Role of Activated Carbon in the Synthesis of Heterocyclic Compounds

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Abstract

A vast number of heterocyclic moieties are used in pharmaceutical research, agricultural science and drug discovery. Several methods are used for the synthesis of heterocyclic compounds. In the present work different nitro heterocyclic compounds possessing diverse biological activity have been successfully synthesized by simple, rapid, new environment friendly method involving the use of calcium nitrate supported on activated carbon prepared from agro waste material by chemical activation method. Activated carbon is a material with high porosity consisting of hydrophobic as well as hydrophilic surface functional groups making them beneficial for catalytic applications. The completion of reaction and purity of products was checked by silica gel TLC. Melting points were determined by open capillary method. Synthesized compounds were characterized by IR and NMR spectra.

Key words: Agriculture waste, calcium nitrate, green catalyst, heterocyclic compounds

Introduction

Environmental pollution is increasing rapidly in the last two decades. Today there is a growing consciousness about the hazardous effect of chemicals on environment and human being and chemical industry is one of the major contributors to this. In order to avoid the impact of chemicals on environment, green reaction conditions in synthetic processes can be adopted. The tight legislation to maintain greenness requires us to prevent the generation of waste, avoid use of auxiliary substances (e.g., organic solvents, additional reagents) and minimize the energy requirement [1].Therefore, to address depletion of natural resources and preservation of ecosystem it is urgent to adopt so called "greener technologies" to make chemical agents for well being of human health. A vast number of heterocyclic moieties are used in pharmaceutical research, agricultural science and drug discovery [2]. Heterocyclic compounds are building blocks in antitumor agents, antiparkinsonism agents and also in creating a number of molecules for treating a heterogeneous family of diseases [3]. Several methods are reported for the synthesis of heterocyclic compound [4-5]. Most of the synthetic procedures suffer from harsh reaction conditions, lengthy procedures, expensive catalyst and side products which may be hazardous and have disposal problems. In order to overcome these hazards, uses of greener technologies are a must. Supports obtained from industrial and agricultural waste may prove beneficial for green synthesis of heterocyclic compounds. There are few reports on new environment friendly methods using silica gel [6] and carbon [7] for their synthesis.D. M. Badgujar have reported new environment friendly nitration method involving the use of bismuth nitrate supported on silica gel as a solid support for synthesis of heterocyclic compounds [8].

Activated carbon is a material with high porosity consisting of hydrophobic as well as hydrophilic surface functional groups making them beneficial for catalytic applications. The surface can be modified

by chemical activation. Although commercial activated carbon is the preferred catalyst/ support, its high cost restricts its use. Therefore designing ways and testing materials for the production of activated carbon through economic ways is the need of hour. Carbons prepared from agro waste materials are found to have good adsorptive properties. The potential of these carbons needs to be assessed in terms of their ability to act as solid supports/catalyst in synthesis of heterocyclic compounds. This study presents new environment friendly method involving the use of calcium nitrate supported on activated carbon prepared from agro waste material by chemical activation method, as a solid support for synthesis of heterocyclic compounds.

Materials and Methods

Experimental

All chemicals used are of AR grade (S. d. Fine Chem. Ltd.,).The completion of reaction and purity of products was checked by silica gel TLC. Melting points were determined by open capillary method. IR spectra were recorded.

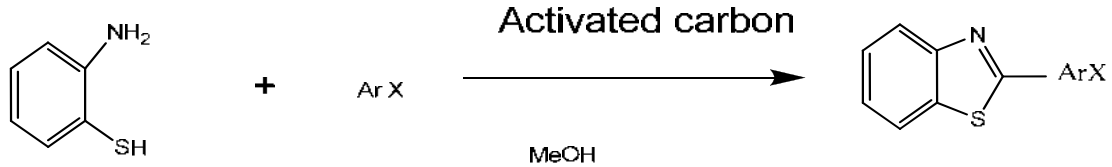
Preparation of Activated Carbon from *Polyalthia longifolia* seeds

The seeds of *Polyalthia longifolia* were collected in Pune, Maharashtra, India. Plant material is authenticated at Botanical Survey of India, Pune, India. Its Voucher Specimen No. is BSI/WRC/Tech/2009/ POLMK1. The seeds were washed, dried in an oven, crushed and powdered. The powder was sieved to get uniform particle size (0.063 mesh). It is stored in air tight bottle. The chemically treated activated carbon (SATM) is prepared from this material [9].

General procedure for the synthesis of 2-aryl benzothiazoles (Scheme 1)

Aldehyde (1 mmol) and *o*-aminothiophenol (1 mmol) are mixed thoroughly in methanol in a round bottom flask. To this solution, prepared catalyst (SATM) was added at room temperature with continuous stirring. The reaction was monitored using TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (30 mL) washed with water (2 x 15 mL), brine solution (1 x 10 mL) and again with water (1 x 15 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum to obtain a crude product which was further purified on silica gel (60-120) column chromatography with hexane: ethyl acetate (8:2 or 9.5:0.5) as eluent. Finally, the products were confirmed by their ^{1}H-NMR, IR spectral data and comparing their melting points with the reported. Similar procedure is used for substituted benzaldehydes such as m-nitrobenzaldehyde, o-chlorobenzaldehyde, p – chlorobenzaldehyde and p-tolualdehyde as reactants to get substituted 2-aryl benzothiazoles.

Scheme 1. Synthesis of 2-aryl benzothiazoles



X = H	**Compound**	**1**
X = m NO_2		**2**
X = O Cl		**3**
X = p Cl		**4**
X = p CH_3		**5**

Results and Discussion

FT-IR spectra and SEM analysis of SATM

FT-IR spectra of SATM prepared from PL seeds display a number of absorption peaks which demonstrate the complex nature of it. IR spectrum displays characteristic peaks of the compound. It clarifies polymeric nature of compounds along with presence of hydroxyl, ketonic, acidic and ester functional groups. Such groups are capable to react with the functional groups of dye molecules.

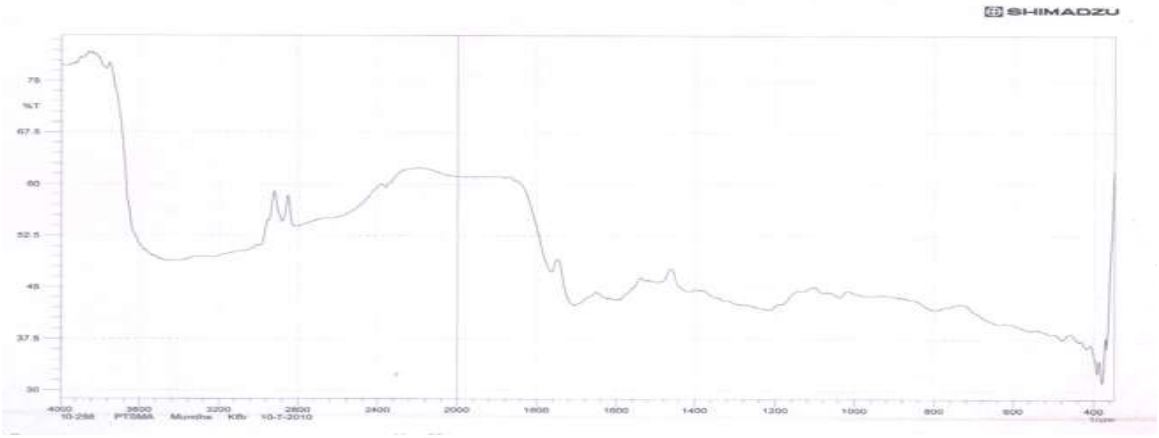


Figure.1.FTIR of SATM of *P.longifolia* seeds

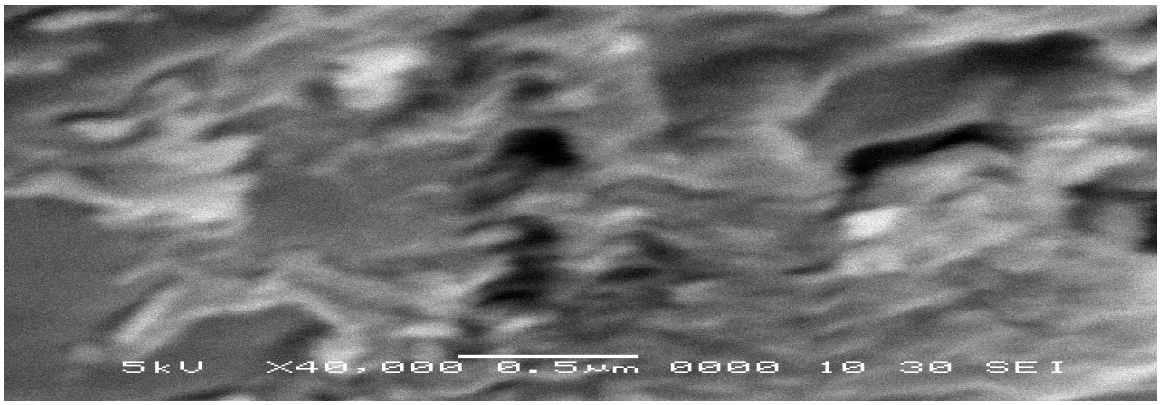


Figure .2 SEM of SATM of *P.longifolia* seeds

^{1}H NMR Spectra

The FT-IR spectrum of SATM **(Fig. 1.)** depicts broad band at 3433 cm^{-1} is of associated –OH bonded polyhydroxyl groups. The peaks at 2881 and 2814 cm^{-1} makes an appearance for C-H stretching of saturated alkanes. The peak at 1703 cm^{-1} is due to conjugated C=O group. Stretching frequency absorption illustrated at 1602 and 1487 cm^{-1} proves the presence of aromatic ring. The peaks at 1217, 1080 and 1036 cm^{-1} are due to presence of – O –C = O acyl oxygen and etherial linkages of ester function confirms the presence of ester group.

Scanning Electron Micrograph of the SATM (**Fig. 2)** seems that cavities present on the surface of SATM, resulted due to heating and acid treatment respectively. This may be due to production of carbon of different porosity from lignocellulosic material present in the PL seeds [10, 11]. Scanning Electron Micrograph of the adsorbent shows different structural features with non-uniform sizes and surfaces.

Synthesis

The synthesis of 2-aryl benzothiazoles has been effected as per **scheme I** using SATM as the catalyst. Reactions were carried out using various substituted benzaldehydes and equilibrium time recorded. The equilibrium time required for each reaction is reported (**Table I**).

Table 1: Relative yields and Melting points at equilibrium time for 2-aryl benzothiazoles using SATM as green catalyst

Compound	Aldehyde	Yield (%)	Time (min.)	M.P. ^{o}C
1	Benzaldehyde	86	45	110
2	m-nitrobenzaldehyde	82	60	182
3	o-chlorobenzaldehyde	79	45	70
4	p-chlorobenzaldehyde	83	45	116
5	p-tolualdehyde	84	60	85

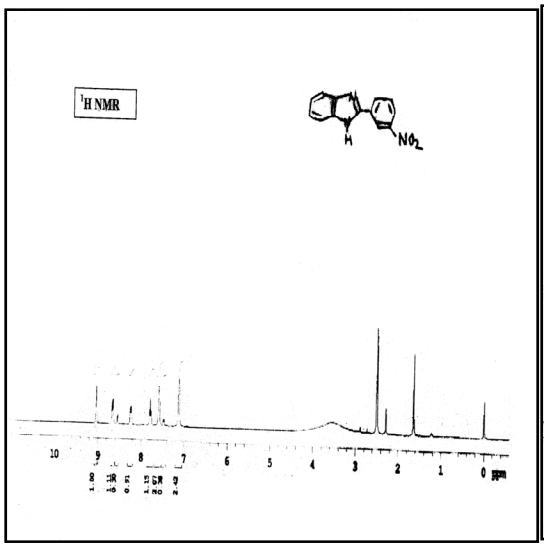


Figure 3. Compound 1

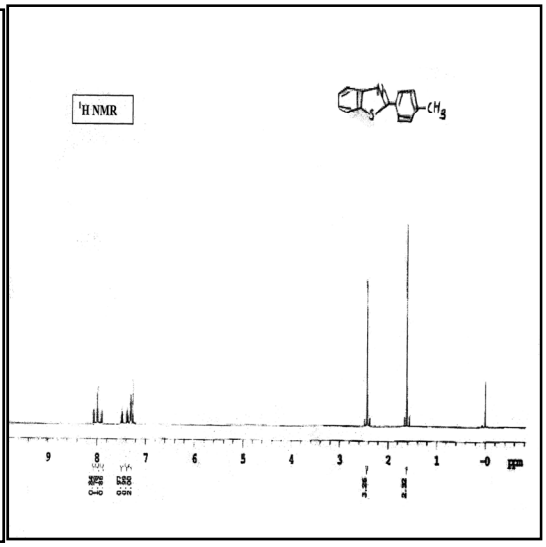


Figure 4. Compound 2

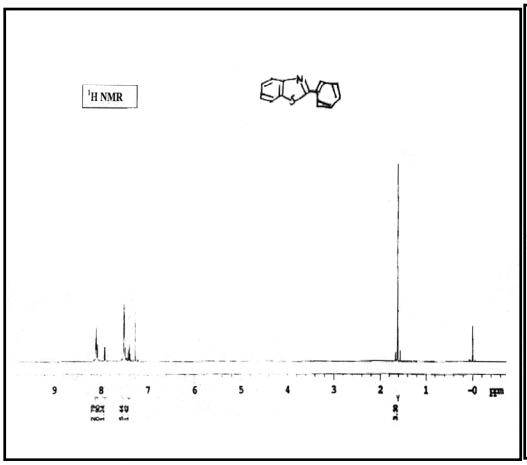


Figure 5. Compound 3

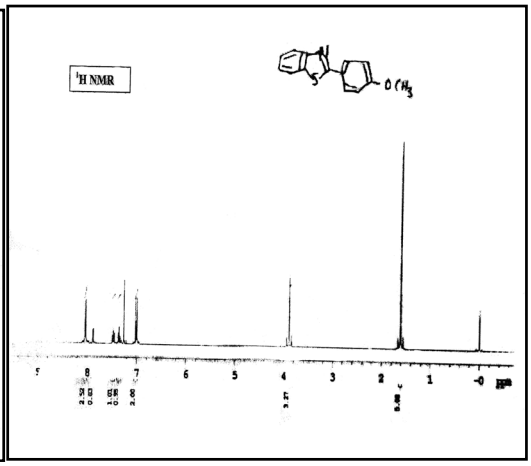


Figure 6. Compound 4

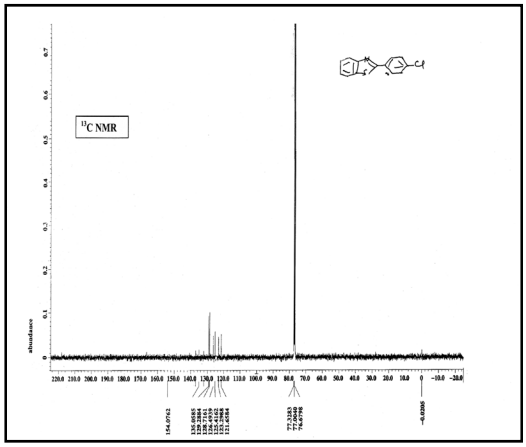


Figure 7. Compound 5

The products are confirmed by comparing their ^{1}H NMR (**Figure 3 to 7**) & IR spectral data those with authentic samples. The results indicate that the carbon catalyses the reaction, as a result higher yields of the product are obtained at lesser reaction times. The carbon catalyst could be recycled thrice to get a good yield.

Conclusion

An eco-friendly and economic process is developed for the synthesis of 2-aryl benzothiazoles with good yields. This preliminary work highlights the potential of carbon from bio- waste as a recyclable catalyst.

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