COMPARISON OF ANTIOXIDANT ACTIVITY OF NATURAL AND SYNTHETIC ZEOLITES

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Abstract

Zeolites are porous mineral with high absorption and ion-exchange capacity. Their molecular structure is a dense network of AlO_4 and SiO_4 that generates cavities where water and other polar molecules or ions are inserted /exchanged. There are several synthetic or natural occurring species of zeolites with unique and outstanding physical and chemical properties which make them extremely useful in various fields including agronomy, ecology, manufacturing and industrial processes. Recently, a more specific application of naturally occurring zeolite, clinoptilolite, has been studied in veterinary and human medicine as an excellent detoxifying, antioxidant and anti-inflammatory agent. The objective of the present study is to evaluate antioxidant activities of natural and synthetic zeolites. The *In vitro* antioxidant activity of zeolites is assessed against hydrogen peroxide (H_2O_2) DPPH, 1,1-diphenyl-2-picryl-hydrazyl free radical (DPPH) scavenging using standard protocols. Synthetic zeolite showed higher antioxidant activity than natural zeolite. It can be concluded that the antioxidant role of zeolites is based on the ability to reduce lipid peroxidation, free radicals levels and to increase total antioxidant status (TAS) in serum.

Keywords: Zeolites, Clinoptilolite, Antioxidant activities, H_2O_2, DPPH scavenging model.

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Introduction

The name 'zeolite' originated from the Greek words 'zeo'(to boil) and 'litos' (a stone). The current nomenclature and classification of zeolite materials has been provided by the Structure Commission of the International Zeolite Association that identifies each material based on its framework with a three-letter mnemonic code; for instance, natural zeolite, Clinoptilolite is denoted as HEU[1].By origin, zeolites can be natural or synthetic. They are aluminosilicate minerals with rigid anionic framework containing well-defined channels and cavities. These cavities contain metal cations, which are exchangeable, or they may also host neutral guest molecules that can also be removed and replaced. The majority of natural zeolites are of volcanic origin and have a general formula, $M_2/n:Al_2O_3:xSiO_2:yH_2O$, where M stands for the extra-framework cation[2]. The mineral structure is based on AlO_4 and SiO_4 tetrahedra, which can share 1, 2, or 3 oxygen atoms. Thus there is a wide variety of possible structures as the network is extended in three dimensions. This unique structural feature is the base for well-known microporous structure of zeolites. Based on the pore size and absorption properties, zeolites are among the most important inorganic cation exchangers and are used in industrial water and waste water treatment, catalysis, nuclear waste treatment, agriculture, animal feed additives and in biochemical applications. Due to their structure, zeolites exhibit versatile adsorptive, cation exchange, dehydrating-rehydrating and catalytic properties[3]. Some zeolites are already been used in antidiarrheal, antibacterial, antifungal drugs and as glucose absorbent in field of medicine. Moreover, previous studies also indicated that the zeolite clinoptilolite exerts anti-cancerogenic and antioxidant effects. The antioxidant role attributed to zeolites, specifically to clinoptilolite, is based on its ability to reduce lipid peroxidation and free radicals levels as well as to increase total antioxidant status (TAS) in serum[4-6]. Reactive oxygen species (ROS) are highly reactive molecules which may be important mediators of some physiological functions and also act as potential peroxidants. Imbalance between ROS generation and antioxidant capacity induces a condition known as oxidative stress which may play major role in initiation and progression of numerous pathologies including cardiovascular dysfunction associated with vascular disease, hyperlipidemia, diabetes mellitus, hypertension and ischemia/reperfusion injury. The potential damage caused by an excess of ROS is controlled by a series of antioxidant defence mechanisms and among them, a key protective role is played by the antioxidant enzymes gluthatione (GSH) peroxidase, superoxide dismutase (SOD) and GSH reductase[7]. Due to their key protective role in preventing or slowing down oxidative damage, antioxidant enzymes could be potential target of zeolites action. To this aim, in present study we have evaluated antioxidant activities of natural and synthetic zeolites.

Chemical reagents

The fine powder of natural and synthetic zeolites was purchased from Maniyar Minerals and Chemicals Bijapur Karnataka, India. All the chemicals of analytical grade used in this study were obtained from Hi Media Laboratories Pvt. Ltd. (Mumbai, India), Sigma-Aldrich Chemical Co. (Milwaukee, WI, USA), SD Fine-Chem Chem. Ltd. (Mumbai, India) and SRL Pvt. Ltd. (Mumbai, India).

Antioxidant activity

DPPH free radical scavenging assay

For DPPH assay, the method used by Gulçin*et al.*, was adopted[8]. A solution of 0.1 mM DPPH in methanol was prepared. 1 ml of this solution was mixed with 2 ml of different concentrations of zeolites. The reaction mixture was vortexed thoroughly and left in dark at room temperature for 30 min. Reduction of the stable DPPH radical was used as a marker of antioxidant capacity of zeolite solutions. The change in colour was measured at 517 nm wavelength using methanolic solution as reference solution. This was related to the absorbance of the control without plant extracts. All the tests were carried out in triplicates.

The percentage inhibition of free radical DPPH was calculated by the following equation:

% inhibition = [(absorbance of control - absorbance of sample)/absorbance of control] × 100%.

Hydrogen Peroxide scavenging capacity

The ability of the zeolites to scavenge hydrogen peroxide was determined according to the method used by Ruch et al [9]. A solution of hydrogen peroxide (40 mM) was prepared in phosphate buffer (pH 7.4). Zeolites (20-100 µg/ml) in distilled water were added to hydrogen peroxide solution (0.6 ml, 40mM). Absorbance of

hydrogen peroxide at 230 nm was determined after 10 minutes against a blank solution containing the phosphate buffer without hydrogen peroxide. The percentage of hydrogen peroxide scavenging for both zeolites and standard compounds were calculated:

% scavenged [H_2O_2] = [(AC – AS)/AC] x 100

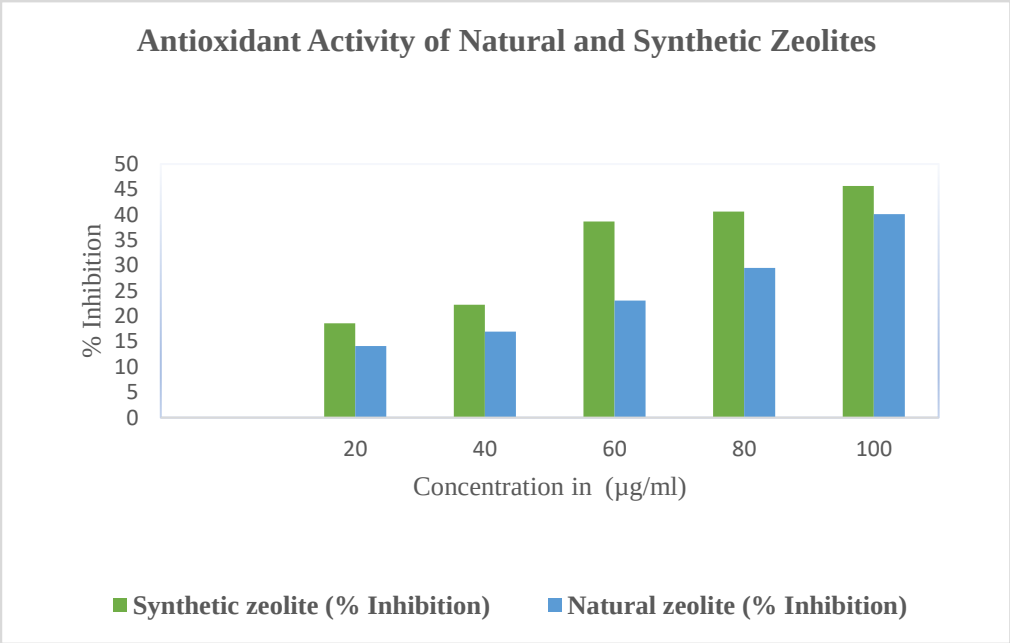
Where AC is the absorbance of the control and AS is the absorbance in the presence of the sample of zeolites or standards.

Result and Discussion

Antioxidant activity of the samples was calculated through DPPH assay and Hydrogen Peroxide scavenging capacity. The % inhibition was calculated as an measure of antioxidant potency. The higher is the value of % inhibition, better is the antioxidant activity. In both tests the values were compared with concentration ranging from 20µg/ml to 100µg/ml. A dose dependent activity with respect to concentration was observed. The value of % inhibition for natural zeolite ranged between14 % to 40 %. These values are less than the % inhibition values observed for synthetic zeolite ranging between18.59 % to 45.65 % (table 1).

Table 1 DPPH assay of synthetic and natural zeolites

S. No.	Conc. (µg/ml)	Synthetic zeolite(% Inhibition)	Natural zeolite(% Inhibition)
1.	**20**	18.59	14.14
2.	**40**	22.27	16.92
3.	**60**	38.64	23.05
4.	**80**	40.64	29.51
5.	**100**	45.65	40.08

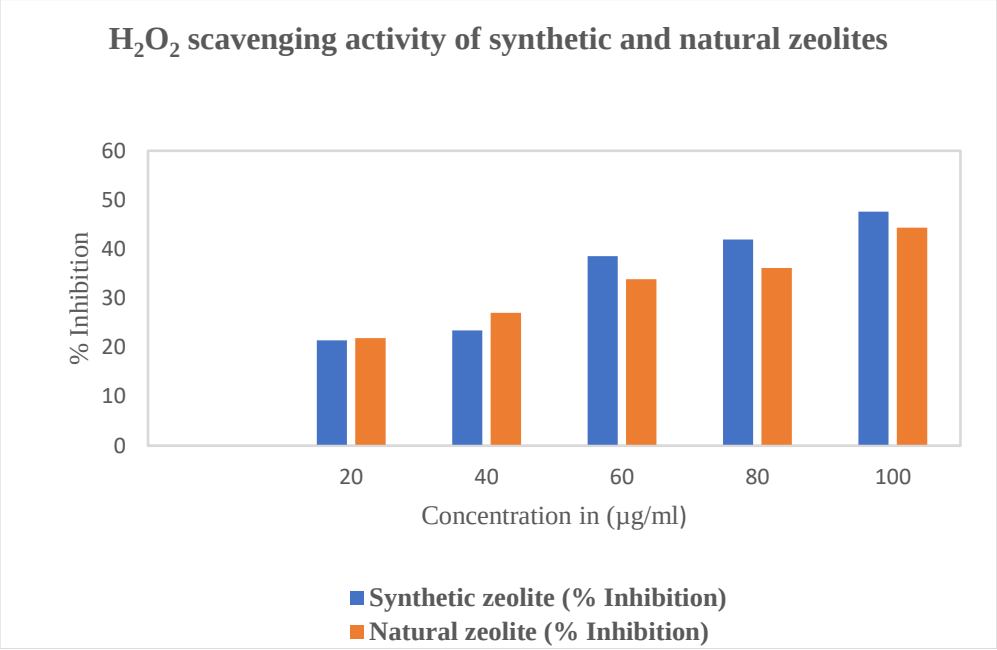


Hydrogen peroxide has strong oxidizing properties. It can be formed in vivo by many oxidizing enzymes such as superoxide dismutase. It can pass through membranes and may slowly oxidize number of compounds. The ability of zeolites to scavenge hydrogen peroxide was determined according to the method used by Ruch et al as shown in Table 2. The results of Hydrogen peroxide scavenging activity of synthetic and natural zeolites show that synthetic zeolites have an effective hydrogen peroxide scavenging activity in comparison to natural zeolites at the concentration 60,80,100(µg/ml).

The hydrogen peroxide scavenging effect of zeolites decreased in the order of synthetic > natural zeolites for these concentrations. Natural zeolites show effective hydrogen peroxide scavenging activity than synthetic zeolites at concentrations 20 and 40 (µg/ml). Hydrogen peroxide itself is not very reactive; however, it can sometimes be toxic to the cell due to formation of hydroxyl radical in the cells.

Table 2 H_2O_2 scavenging activity of synthetic and natural zeolites

S. No.	Conc. (µg/ml)	Synthetic zeolite (% Inhibition)	Natural zeolite (% Inhibition)
1.	**20**	21.46	21.90
2.	**40**	23.43	27.05
3.	**60**	38.55	33.84
4.	**80**	41.94	36.14
5.	**100**	47.64	44.35



Conclusion

According to data obtained from the present study, synthetic zeolite was found to be an effective antioxidant in different in vitro assay including DPPH radical and hydrogen peroxide scavenging at higher concentrations. Natural zeolite shows more hydrogen peroxide scavenging activity than synthetic zeolite at lower concentrations,

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