters and has become one of the issues for the countries all over the world due to the fact that they pose toxicity. Therefore, it is important and necessary to search for an effective method to treat wastewater. Owing to public health interest, it is in demand to develop effective and convenient treatment methods. Among the commonly used technologies, azo-dye removal by adsorption is regarded as an effective and simplest process. Polymer-based adsorbents are of particular importance owing to the possibility to design their surface morphology, mechanical rigidity and adjustable surface chemistry.

Despite these advantages, only limited research has been focused on polymer-based sorbent materials for removal of azo-dye pollutants. On the other hand, antibacterial materials utilizing polymeric frameworks have attracted growing attention in multitude of healthcare applications because of a number of benefits. All these provide sufficient impetus to find new polymeric materials desire for hygiene applications.

To this end, the author believes that novolac type phenolic resin-based materials are the most promising candidates for functioning because of its fascinating chemistry. The author envisages that combining the merits of such resin in newly formed materials might be more rewarding in separation science and antimicrobial applications.

1.2 Phenolic resin

1.2.1 Synthesis of Phenolic Resin

The chemistry and properties that are desirable for resolving challenges in

phenolic resin-based advanced materials require the knowledge about the formation of phenolic resin or phenol formaldehyde resin (PF). Phenolic resin or phenol formaldehyde resin (PF) is synthetic polymer obtained by the condensation of phenol or its derivatives with formaldehyde[1.1-1.3].

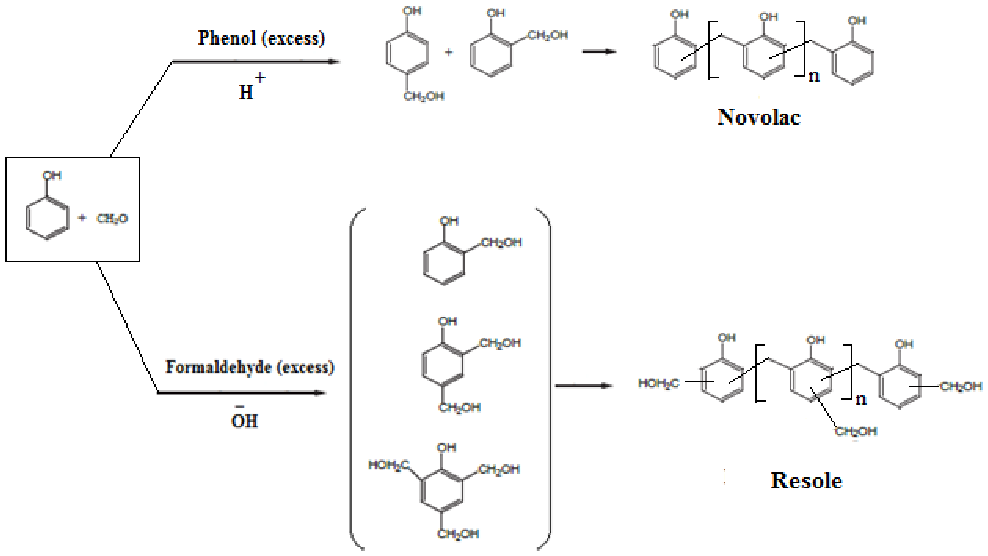
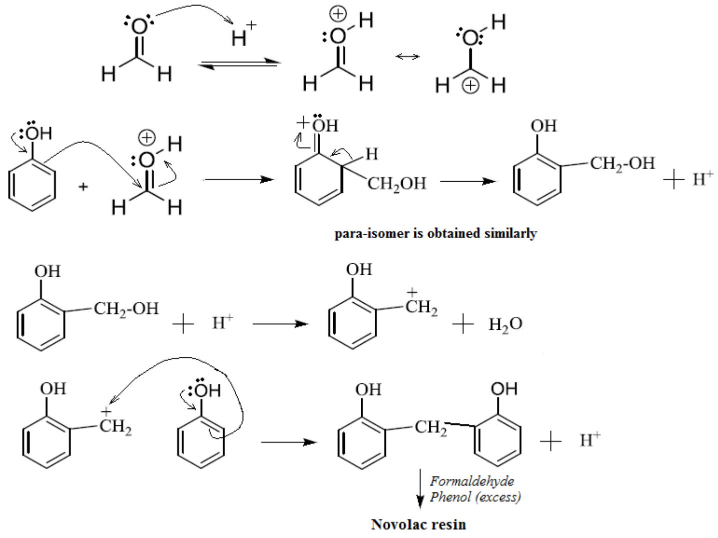


Figure 1.1: Typical structures of novolac and resole resin

Depending on conditions used in the synthesis (e.g., molar ratio of formaldehyde to phenol, type of catalyst, pH) there are two types of phenolic resins, the resole resin and the novolac resin. Novolac is synthesized in the presence of acid catalyst like para-toluene sulphonic acid, oxalic acid or sulphuric acid from the condensation reaction between phenol and formaldehyde with excess of phenol. It is formaldehyde deficient resin. In contrast, resole is typically synthesized under alkaline condition from the condensation reaction between phenol and formaldehyde with excess of formaldehyde. It is phenol deficient resin (Figure 1.1). During the resin synthesis, phenol is first reacted with formaldehyde to form the initial hydroxymethyl-substituted phenol called methylol phenol undergoing subsequent condensation. The difference between these two types of resins is the presence of the reactive methylol groups and, occasionally dimethylene-ether linkage in the resoles instead of the condensation products linked with methylene bridges, as in the case of novolacs. Resole resin possessing reactive hydroxymethyl groups has the ability of self polymerization at high temperatures. So it is known as the one-step resin. However, novolac is non-hydroxymethyl-bearing resin requiring more formaldehyde to achieve cure. Hence it is known as the two-step resin exhibiting more stability than resole. Throughout the research work, novolac type resin is used as the main component of materials developed.

1.2.2 Novolac type Phenolic Resin and research rationale

Phenol has a functionality of three and reacts with formaldehyde at *ortho*- and *para*- positions. An accepted belief is that *para*- position is more reactive than *otho*- positions. Delocalization of the nonbonding electron pairs on the oxygen of phenol into the aromatic ring produces electron-rich sites at these positions, which activates these sites. The reaction with formaldehyde can thus produce essentially three different kinds of methylene linkages such as *ortho-ortho*, *ortho-para*, and *para-para*. Novolac chain with ten phenol groups accounts statistical possibility of more than 10,000 isomers. The separation of pure phenolic compounds from phenolic resin becomes nearly impossible. The complexity of the isomeric compositions leads to amorphous materials.The mechanism of the reactions leading to the formation of novolac phenolic resin is given in Scheme 1.1. In presence of acid electrophilic attack of the conjugate acid of formaldehyde on phenol occurs. This primary ring substitution reaction produces the hydroxymethyl phenols[1.1,1.2,1.4,1.5]. Hydroxymethyl group generated is very unstable in the acidic medium and converts to benzylic carbonium ions. It will react at the *ortho*- or the *para*-position of phenol producing methylene bridge between rings. On further condensation fusible and soluble low to medium molecular weight novolac resin is formed where *ortho*- and *para*- links occur at random.



Scheme 1.1: Acid catalysed process in phenol-formaldehyde system: Formation of novolac resin

This resin is important for its outstanding properties such as ease of processibility, strong adhesion to various substrates, chemical and corrosion resistance, good mechanical properties, and dimensional stability. These wide-ranges of advantageous properties make this resin highly useful for various applications in different sectors ranging from commodity materials to advanced technology applications. Furthermore, opportunities for appending new reactive groups like epoxy to phenolic hydroxyl substituent occur, which is a benefit of this system. Modification of novolac is thus an accessible procedure to provide new era of making novolac resin-based materials with modulated functionalities for applications in diverse high-tech fields.

1.3 Polymers to remediate azo-dye containing waste waters

1.3.1 Introduction

The harmful effects of human activity on the environment are increasing day by day. Water pollution is one such environmental issue that affects water bodies. The fresh water resources are contaminated with different types of pollutants. Approximately 2.5% of the total water body is fresh water. The rest is salted water. If this much water is polluted human civilization will be in great trouble. Out of the total fresh water 69% is frozen in ice caps located on Antarctica and Greenland[1.6]. Therefore only 30% of the total freshwater is available for human consumption. The life on earth is very much dependent on the amount of fresh water available. It is an important resource for human civilization to carry on further. However, investigations revealed health and hygienic problems of more than 25% of the total world population related to freshwater pollution and the percentage continues to climb[1.7]. Discharge of wastewater contaminated with various pollutants from industrial sectors is a considerable pollution concern of freshwater supplies. A particular note is the organic pollutants like synthetic dyes discharged from several industries because many of them are known to pose serious health risks. Azo dyes are reported to be the largest and most versatile class of synthetic dye stuffs used as coloring agents in various industries and hence accounts for greater risk of their toxic effects affecting the society[1.9,1.10]. Therefore, removal of azo-dyes from wastewaters before discharging has become worldwide focus of attention.

1.3.2 Azo dyes and their effects on environment and human health

Azo-dyes must carry one or more azo functionality (-N=N-) offering the dye color, called chromophores ("chroma" means colour and "phore" means bearer), as well as an electron withdrawing or donating substituents that cause or intensify the coloring capacity of the chromophores, called auxochromes ("auxo" means augment). Prominent types are: a) Acid dyes are used for polyamide and protein substrates such as wool, silk and nylon. b) Disperse dyes are used for hydrophobic substrates such as polyester clothes and acetate.

c) Direct and reactive dyes are used for cellulosic substrates such as cotton, rayon, linen, and paper. Generally, the synthesis of azo dyes involves two steps. Step-I is the generation of diazo compound from an aromatic amine (i.e. Ar-NH2 → $Ar-N_2^+$), a process known as diazotization, and step-II is the reaction of the diazo compound with a phenol, naphthol, aromatic amine to produce the corresponding azo dye, This process is known as diazo coupling reaction (e.g. $Ar-N_2^+ + Ar'-OH \rightarrow Ar-N{=}N-Ar'-OH$). This process is suitable for the synthesis of azo-dyes that possess complex aromatic molecular structure and exhibit structural diversity. Thus the essential precursors of azo dyes are structurally variable aromatic amines. Chemical structures of some typical azo dyes are illustrated in Figure 1.2.

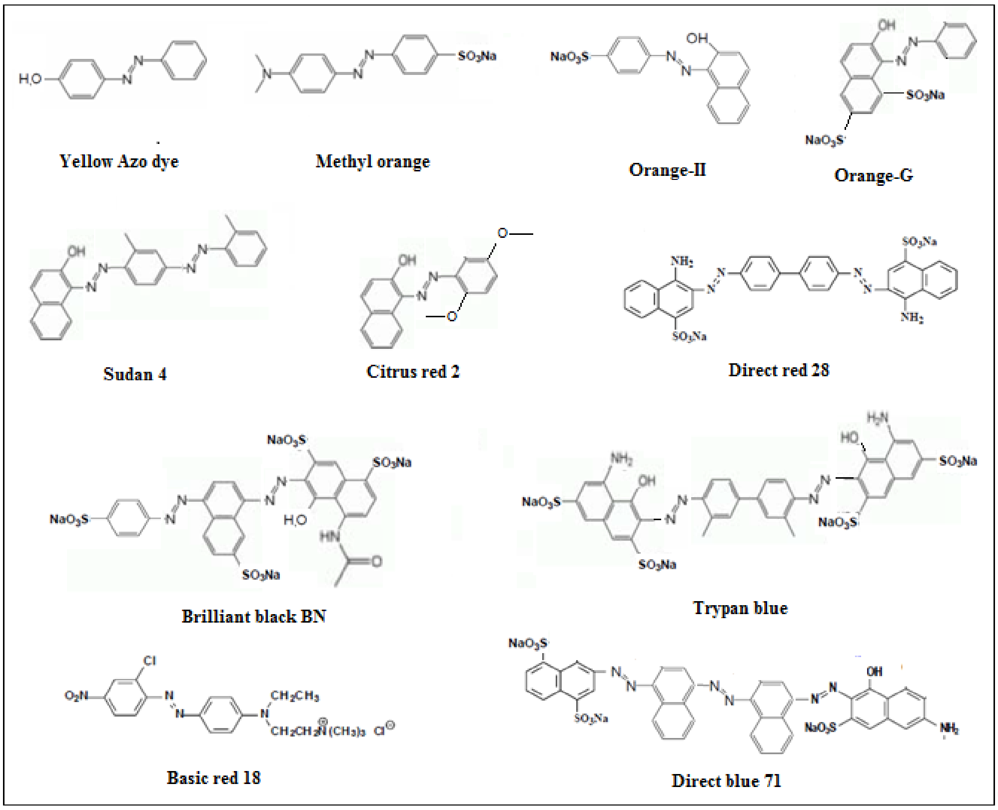


Figure 1.2: Chemical structures of some typical azo-dye colorants

Azo-dye colorants possess reactive groups that enable good bonding to the substrates being processed in textiles, printing, rubber, cosmetics, plastics, leather industries. It is estimated that a massive amount of azo dye colorants is being wasted from these industrial sources and get discharged into the water streams during overall production and utilization[1.9,1.12].

Since these colored compounds have a synthetic origin and complex aromatic molecular structures, which make them inert and resistant to biodegrade when discharged into waste streams, their undesirable nature has attracted considerable attention. Their presence in low concentrations in wastewater is highly visible reducing sunlight penetration, photosynthesis efficiency and dissolved oxygen concentrations thereby becomes hazard to aquatic organisms[1.13-1.15]. Furthermore, some azo-dyes and their enzyme-mediated degradation products may be mutagenic and/or carcinogenic and toxic[1.16-1.21]. Dermal, systemic and bacterial biotransformation is associated with reductive cleavage of azo bonds and consequent release of aromatic amines metabolites, which may have toxicological properties, particularly mutagenic and/or carcinogenic and allergenic potential[1.22,1.23]. For instance, benzidine-based azo-dyes such as Direct Red 28 was noted to produce human urinary bladder carcinogen benzidine, if ingested (Figure 1.3)[1.24,1.25].

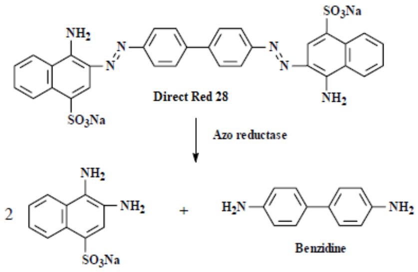


Figure 1.3: Reductive-cleavage of Direct Red 28 using an azo-reductase enzyme

Aromatic amines get metabolically oxidized further to reactive electrophilic species which can irreversibly attach to DNA with consequent end in mutation[1.26-1.28]. However, toxicity of such amines depends on the metabolic activation to reactive electrophilic intermediates that damage DNA. Varieties of azo dyes bearing free aromatic amine groups in their structures can be metabolically oxidized without azo reduction and showed mutagenic response[1.26]. Other mechanism of azo dye carcinogenicity indicated the activation via direct oxidation of the azo linkage to highly reactive electrophilic diazonium salts[1.26].

Thus the carcinogenicity can be a result of direct action by the azo-dye itself, or the formation of aromatic amines generated during the reductive biotransformation of the azo bond, or even caused by the metabolically generated reactive species[1.21,1.29]. According to Chequer et al., exposure of azo dye Disperse Red 1 (DR1) causes biotransformation to products exhibiting the genotoxic and mutagenic potential[1.20]. According to the European Commission Regulation 552/2009/EC, all azo dye colorants based on carcinogenic aromatic amines are restricted for use in textile and leather articles[1.30,1.31]. Therefore, the importance of their removal from water bodies is obvious.

1.3.3 Azo dye containing wastewaters

Azo dye containing wastewater from various industrial outlets such as textile, leather, paper, printing, food, cosmetics, paint, pigments, petroleum, solvent, rubber, plastic, pesticide, wood preserving chemicals and pharmaceutical industries etc under uncontrolled and unsuitable condition is a serious threat to the receiving water bodies and is a main environmental problem. The discharge of azo dye containing wastewaters into the environment without proper treatment may have a serious health hazard to humans and aquatic living creatures. The textile industry is the largest manufacturer of azo-dye containing wastewaters because of the large volume of water involved in the dyeing process. It is estimated that approximately 93% of the intake water comes out as heavily colored wastewater from this industry[1.32]. During this processing, inefficiencies in bonding to the fabrics result in large amounts of azo-dyestuff being directly lost to the wastewater[1.33], which ultimately finds its way into the water streams. This leads to disruption of the total ecological or symbiotic balance of receiving water streams. Thus, studies concerning the feasibility of treating dyeing wastewater before discharging into environment are very important.

1.3.4 Wastewater-treatment methods

During the past several decades, a number of chemical, biological and physico-chemical treatment methods were adopted to decrease the color contents from wastewater.

1.3.4.1 Chemical Methods

Different chemical oxidation strategies have appeared in the last decades to treat colored wastewaters. These strategies can be divided into two categories: (a) classical chemical treatments (b) advanced oxidation processes (AOPs)[1.34]. Classical chemical treatments usually include the addition of an oxidizing agent (chlorite, hydrogen peroxide and ozone) to the water containing the dye pollutant. The concept of AOPs was first pioneered by Glaze and co-workers in 1987 as near ambient temperature and pressure wastewater treatment processes. The AOPs methods are based on the formation of very powerful oxidizing agents such as hydroxyl radicals (OH•) in solution. The OH•/H_2O has a very strong oxidation potential to start cascade of oxidation reactions that can decompose a variety of azo-dye compounds in wastewater. Fenton (a solution of hydrogen peroxide and ferrous iron catalyst) and photo-Fenton (H_2O_2/UV) processes are the most important AOPs[1.35,1.36]. In photo-Fenton process light accelerates the reaction increasing the rate of degradation of contaminants as an extra dose of HO• are generated. All these methods have their advantages and disadvantages as highlighted in Table 1.1 in the treatment of dye contaminated waters.

Table 1.1: Advantages and disadvantages of chemical oxidation methods of dye removal

	Method	Advantage	Disadvantage	References
Chemical oxidation	Conventional oxidation processes by oxidising agents such as ozone, hydrogen peroxide and chlorite	Simple, initiate and accelerate the azo bond cleavage; Ozonation: applied in gaseous state, no alteration of volume.	Expensive due to employment of a large amount of oxidants; release of toxic by-products, *e.g.*, aromatic amines; not applicable for all types of dyes.	[1.37]
	Advanced oxidation processes (AOPs): Fenton/photo Fenton type	Fenton type: cheap and represents high chemical oxygen demand removal and decolourisation efficiency.	Production of sludge with a high content in iron and iron deactivation by the formation of complexing agents	[1.35,1.36]
		Photo Fenton type: no sludge formation and high chemical oxygen demand removal in a short retention time	Not effective for all types of dyes; formation of by products and inefficient use of UV light can increase the cost of the process	

1.3.4.2 Biological Methods

Biological methods, which utilize the ability of bacteria, fungi, or its combination system, are often the most economical alternative compared to other processes[1.38-1.40]. Microorganisms that produced enzymes may be used in decomposition and ultimate mineralization of dye pollutants. The ability of bacterial cells to metabolize azo dyes to a significant level in anaerobic, aerobic or combined treatment processes is on the front line and priority research area in environmental sciences. Attempts to isolate bacterial cultures capable of degrading azo dyes started back in 1970 with reports of Bacillus subtilis[1.41] and since then many researches offers use of numerous bacteria and fungi capable of azo-dye decolorization, either in pure cultures or in consortia involving secretion of enzymes such as azoreductase etc[1.40,1.42]. However, some shortcomings as listed in Table 1.2 are associated in this method.

Table 1.2: Advantages and disadvantages of biological methods of dye removal

	Method	Advantage	Disadvantage	References
Biological	White-rot fungi	Economically feasible, environmentally benign approach	Not applicable for all dyes, special azo dyes, technical constraints, slow process	[1.43]
	Microbial cultures	Low operation cost	Produce toxic aromatic amines, slow process, unable to cope with larger volume of wastewater	[1.44]
	Microbial biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors(pH, salts, temperature)	[1.45]

1.3.4.2 Physico-chemical Methods

Over the years, numerous treatment practices were devoted to remove azo-dyes from effluent. Studies have mainly concentrated on the development of economical and effective removal process. From this view point, several physico-chemical methods[1.46-1.52] such as adsorption, filtration, coagulation, chemical flocculation, *etc* are employed worldwide. The advantages and drawbacks of these methods are presented in Table 1.3. Among these techniques, adsorption has been proved as the most economical, effective and widely used method for removing different types of azo-dye contaminants from wastewaters without the formation of harmful substances. This process provides an attractive alternative for the treatment of polluted waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. It has also been found to be superior to other technique for wastewater treatment in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation. The adsorbable solute that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is adsorbent. Decolorization by adsorption is a surface phenomenon involving two common mechanisms, surface adsorption and ion exchange[1.53], and is associated with a number of influential physiochemical factors, such as dye / sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time[1.54]. So far, several adsorbents have been explored for wastewater decolorization[1.52]. In recent years, attention has been directed toward polymer-based adsorbent materials.

Table 1.3: Advantages and drawbacks of physico-chemical methods of dye removal

	Method	Advantage	Disadvantage	References
Physico-chemical	Coagulation/ Flocculation	Simple, economically feasible, satisfactory removal of disperse, sulphur and vat dyes	Removal is pH dependent, High sludge production, high cost of ferrous sulphate and ferric chloride, handling and disposal problems	[1.55]
	Membrane filtration	Removes all dyes types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes	[1.56]
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, expensive regeneration, not effective for all dyes	[1.56]
	Adsorption	Economical and environmentally safe, removal of wide variety of dyes, effective production of high-quality treated effluent	Some adsorbents are very expensive	[1.56,1.57, 1.58]

1.3.5 Polymeric adsorbents as effective materials for wastewater treatment

Polymeric materials represent an interesting and attractive alternative as adsorbents for removal of dyes from wastewater. They deserve particular attention because of their particular structures and physicochemical properties, like hydrophilicity, swellability, porosity, mechanical rigidity, chemical stability, adjustable surface chemistry, easy processibility, and feasible regeneration[1.59]. Surface modification of polymeric adsorbents can be made by inserting ligands to obtain specific sorbents. From this point of view, the polymeric adsorbents could be anticipated to provide a particularly useful feature when employed for the removal of azo dyes from wastewater.

1.3.6 Adsorption of azo dyes on polymeric materials: Literature Review

Worldwide attempts have been made to find out polymeric adsorbents for azo dyes. M. Yilmaz *et al* reported interesting examples of calyx[4]arene-based oligomers and demonstrated their azo-dye removal abilities[1.60]. An extensive review on “Adsorption of azo dyes on polymer materials” has been published by A. R. Nešić *et al* in recent years[1.61]. This article presented a substantial amount of review material covering up-to-date polymeric materials, both synthetic and natural by origin, as adsorbents for azo dyes, including several articles published by 2013. In the same year, H. Gao *et al* developed functional ionic liquid cross-linked polymer for removal of anionic azo dyes from aqueous solution[1.62]. As another example, S. S. Li *et al*. synthesized[1.63] porous polyurea absorbent as attractive candidate for removal of azo dyes. In the last few years (after 2013), researchers have attempted to prepare a number of polymeric adsorbents for removal of azo dyes from aqueous solutions. Y.V. Shalaeva *et al* reported amidoamine calix[4]resorcinarene-based oligomers and polymers as efficient sorbents of azo dyes[1.64]. A new copolymer of acrylamide with allyl methacrylate [poly(acrylamide-co-allyl methacrylate) (Poly(AA-co-AMA)] was cited by Y. Yildirim *et al* and employed for the removal of azo dyes[1.65]. As another example, G. Liao *et al* developed a rich-amine porous organic polymer *via* the Schiff base reaction with melamine and terephthalaldehyde as the monomers[1.66]. The created polymer was capable of adsorbing azo dyes (methyl orange) from aqueous solution. The use of chitosan derivatives as adsorbents to the azo dye removal process cited to date by excellent review[1.67]. Very recently, M. Blachnio *et al* devised chitosan−silica hybrid composites for removal of sulfonated azo dyes from aqueous solutions[1.68]. Cross-linked polymer derived from β-cyclodextrin and hydroxypropyl- β –cyclodextrin was recently adopted by J. A. Gabaldón *et al* as adsorbent of azo dye (Direct Red 83:1), for water treatment applications[1.69]. This background information in this specific topic clearly demonstrates the potential of polymeric materials as adsorbents to remove azo dyes from wastewaters.

1.4 Antimicrobial Polymer-Metal Nanoparticle Hybrids

1.4.1 Introduction

Microbial infections have become again a public health concern, which has attained significant interest in the development of antibacterial materials. However, conventional antibiotic therapies are less efficient owing to the overuse of antibiotics and the emergence of bacterial resistance to antibiotic, resulting in poor treatment efficacy and the significantly increasing cost of healthcare[1.70,1.71]. Thereby, development of new generations of antimicrobial agents is highly demanding for effective killing of pathogenic bacteria. Metal nanoparticles (NPs) have received great attention for their enhanced antimicrobial effects as compared to traditional materials[1.72]. In this context, polymer–nanoparticles hybrid opens a new window of possibility in the development of new-age antimicrobial materials[1.73]. For the past few decades, silver nanoparticles (AgNPs) have attained a special focus for a wide range of applications, particularly in the biomedical field, due to their broad spectrum antibacterial properties[1.74-1.76]. In this context, immobilization of AgNPs onto polymeric substrates emerges a route to further extend applications in the medical field such as antimicrobial materials for wound dressing.

1.4.2 A general overview of metal nanoparticles

Nanoparticles are submicron scale entities (1-100 nm)[1.75]. The term "*Nano*" is derived from Greek word dwarf meaning extremely small. The particles have sharp and uniform size in the nanometer range. Metal nanoparticles are generally categorized as inorganic nanoparticles. In the area of nanoscience and technology it has much importance as it has superior material properties with versatile functions. Typically, nanoparticles are synthesized via two different methods: "*Bottom-up*" and "*Top-down*" approaches[1.76-1.78]. The "*bottom-up*" or constructive approach involves the build-up of material from atom to clusters to nanoparticles. Examples of this approach include self-assembly of monomer/polymer molecules, chemical or electrochemical nanostructural precipitation, sol–gel processing, laser pyrolysis, chemical vapour deposition (CVD), pyrolysis and bio-assisted synthesis etc. The "*Top-down*" or destructive approach refers to the reduction of a bulk material to fine nanometric scale particles. The most commonly used top-down methods are mechanical milling, nanolithography, laser ablation, sputtering, thermal decomposition and grinding.

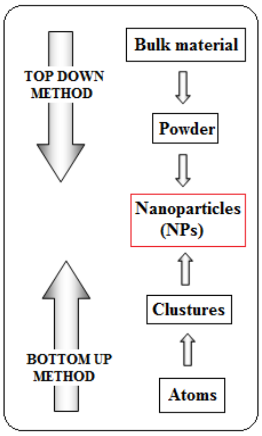


Figure 1.4: Schematic diagram of nanoparticles (NPs) synthesis (top-town and bottom-up methods)

A schematic diagram of the process is presented in Figure 1.4. In general, nanoparticle synthesis methods can be divided in three groups: physical methods, chemical methods, and bio-assisted methods.

Due to distinctive properties such as small dimension, exceptional surface properties like high surface area to volume ratio, shape, spacing, confined sizes, color, reactivity and sensitivity to environmental factors, NPs have shown great potential for diverse applications[1.79]. They have unique characteristics such as surface Plasmon resonance (SPR)[1.80,1.81] playing a key role of optical properties. SPR is the resonant oscillation of the conduction electrons in the nanoparticles excited by incident photons. These special properties make NPs as crucial components of nanotechnology and nanoscience.

1.4.3 Antimicrobial metal nanoparticles

With the introduction of nanotechnology, metal nanoparticles offer promise as antimicrobial agents against a broad spectrum of micro-organisms, including several antibiotic-resistant bacterial strains[1.82]. In this context, noble metal nanoparticles have attracted significant interest because they have proven to be very useful in medical applications due to their well-known antibacterial, antifungal and antiviral properties[1.83]. Their high surface area to volume ratio is related the adherence to the surface of micro-organism and membrane functions. Information on the exact mechanisms for antimicrobial activity is still being the subject of rigorous research. However, proposed possible mechanisms in this regard: metal nanoparticles can exert their effect on microbial cells by generating membrane damage, oxidative stress, and injury to proteins and DNA[1.82].

1.4.4 Silver nanoparticles (AgNPs) as antimicrobials

Silver has been an excellent antimicrobial and has been used since ancient time to discourage contamination of microbes. Silver in its metallic state is inert but ionized state (Ag^+) is capable of killing about 650 microorganisms from different classes such as gram-negative and gram-positive bacteria, fungi or viruses[1.84]. The unique physical and chemical properties of silver nanoparticles (AgNPs) only increase the antimicrobial efficacy of silver. With the development of nanotechnologies, AgNPs have attracted remarkable attention for applications in biomedical field because of their superior antimicrobial activity[1.85-1.87]. Though there are multifaceted mechanisms attributed to the antimicrobial activity shown by AgNPs, the exact mechanism of action remains heavily debated[1.88,1.89]. It is suggested the silver ions (Ag^+) released from AgNPs may contribute to antimicrobial activity[1.90]. The most known mechanisms of AgNPs involve[1.91]: (i) disruption of the integrity of the bacterial cell wall and membrane causing membrane damage (ii) interaction with thiol and amino groups causes damage of enzymes and proteins affecting cell viability (iii) silver ions released from AgNPs can bind to phosphorus moieties in DNA, leading to inactivation of DNA replication and (iv) reactive oxygen species (ROS) generation by silver nanoparticles and silver ions, causing damage to the intracellular structures, in particular mitochondria and DNA. Owing to antimicrobial capability, AgNPs are considered crucial components of medical field.

1.4.5 Polymer-silver nanoparticles hybrid as antimicrobial material

AgNPs have attracted interest for development of new age antibacterial agents. However, long-term application of AgNPs might suffer from their tendency to form aggregates reducing effectiveness. Additionally, AgNPs lack mechanical property, which is not desired for many material and biomedical applications. In this context, the polymers have been proven to be good host for AgNPs to develop useful composite materials exhibiting synergistic, unique and potentially useful properties that are not found in the individual components. It sounds evident that the polymer matrix can provide notable features: it imparts stability and minimizes aggregation of AgNPs exhibiting antibacterial activity. More importantly, the usage of polymeric support matrix is believed to prolong the activity of AgNPs by controlling the escape of the nanoparticles to the media and hence controls the microbiological risk. Therefore, the development of hybrid materials of polymers with AgNPs has attracted considerable interest for a wide range of biocidal applications[1.92-1.99]. The *in-situ* synthesis method, which is commonly used toward the manufacturing of hybrids, is based on the reduction of silver ions that are dispersed in polymer matrices. Another approach involves mixing *ex-situ* synthesized AgNPs with the polymers. Hence, the use of polymers acting as matrices and stabilizers is an insightful approach and attracts special interest in the era of new antibacterial agents.

1.5 Objectives, outcomes and author's achievements

The objective of this research program is to develop novolac type phenolic resin-based materials with special emphasis to their applications such as adsorptive removal of azo dye pollutants and antibacterial activity. With this aim, novolac type epoxy resin precursor has been successfully developed and the following objectives have been undertaken:

i) Novolac type phenolic resin-based network materials for removal of azo dyes from aqueous solutions.
ii) Novolac-based polymer- silver nanoparticles hybrid: An effective antibacterial material.

All these materials were fully characterized. The azo-dye removal performance of all these well-characterized network materials as adsorbents was evaluated and presented in this dissertation. Furthermore, The antibacterial effectiveness of hybrid against representative Gram-positive / Gram-negative bacteria was estimated and presented in this dissertation. Author is confident that the newly designed novolac type phenolic resin-based materials presented in this dissertation add a body of knowledge pertaining to biomedical field, separation, environmental and materials sciences. From these accomplishments, there have been several outcomes, the results of which have been published in refereed journals and presented at conferences.

1.6 Thesis Organization

The dissertation highlights the novolac type phenolic resin-based materials design strategies, adsorption performances to remove azo dyes from aqueous medium, antibacterial activity relating to health care applications. The thesis is comprised of six chapters to communicate the findings of this investigation and is presented as follows:

Chapter-1, as seen above, gives an overview of the author's motivation for undertaking this research, the general aspects of phenolic resin, its versatile properties and the basis of its selection in designing new materials toward azo dye decolourization and antimicrobial applications. This chapter also outlines the general aspects of antimicrobial polymer–metal nanoparticles hybrids in the context of author's achievement on novolac type phenolic resin-based materials. Finally, objectives, outcomes and author's achievements and the organization of this thesis are presented.

Chapter-2 describes the synthesis and characterization of novolac type phenolic resin-based network polymers and their potential application in adsorptive removal of selected azo dye molecules from aqueous medium.

Chapter-3 presents in detail the synthesis and characterization of iron(III) loaded novolac-based networks and their efficacies as adsorbent materials for removal of azo-dyes from aqueous solution.

Chapter-4 reports the successful synthesis of novolac-based network polymer sorbent with 3-aminopyridine unit for adsorptive removal of a variety of azo dyes, i.e., methyl orange, orange-G and Orange-II.

Chapter-5 deals with the the preparation of an antibacterial hybrid of functionalized novolac polymer with Silver nanoparticles (AgNPs). The antibacterial effectiveness of the resulting hybrid against Gram-positive and

Gram-negative bacteria was estimated. The results provide evidence of hybrid to achieve designated goal in its antibacterial application.

Chapter-6 in brief gives overall conclusion on the endeavor towards design, synthesis, characterization and properties of newly developed novolac type phenolic resin-based materials.