A low cost, well-designed catalytic system derived from household waste "egg shell": synthesis of quinoxaline derivative under green path

Gautam Kumar [a], MD. Altaf Raj [a], M. Bharathi [a] [*]

[a] *Department of Pharmaceutical Engineering*

Vinayaka Mission's Kirupananda Variyar Engineering College,

Vinayaka Mission's Research Foundation (Deemed to be University), Salem-636308, Tamil Nadu, India.

[*] Corresponding author E-mail: bharathi@vmkvec.edu.in

Abstract

The synthesis of quinoxaline derivatives is made more environmentally friendly and productive with the use of cheap, biodegradable eggshell powder (ESP) as a heterogeneous catalyst under ultrasonic irradiation. Numerous benefits are offered by this ecologically friendly technology, including mild reaction conditions, a quick reaction time, a great yield of up to 98%, ease of operation, catalyst stability, heterogeneous nature, and simple catalyst retrieval using filtration. Up to four cycles of catalyst reuse are possible without notably lowering catalytic activity. FT-IR, TGA and SEM were among the analytical methods used to characterize the catalyst.

Keywords: Heterogeneous catalyst, eggshell powder, quinoxaline, green synthesis, ultrasonic irradiation

1. Introduction

Catalysts play a fundamental role in chemical reactions by facilitating the conversion of reactants into products while remaining unchanged themselves. Their ability to increase reaction rates, modify reaction pathways, and enhance selectivity has profound implications in various industrial processes, environmental remediation, and synthesis of valuable chemicals. This introduction provides an overview of catalysts, their significance, and the different types commonly encountered in chemical transformations.

Catalysts are substances that accelerate the rate of a chemical reaction by providing an alternative reaction pathway with lower activation energy, thereby lowering the energy barrier for the reaction to occur. Unlike stoichiometric reagents, which are consumed in the reaction and undergo permanent chemical changes, catalysts participate in the reaction transiently, allowing them to catalyze multiple reaction cycles.

The importance of catalysts in modern society cannot be overstated, as they enable the efficient production of essential chemicals, fuels, and materials, while minimizing energy consumption and waste generation. From industrial processes such as petroleum refining, ammonia synthesis, and polymerization to environmental applications like catalytic converters for automotive emissions control, catalysts play a crucial role in shaping the global economy and mitigating environmental impacts [1-4].

Catalysts can be broadly categorized into ***heterogeneous and homogeneous catalysts*** based on their physical state and distribution relative to the reactants. Heterogeneous catalysts are typically ***solid materials that interact with gaseous or liquid reactants***, while homogeneous catalysts are molecular species ***dissolved in the same phase as the reactants***. Each type offers distinct advantages and limitations depending on the specific reaction requirements and operating conditions.

In addition to their physical state, catalysts can also be classified based on their mechanism of action, such as acid-base catalysis, redox catalysis, or enzyme catalysis. These mechanisms involve different interactions between the catalyst and reactants, leading to diverse catalytic behaviors and applications.

Waste eggshells, abundant and readily available byproducts of the food industry [5-7], have gained attention as potential heterogeneous catalysts due to their unique composition and surface properties [8-9].

1.1 Composition: Eggshells primarily consist of calcium carbonate ($CaCO_3$), along with small amounts of proteins and other organic compounds. This composition provides eggshells with inherent basicity and surface functionality, making them suitable candidates for catalytic applications.

1.2 Catalytic Activity: The basic nature of CaO derived from eggshells makes it effective in catalyzing various chemical reactions, including trans-esterification, biodiesel production, esterification, and hydrolysis. The porous structure of eggshell-derived CaO enhances mass transfer and accessibility of reactants, leading to improved catalytic performance.

1.3 Sustainable Catalyst: Utilizing waste eggshells as a heterogeneous catalyst offers environmental and economic benefits by repurposing a waste stream and reducing the reliance on conventional catalysts derived from non-renewable resources. Additionally, eggshell-derived catalysts can be easily regenerated and reused, further enhancing their sustainability [6].

1.4 Applications: Waste eggshell-derived catalysts have found applications in diverse chemical transformations, including the conversion of biomass-derived feed-stocks into value-added chemicals, treatment of wastewater [10-12] and pollutants, and synthesis of biofuels and fine chemicals [13,14] in **Fig: 1**. Their versatility and effectiveness make them attractive options for green and sustainable catalytic processes.

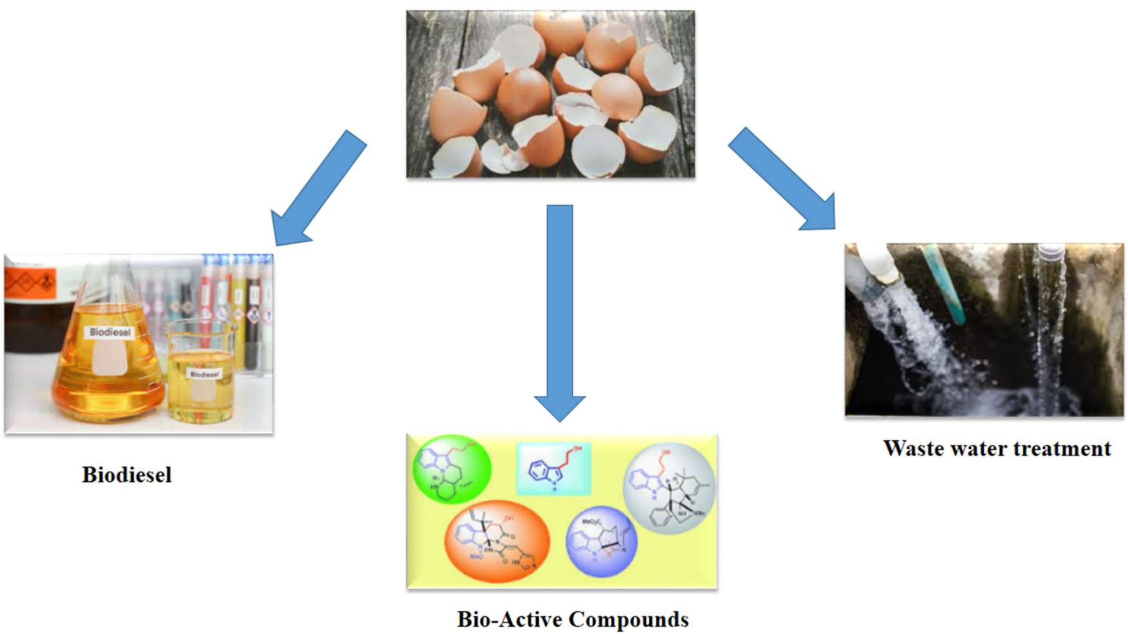


Fig: 1 Application of waste-egg-Shell

Quinoxaline derivatives are a class of organic compounds featuring a bicyclic structure composed of benzene and pyrazine rings fused together. They exhibit diverse pharmacological activities and find applications in various fields including medicinal chemistry, material science, and organic synthesis. It exhibit a wide range of biological activities, including antibacterial, antifungal, antiviral [15], antitumor, antiparasitic, anti-inflammatory, anticonvulsant, and antioxidant properties. These diverse pharmacological activities make them promising candidates for drug discovery and development. It have a wide range of applications across various fields due to their diverse chemical properties and biological activities.

1.1.1 Medicinal Chemistry:

- **Drug Discovery**: It serve as important scaffolds for the development of pharmaceuticals. Their structural diversity allows for the synthesis of compounds with specific biological activities.
- **Anticancer Agents**: It exhibit promising anticancer activity by targeting various pathways involved in cancer progression, such as protein kinases, DNA replication [16], and apoptosis.
- **Antibacterial and Antifungal Agents**: It demonstrate potent antibacterial and antifungal properties, making them potential candidates for the development of new antibiotics and antifungal drugs.
- **Antiviral Agents**: Certain quinoxaline derivatives have shown activity against viruses, including HIV [17], herpes simplex virus (HSV), and hepatitis C virus (HCV), highlighting their potential as antiviral agents.

1.1.2. Material Science:

1.1.2.1.Organic Semiconductors [18]: It possess favorable electronic properties, making them suitable for use in organic semiconductor devices such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs).

1.1.2.2. Fluorescent Dyes: It displays fluorescence properties, making them useful as fluorescent probes for biological imaging and sensing applications.

Electrochromic Materials: It can undergo reversible color changes in response to an applied voltage, making them valuable for applications such as smart windows, displays, and electrochromic devices.

1.1.3. Agrochemicals:

1.1.3.1.Pesticides and Herbicides [19]: Quinoxaline derivatives have been investigated for their potential as agrochemicals, including insecticides, fungicides, and herbicides, due to their pesticidal activities against agricultural pests and pathogens.

1.1.4. Flavor and Fragrance Industry: It contribute to the flavor and fragrance profiles of natural and synthetic products. They are used as key components in perfumes, cosmetics, and food flavorings.

1.1.5. Research Tools: These are utilized as research tools in chemical biology and drug discovery. They enable scientists to investigate biological pathways, elucidate drug-target interactions, and develop new therapeutic strategies.

Herein, we synthesis a quinoxaline derivatives using waste egg-shell as a heterogeneous catalyst under greener way.

2. Experimental

2.1 Materials and Instruments

Ortho-Phenylene-di-amine, Benzil and ethanol were acquired from Aldrich and SRL. The IR spectra of prepared samples were examined on an Avatar 370 model FT-IR spectrometer with KBr pellets. Powder X-ray diffraction data were recorded on Bruker AXS D8 Advance diffract meter. The SEM micrographs were obtained on the JEOL Model JSM 6390LV microscope. The TG/DTA micrographs were recorded on Perkin Elmer at the temperature range 0-900 ºC.

2.2 Synthesis of eggshell powder

Waste eggshells was collected from the household and some food market. It was rinsed with warm water. The adhering membrane was separated manually. Then, the eggshells were washed with distilled water and withered at 120°C for 1 h and were squeezed by mortar. The obtained raw powder material was illustrated as an eggshell powder (ESP). The raw eggshell powder was calcinated at 550 ºC for 1 h with the rate of 2 ºC/min. It was used to remove the impurity and finally got the pure eggshell powder (ESP)(**Fig:2**).

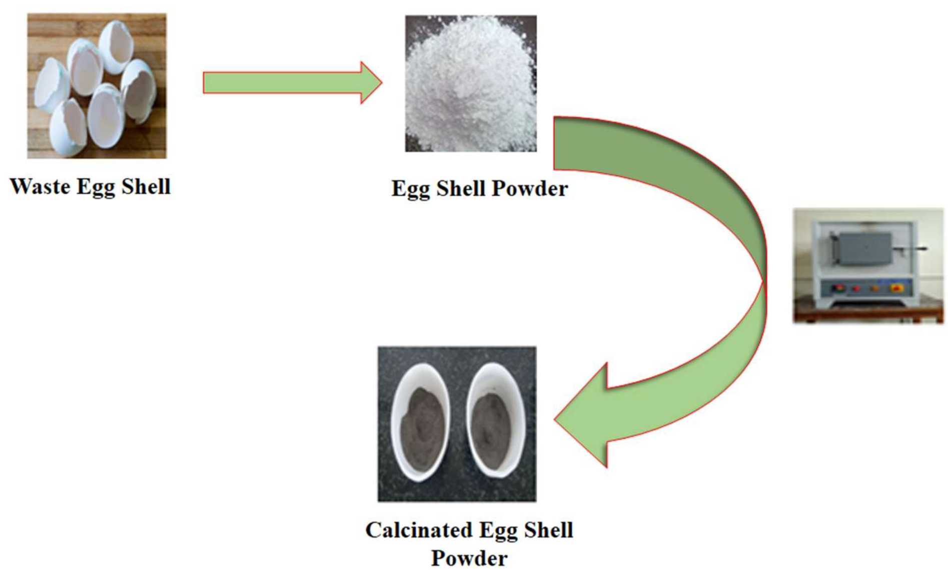
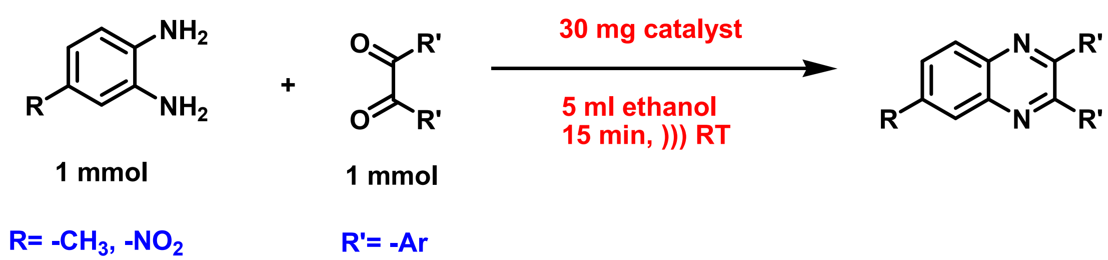


Fig: 2 Synthesis of Egg Shell Powder

2.3 Synthesis of quinoxaline derivatives

1 mmol of various substituted diamine and 1 mmol of diketone was dissolved in 5 ml of ethanol solvent with 30 mg of eggshell as a heterogeneous catalyst under ultrasonication for 15 min at room temperature and the course of the reaction was monitored by TLC. Finally, the reaction mixture was cooled and the catalyst was removed by filtration, then crude mixture was purified by crystallization to give the desired products was calculated.



Scheme. 1 Synthesis of quinoxaline derivatives

3. Results and discussion

The prepared new heterogeneous catalysts were characterized by FT-IR SEM-EDX and TGA analysis.

3.1. FT-IR

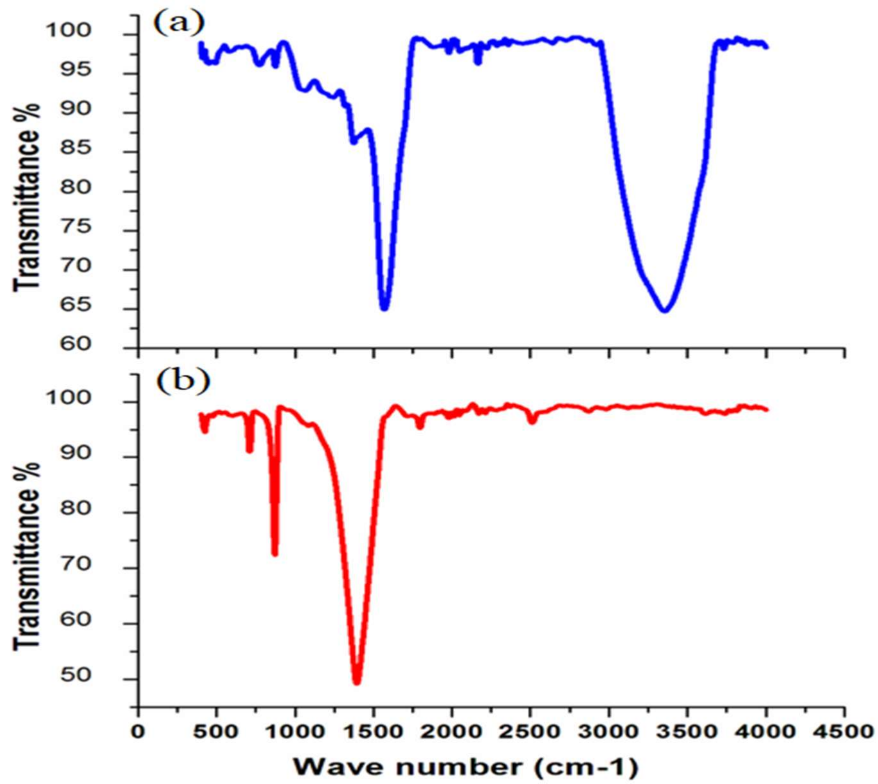


Figure. 3.1 FT-IR spectrum of (a) un-calcinated eggshell (b) Reused Catalyst

Fig 3.1(a) demonstrates the infrared spectra of un-calcinated eggshell powder and characteristic absorption band displayed at 3646 cm^{-1}, which is due to the stretching absorbance of –OH group in Ca $(OH)_2$ produced by through absorption of water by CaO. The prominent absorption band associated with the stretching vibrations of bonds of C–O and O–C–O linkages is at 1407 and 889 cm-1. Besides, the absorption band existing at 705 cm^{-1} can be assigned to the Ca–O bond. These findings indicate that the calcium oxides and carbonates were p.resent and well-dispersed in the eggshell material of three compounds. The figure 3.1(b) shows the same peaks but the intensity is decreased due the reused the catalyst

3.2. SEM-EDX

The eggshell powder (ESP) material was analyzed by SEM for identifying the morphology as illustrated in **Fig. 3.2 a**. The cavities' appearance of SEM micrographs indicates the uniform distribution of small particles on the shell surface. The elemental composition of the eggshell was confirmed from energy dispersive (EDX) analysis (**Fig. 3.2 b**). It composed of O and Ca as major elements.

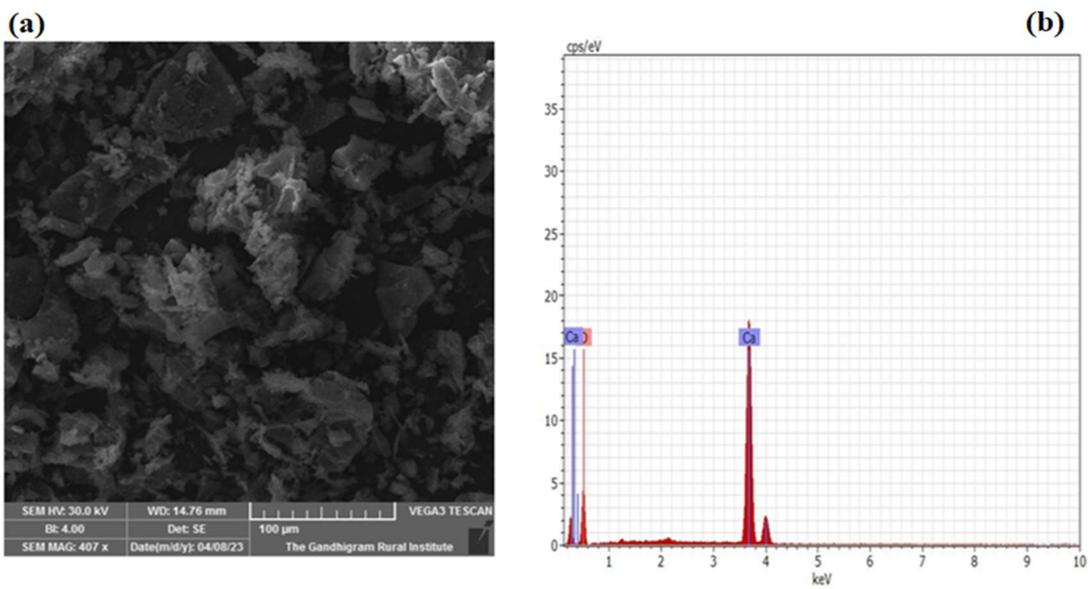


Figure. 3.2 SEM and EDX image of eggshell

3.3. Catalytic activity of eggshell

The catalytic activity of eggshell was evaluated for the synthesis of quinoxaline derivatives from diamine and diketone.

In order to optimize the suitable reaction conditions for the synthesis of quinoxaline derivatives, we have chosen o-phenylenediamine and benzil as model reactants. Hence, we have used eggshell as a heterogeneous catalyst (30 mg) in the reaction that produces the corresponding product in excellent yield (**Table 3.1**, **entry 1**) in 15 min. Then, we have found out the suitable solvent, temperature, time and catalyst amount. The reaction was carried out in ethanol, methanol and water under ultrasonic irradiation with various temperature ranges such as RT and 60 ^{o}C for 5, 10 and 15 min. Then, we found out that ethanol was the better one in terms of yield, time and temperature.

To optimize the amount of catalyst required for the reaction, we have carried out the reaction using different amount of catalyst like 20 mg, 30 mg and 40 mg (**Table 3.1, entry 4**). The yield of the product was progressively increased with the catalyst amount from 20 mg to 30 mg but moderate yield was obtained in the presence of 40 mg catalyst compared to 30 mg of catalyst. This optimization results reveals that 30 mg of catalyst, ethanol solvent and RT for 30 min were found to be most suitable for this reaction.

Under optimized conditions, the catalytic activity of eggshell was explored through the synthesis of quinoxaline derivatives in the presence of various substituted diamine and diketone then the results are given in the (**Table 3.2**). The catalyst showed good activity and gave better yield. We have reused the heterogeneous catalyst for the catalytic studies up to four cycles without any significant loss in the yield.

Table 3.1 Effect of solvent, temperature, time and catalyst amount for the synthesis of quinoxaline derivatives

Entry	Solvent	Temperature (^{o}C)	Catalyst Amount (mg)	Time (min)	Yield (%)

1	Ethanol	RT/60 ºC	30	15	**98**/67
2	Methanol	RT/60 ºC	30	15	74/53
3	Water	RT/60 ºC	30	15	29/11
4	**Ethanol**	**RT**	**30**	**15**	**98**
5	Ethanol	RT	30	5	45
6	Ethanol	RT	30	10	75
7	Ethanol [a]	RT	-	15	**36**
8	Ethanol	RT	20	15	40
9	Ethanol	RT	40	15	73

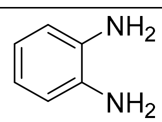
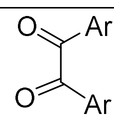
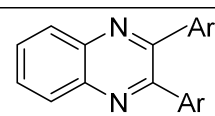
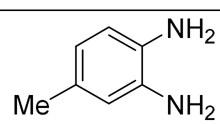
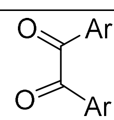
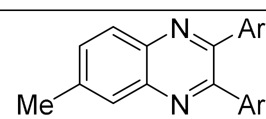
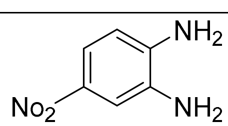
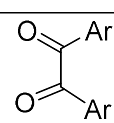
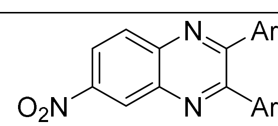
a) Reaction was carried out in the absence of catalyst under room temperature.

Table 3.2 Synthesis of various quinoxaline derivatives by eggshell as a catalyst.

Further, the catalytic activity and recyclability of ESP were examined. The catalyst material and products were separated by simple extraction with ethyl acetate after completion of the reaction. Then, the separated material was recycled up to four cycles and without any decline in its catalytic activity and summarized in **Table 3.3**

Table 3.3 Reusability of eggshell as a catalyst

Cycle	**Fresh**	**1st**	**2nd**	**3rd**	**4th**
Yield (%)	**98**	**98**	**90**	**83**	**81**

Entry	**Diamine**	**Diketone**	**Product**	**Yield (%)**
1				**98**
2				67
3				50

4. Conclusion

We have synthesized and characterized of heterogeneous catalyst, egg shell. The catalyst was used for the synthesis of quinoxaline derivatives under green pathway i.e, using ethanol as a solvent and ultrasonic irradiation method. It shows good to excellent yields and also recovered easily. Hence, the catalysts were successfully used for the catalytic reaction upto four cycles without any significant loss in the yield of the product.