2. Scope of the work

A wide verity of toxic inorganic and organic chemicals is discharged to the environment as industrial effluents, causing serious air, water and soil pollution. Heavy metals, organic chemicals, and dyes are the most notorious contaminants in aquatic environments because of their huge volume of production, slow biodegradation, discoloration and toxicity [159]. With the increasing demand for economical large scale water treatment facilities, the development of efficient catalysts and adsorbents for the removal of dyes, organic wastes, and heavy metals that exhibit fast kinetics at high flow rates would be of great significance.

In recent years, the research in material science basically deals with the three things i.e. synthesis, development, and application. In the catalytic material, the rate of a reaction increases and reaches the end point easily. Mesoporous materials are one such material, synthesized by supramolecular self-assembly of various metal oxide precursors [160] and effectively used as a solid supports or hosts for a variety of catalytic groups [161] due to their well ordered mesopore structure and exceedingly high surface area.

Not only metal but also incorporation of various metal oxides into the MCM-41 and impregnation of metal onto the mesoporous support material (mesoporous metal oxide-MCM-41), enhances the adsorption, catalytic activity (photocatalysis, photo-Fenton process). These modified/design metal-mesoporous metal oxide-MCM-41 aid to degrade or adsorb organic and inorganic pollutants (phenolic compounds, dyes and hexavalent chromium etc) by the process of photocatalysis, photo-Fenton and adsorption. Hence, design of metal - metal oxides modified MCM-41 is an important area of research.

Organic dyes are one of the notorious contaminants in aquatic environments because of their huge volume of production from industries, slow biodegradation, decoloration and toxicity [162]. Over 700,000 tons of dyes and pigments are produced annually worldwide, of which about 20% are in industrial effluent from the textile dyeing and finishing processes [163]. These pollutants are not only harmful to environment but also hazardous to human health. The adversity of dyes even at trace level attracts the environmentalist and scientist to develop suitable processes for their control. The best alternative is photocatalysis because of cost-effectiveness, non-toxic,
eco-friendly, reproducibility. For photocatalytic dye degradation, the material must be semiconducting. Various semiconducting oxides such as TiO$_2$ [54], Fe$_2$O$_3$, ZnO [58], CdSe, ZrO$_2$ [164], WO$_3$, SnO$_2$, etc. have been used as photocatalysts. These semiconducting oxides modified with metals and other metal oxides are also active for photocatalytic dye degradation, in which dyes are excited by absorbing light photons and immediately inject electrons into the conduction band (CB) of semiconductor leads initiating the dye degradation. Likewise, in the adsorption process, the adsorption of dyes occurs efficiently if the adsorbent is highly porous and contains a high surface area. Although both semiconducting and mesoporous materials show efficient photocatalytic and adsorption activity towards dye removal, but there is still some gaps in photocatalysis and adsorption study. This is because of the low surface area of semiconducting materials which gives less interaction of dye molecules with catalyst surface and decreases the activity. In order to avoid these problems, researchers and environmental scientist are in search of alternative materials which can behave both as photocatalyst and adsorbent. It has also been reported that metal ions such as Ag$^+$, Cu$^{2+}$, Cr$^{6+}$, Hg$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ are incorporated to increase the photocatalytic activity of TiO$_2$ [165]. When the mesoporous support modified with the above metal ions, it could act as a semiconducting materials and degrade organic dyes. That means here a single material is developed which has semiconducting as well as high mesoporous surface property. Cu incorporated mesoporous Al$_2$O$_3$–MCM-41 could behaves as a photocatalyst as well as adsorbent and degrade organic dyes by the formation of hydroxyl radicals.

Phenols and Phenolic compounds (phenol, 2-chloro-4-nitrophenol, and 4-chloro-2-nitrophenol) are major threats to aquatic life [166] because these are highly carcinogenic and poisonous for all ecosystems [167-169]. Different methods such as ozonolysis, photosynthesis, photocatalytic decomposition, reverse osmosis, ion exchange, precipitation, and electrodialysis have been implemented for their removal [170-172]. However, the control of organic pollutants such as phenol with the aid of a catalyst has been a particular research interest. Numerous catalytic processes have been reported as realistic methods for the control of phenolic contamination. These processes are referred to as advanced oxidation processes (AOPs) [173]. Photo-Fenton oxidation, as an AOP, is one of the most advanced and vital methods for the degradation of organic pollutants. The notable benefits of Fenton-type processes are
their ability to convert a broad range of pollutants to harmless or biodegradable products and the fact that they involve relatively cheap reagents that are safe to handle and eco-friendly. Photo-Fenton process proceeds in presence of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ in presence of light ($\text{h}\nu$). Homogeneous photo-Fenton process has lots of drawbacks i.e. separation problem and reusability. Hence, heterogeneous photo-Fenton process is an alternative to homogeneous advanced oxidative process. Iron supported with high surface mesoporous materials are known to be efficient heterogeneous photo-Fenton catalyst [174]. Iron oxide supported on mesoporous materials like $\text{MnO}_2$ and silica (MCM-41) act as an efficient photo-Fenton catalyst because mesoporous materials have high textural property, thermal stability and also chemically stable. In that context, iron incorporated manganese oxide-silica support ($\text{Fe}^{2+}/\text{MnO}_2$–MCM-41) can be considered as a heterogeneous photo-Fenton catalyst for removal of phenolic compounds. Moreover, $\text{Cu}^{2+}/\text{Al}_2\text{O}_3$–MCM-41 can also act as a photo-Fenton like catalyst for degradation of phenolic compounds.

The presence of heavy metals in aquatic bodies has been known to cause pollution problem. These metal ions are non-degradable. Among these inorganic pollutants chromium is an important industrial metal that is considered a priority pollutant by US environmental protection agency. Chromium occurs mainly in two common oxidation states in nature, Cr (VI) and Cr (III). Out of which hexavalent chromium is 100 times more toxic than the other [175]. The removal of chromium from waste water is generally accomplished by employing various chemical and physical means such as hydroxide precipitation, ion exchange, adsorption and membrane process. Recently, a new technology, based on photocatalysis to eliminate Cr (VI) ions, a toxic pollutant in the environment was applied using solar energy [176, 177]. The photocatalytic reduction of Cr (VI) using semiconductor particles at lower pH has been widely used. The photocatalysts used are mainly CdS, ZnS, WO$_3$, TiO$_2$, ZnO; titania modified mesoporous silicate, sulphated titania [178-183]. So, heterogeneous catalysis and photochemistry principles were used to explain these processes. Here, Cu incorporated $\text{ZrO}_2$-MCM-41 could behaves as a semiconducting like visible light active material and also used for the photo reduction of hexavalent chromium Cr (VI).

The direct oxidation process of benzene to phenol would be the most economical route, until now only the indirect manufacturing process have been operated. The reason is that, the activation of C-H bond in benzene is difficult due to its
resonance stability. In recent years there has been a growing research interest in finding a suitable solid catalyst for the selective oxidation of benzene to phenol under mild reaction conditions with clean oxidants such as O\textsubscript{2} & H\textsubscript{2}O\textsubscript{2}. Because of their regular, hexagonal mesoporous structure and potential application in catalytic reactions, MCM-41 molecular sieves have attracted a considerable scientific attention. The catalytic properties of these materials can be significantly improved if specific transition metal cations, anions or metal complexes are introduced into the structure. Recently various efforts have been devoted to study the catalytic properties of the so-called redox molecular sieves in the liquid phase oxidation of organic compounds [184-185]. In the present study the catalytic activity Cu modified mesoporous ZrO\textsubscript{2}-MCM-41 was studied towards oxidation of benzene.

2.1. Objectives of the study

The main objective of the present investigation is to synthesize and design high surface area mesoporous metal oxide (Al\textsubscript{2}O\textsubscript{3}, MnO\textsubscript{2}, and ZrO\textsubscript{2}) modified MCM-41 and Fe, Cu etc promoted mesoporous metal oxide modified MCM-41 (Al\textsubscript{2}O\textsubscript{3}-MCM-41, MnO\textsubscript{2}-MCM-41, and ZrO\textsubscript{2}-MCM-41). The focus is to apply these materials as an adsorbent and a heterogeneous catalyst for adsorption, photocatalysis and photo-Fenton processes in order to remove the organic and inorganic pollutants. I have taken the help of various advanced instrumental techniques for the detail characterization and identification of active sites.

1) Synthesis of Cu/Al\textsubscript{2}O\textsubscript{3}-MCM-41 for enhanced photocatalytic and adsorptive degradation of organic dyes.

2) Quick photo-Fenton degradation of phenolic compounds by Cu/Al\textsubscript{2}O\textsubscript{3}–MCM-41 under visible light irradiation: small particle size, stabilization of copper, easy reducibility of Cu and visible light active material

3) Design and synthesis of mesoporous nanocomposite meso-MnO\textsubscript{2}-MCM-41: a promising material for photocatalytic and adsorption study on degradation of organic dyes under visible light.

4) Fabrication of Fe/MnO\textsubscript{2}-MCM-41 as photo-Fenton like catalyst for the degradation of phenolic compounds.

5) Synthesis of Cu/ZrO\textsubscript{2}-MCM-41 and its catalytic activity towards hexavalent chromium under visible light.

6) Hydroxylation of benzene by mesoporous Cu/ZrO\textsubscript{2}-MCM-41.