Present work was aimed to utilize agricultural waste - wheat straw. Silica was extracted from wheat straw thorough microwave digestion followed by calcination. Microwave digestion was found to be an alternative method to incineration or burning of wheat straw as the later process is a big menace. Scheme of extraction of silica from wheat straw is shown in Fig.1. Wheat straw from wheat plants was treated with hydrochloric acid in a microwave digester. After washing, product was calcined and characterized. Particle size distribution, surface area, porosity, crystallinity, chemical and morphological studies were carried out for characterization of silica. SEM, EDX, TEM, XRD, FTIR, TGA were also used to characterize the material. Mesoporous, amorphous, nano sized, pure silica was obtained from the process followed.

Fig.1. Extraction silica from wheat straw

Silica obtained through this process was used as solid acid catalyst in the synthesis of two bio active materials 1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile and 7-hydroxy-4-methylcoumarin as shown in Fig.2.

Synthesis of 1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile, and its derivatives, was a single pot reaction in aqueous media. Equimolar quantities of aromatic
aldehydes, ethyl acetoacetate, hydrazine hydrate and malononitrile were taken in each case. Good yield was obtained in very short duration at 80 °C. Acidic nature and mesoporous nature of silica might have resulted in the good yield.

Synthesis of 7-hydroxy-4-methylcoumarin by Pechmann condensation method was carried out with resorcinol and ethylacetoacetate. Good yield was obtained at 80 °C using wheat straw extracted silica, without any functionalization using as catalyst. It was solvent free reaction. Reaction mechanism, supported by DFT calculations, has been proposed. A number of bioactive materials can be synthesized using this green catalyst.

Fig. 2. Applications of wheat straw silica (WS-nSiO$_2$) as catalyst in pyranopyrazoles and coumarin synthesis

Key words: Wheat straw, mesoporous nano silica, microwave digestion, 1,4-dihydropyrano[2,3-c]-pyrazole-5-carbonitriles, 7-hydroxy-4-methylcumarin
Organization of Thesis

Thesis is divided in four chapters. Introduction of the topic and relevant literature review has been presented in chapter 1. Literature review consists of available thermal and chemical methods for production of silica from agricultural waste. Methods of extraction of silica from agricultural waste have been summarized in part 1.2. Applications of silica have been summarized in part 1.3, followed by work on literature review on pyrano[2,3-c]pyrazole-5-carbonitrile derivatives and coumarin derivatives.

Materials used and methods followed in the work have been given in chapter 2. Chapter 2 contains three parts. Extraction of silica by using microwave induced combustion followed by calcination at various conditions has been discussed in Part I. Characterization techniques used for extracted silica has also been presented. Details of the green protocol followed for preparation of 1,4-dihydropyrano[2,3-c]-pyrazole-5-carbonitrile and synthesis of 7-hydroxy-4-methylcumarin catalyzed by WS-nSiO₂ has been reported in part II and part III, respectively. Methods followed for estimating the yield and the characterizations of products by TLC, 1H NMR, 13C NMR, IR etc. has been reported in part III.

Results obtained and discussions thereon have been presented in chapter 3. This chapter consists of three parts. Characterization of wheat straw and silica obtained from wheat straw using Particle Size Distribution (PSD), Surface area and Porosity analysis, X-Ray Diffraction Analysis (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Analysis (EDX), Fourier Transforms Infrared (FTIR) Analysis and Thermo Gravimetric Analysis (TGA) have been presented in part I. The result and discussion on the synthesis of 7-hydroxy-4-methylcoumarin and 1,4-dihydropyrano[2,3-c]-pyrazole-5-
carbonitriles using silica have been given in part II and III, respectively.

Chapter 4 gives the summary of the experiments and results of the research work. Conclusion drawn from the research work and future scope of work has been included. Annexure and list of papers published out of this work are given at the end.