ABSTRACT

Nanomaterials have consistently been receiving considerable amount of attention due to their wide range of applications. Metal oxide nanoparticles (NPs) exhibit a variety of physical and chemical properties with versatile applications as dyes, agrochemicals, semi-conductor and optically active ligands, drugs, catalyst, environmental decontaminants etc. The present work is focused on the synthesis of metal or metal oxide NPs and their characterization followed by their applications in the field of catalysis in organic synthesis and environmental remediation in removal of chemical contaminants from water, which may be outlined as follow:

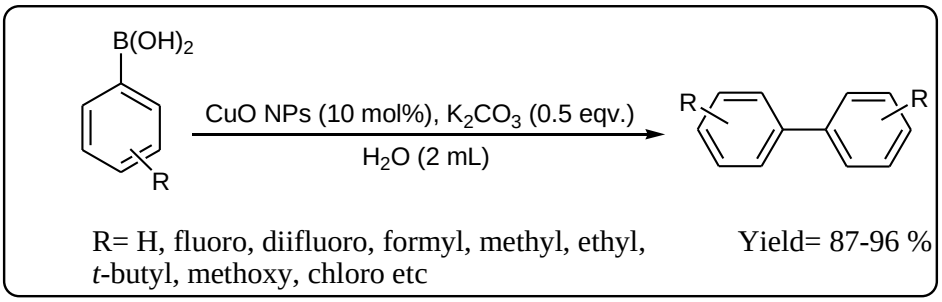
The present thesis consists of 8 chapters with the contents as outlined below:

Chapter 1 provides a general account on NPs as well as their synthesis and properties. The special emphasis is given on the synthesis of metal oxide NPs and their characterization as well as application in several fields like catalysis, adsorption, etc. Finally, the aims and objectives of the work have been highlighted.

The characterization of a material is the connecting bridge between the synthesis of material and its applications in different fields. Hence, **Chapter 2** describes the materials and methods used in the whole work. Characterization techniques *viz*. NMR, SEM, TEM, FT-IR, XRD, BET, EDAX etc. are utilized in the study of structure, morphology, property evaluation of the synthesized NPs, monitoring of reactions and identification of synthesized organic compounds.

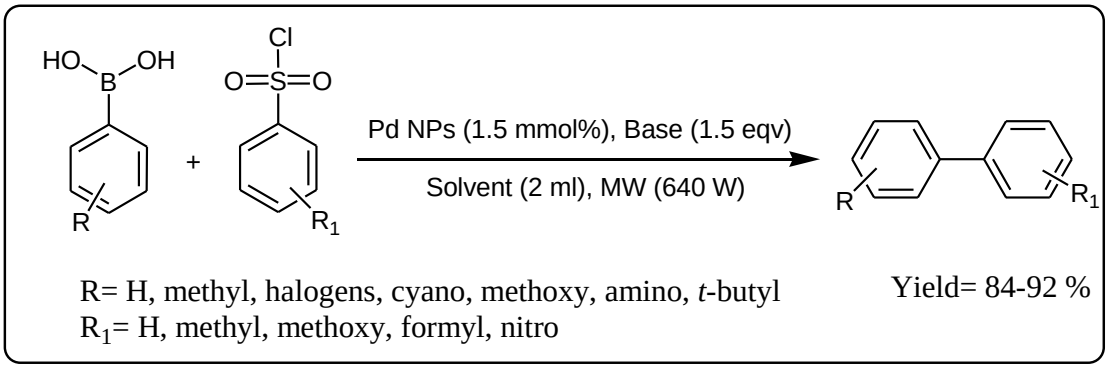
Chapter 3 deals with a simple *in-situ* soft chemical synthesis of rod-shaped CuO NPs, characterization and study of its catalytic performance in the aerobic homo-coupling of arylboronic acids to synthesize symmetrical biphenyls. Phenylboronic acids bearing electron-withdrawing groups like fluoro, difluoro and formyl provided corresponding homo-coupling products in good to excellent yields (92–96%, Scheme 1). We also investigated the homocoupling reaction of aromatic boronic acids bearing electron-donating groups. Phenylboronic acids bearing methyl, ethyl, *tert*-butyl, methoxy etc. groups afforded desired products in 87–93% yields. The catalyst is simple to prepare, environmentally benign, efficient, easy to recover, reusable, stable and heterogeneous in nature. The good selectivity of homo- coupling over the Suzuki cross-coupling shows potential application in

the synthesis of biphenyls.



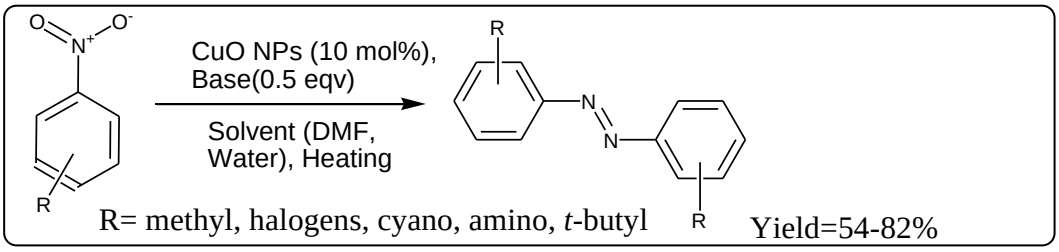
Scheme 1: General representative scheme for the synthesis of biphenyls

Chapter 4 is focused on the synthesis of hetero-biphenyls (cross-biphenyls) from substituted arylboronic acids and aryl sulfonyl chlorides using palladium NPs under microwave irradiation. The principal advantage of this reaction is that it requires shorter time with desulfurization of aryl sulfonyl chloride. Possibly, the desulphurization could be exploited to inhibit environmental pollution caused by sulphur containing organic substances. This method deals with cross-coupling of benzene sulfonyl chlorides and arylboronic acids containing substituents like methyl, halogens, cyano, amino and *t*-butyl groups (Scheme 2). *In-situ* generated Pd NPs could be reused under optimized conditions with only a minor loss in its activity. The reaction is one of the examples of *in-situ* generated **N**anoparticle-catalyzed **O**rganic **S**ynthesis **E**nhancement (*i*-**NOSE**) approach. The simplicity of catalyst preparation, its stability, substrate specificity, easy recovery and regeneration clearly indicates that the catalyst could be reused in various type of catalytic reactions and industrial processes.



Scheme 2: General representative scheme for the synthesis of cross-biphenyls

Chapter 5 describes the one-step wet chemical synthesis of azo-biphenyl compounds from nitroaromatic compounds in presence of DMF-water as mixed solvent and CuO NPs as catalyst. There is sufficient reports evidence that azo-aromatic compounds need at least two-step reaction to form from its nitro-analogs. CuO NPs have been synthesized through simple wet chemical procedure and well characterized with the help of SEM, TEM, FT-IR etc. Sufficient amount of azo-biphenyl is formed in addition to small amount of azoxy-benzene and aniline. We investigated the formation of azobenzene reaction from nitrobenzene bearing electron donating as well as electron withdrawing groups. Nitrobenzene bearing methyl, *tert*-butyl and methoxy groups afforded desired products in 73–81% yields (Scheme 3). Nitrobenzene bearing electron-withdrawing groups like fluoro, chloro and iodo groups provided corresponding azobenzene products in poor yields (54.4–71.3%).The nanocatalyst is reusable and environmentally friendly in nature. In conclusion, we have successfully developed a simple and efficient CuO NPs catalyzed methodology toward the formation of azobenzene compounds directly from the corresponding nitroaromatic compounds. This protocol is relatively inexpensive and environmentally friendly manner. This reaction skips two-step synthesis of azobenzene compounds from nitroaromatics and opens a convenient synthesis procedure.



Scheme 3: General representative scheme for the synthesis of azobenzene

Chapter 6 is concerned with synthesis of non-magnetic iron oxide hydroxide nanoparticles with flower like morphology and its application to remove arsenic from contaminated water. It is found to play as an effective adsorbent media to remove As(III) from 300 μgL^{-1} to less than 10 μgL^{-1} from drinking water over wide range of pH. TEM image clearly reveals that the NPs in having flower like morphology with average particle size less than 20 nm. The material can be regenerated upto 70% using dilute hydrochloric

acid and it would be utilized for de-arsenification purposes. Novelty lies on the fact that the iron oxide material is stable at low pH with profound activity.

Chapter 7 deals with a simple in-situ soft chemical synthesis route towards nanoscale copper (II) oxide, its characterization and adsorption studies on removal of lead from drinking water. Adsorption studies reveals that the Pb(II) uptake onto CuO is a fast process and >70% of the uptake occurred within the first 10 min contact time and attained >92% in 60 min. Thermodynamic parameters and isotherm studies have been performed and adsorption is found to be heterogeneous, multilayer in nature. Reusability study also has been done for practical application in environment.

Chapter 8 summarizes all the results obtained in preceding chapters. A brief note on future work extendable from the findings of the thesis work is also given.