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Synthesis and Characterization of Silica Sulphonic Acid from Rice Husk Ash and its use in the Synthesis of 4-Methylcoumarin Derivatives

تخليق وتشخيص حامض سلفونيك - سيليكات من رماد قشرة الأرز
وإستخدامه لتخليق مشتقات 4-ميثيل كومارين

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بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

قال تعالى:

نَزَّلْنَا فَعُورَ جَاتٍ مِّنْ نَّشَآءٍ وَفَوْقَ كُلِّ ذِي عِلْمٍ عَظِيمٌ {

صدق الله العظيم

سورة يوسف [76]

Dedication

To my lovely family members

Acknowledgments

First of all, praise to Almighty Allah for giving me the strength and health to complete this dissertation .

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ABSTRACT

In this work, Rice Husk Ash Silica sulphonic acid materials(RHA-SO₃H and RHA-SiO₂/SO₃H) were synthesized at ambient conditions from direct reaction of chlorosulphonic acid and RHA sodium silicate or post reaction of RHA silica(RHA-SiO₂)and chlorosulphonic acid, respectively. The two materials were characterized by FT-IR spectroscopy and conventional volumetric acidity measurement. The FT-IR indicated the successful incorporation of sulphonic species to the silicate surface of both materials, but with higher extent in the silicate of post-modified method(RHA-SiO₂/SO₃H). This was further evident through acidity measurement and the results showed that the post-modified material exhibited , extremely, higher Bronsted acidity over the directly-modified material(RHA-SO₃H). Synthesized RHA-SiO₂/SO₃H solid acid material was used to catalyze the synthesis of 4-methyl coumarin derivatives via Pechmann condensation reaction of phenols and ethylacetoacetate(EAA). Various reaction parameters were studied for the production of high yields of coumarin derivatives which include molar ratio, type of phenol, catalyst loading, reaction time and re-usability . Optimum yield of 99 % coumarin was obtained when conducting the reaction between resorcinol and EAA with molar ratio of 1:2 at 80 °C for one hour using 0.1 g of the synthesized catalyst. Moreover, RHA-SiO₂/SO₃H catalyst was found reusable for this reaction several times without any significant changes in its catalytic performance.

المستخلص

في هذه الدراسة, تم تخليق مادتي (مجموعة سلفونيك- رماد قشرة الإرز) و (مجموعة سلفونيك/سيليكات رماد قشرة الإرز) من خلال التفاعل المباشر لحمض كلوروسلفونيك مع سيليكات الصوديوم أو من خلال التفاعل المتقدم كلوروسلفونيك إلي السيليكات الناتجة من رماد قشرة الأرز علي الترتيب. المادتين تم تشخيصهما بجهاز مطيافية الأشعة تحت الحمراء و قياسات الحمضية الحجمية التقليدية. حيث دلت مطيافية الأشعة تحت الحمراء علي نجاح إندماج مجموعة السلفونيك علي سطح السيليكات للمادتين ولكن بتواجد أعلي في المادة الناتجة بالطريقة المتقدمة و علاوة علي ذلك أوضحت نتيجة قياسات الحمضية علي أن هذه الطريقة تحتوي علي حمضية برونستيد أكثر من الطريقة المباشرة. تم إستخدام مادة مجموعة سلفونيك/ سيليكات رماد قشرة الإرز الحمضية الصلبة في تفاعل كل من الفينولات مع الايثايل اسيتواسيتيت لإعطاء مشتقات مركب 4-ميثايل كومارين. تمت دراسة تأثير عدد من عوامل التفاعل منها النسب المولية للمتفاعلات, نوع الفينول, كمية الحفاز المستخدمة, زمن التفاعل و إمكانية إعادة إستخدام الحفاز لتحفيز تفاعل آخر. حيث كان أعلي مردود 99% عند تفاعل الريسورسينول(فينول) مع الايثايل اسيتواسيتيت بنسبة مولية 2:1 وكتلة حفاز 0.1 جرام لمدة ساعة. علاوة على ذلك, وجد ان حفاز مجموعة سلفونيك/ سيليكات رماد قشرة الإرز الحمضية الصلبة يمكن إستخدامه في التفاعل المذكور عدة مرات دون أن تظهر عليه تغيرات كبيرة في خصائصه ونشاطه.

Table of Contents

الآية	I
Dedication	II
Acknowledgments	III
Abstract(English)	IV
Abstract (Arabic)	V
Table of contents	VI
List of Tables	IX
List of Figures	X
List of Schemes	XI

Chapter One Introduction and Literature Review

1.1	General Introduction	1
1.2	Silica	3
1.3	Coumarins	4
1.3.1	Industrial importance of coumarins	5

1.3.2	Pechmann condensation Reaction	5
1.4	Catalysts	6
1.4.1	Homogeneous catalysts	6
1.4.2	Heterogeneous catalysts	7
1.5	Rice husk	7
1.6	Literature Review	8
1.7	Objectives	14

Chapter Two Materials and Methods

2.1	Materials	16
2.2	Methods	16
2.2.1	Pre- treatment of RH	16
2.2.2	Preparation of silica	17
2.2.3	Preparation of the catalysts	17
2.2.3.1	Direct modification	17
2.2.3.2	Post modification	18
2.2.4	Catalyst characterization	18
2.2.4.1	FT-IR Spectroscopic Analysis	18
2.2.4.2	Acidity Measurement	18
2.2.5	Catalytic Reactions	19
2.2.5.1	Pechmann condensation Reactions	19
2.2.5.2	The reusability of the catalyst	20
2.2.5.3	Gas Chromatography(GC)	20

Chapter Three
Results and Discussion

3.1	Catalyst characterization	22
3.1.1	FT-IR spectroscopy	22
3.1.2	Acidity measurement	25
3.2	Pechmann catalytic condensation of phenolic compounds	26
3.2.1	Effect of type of phenolic compound	26
3.2.2	Effect of solvent	27
3.2.3	Effect of reactants molar ratio	28
3.2.4	Effect of catalyst loading	30
3.2.5	Effect of reaction time	30
3.2.6	Reusability of the catalyst	31
3.3	Characterization of 7-hydroxy 4-methyl coumarin	32

Chapter Four
Conclusion and Recommendations

4.1	Conclusion	33
4.2	Recommendations	34
-	References	35
-	Appendices	40

List of Tables

Table		Page
3.1	Acidity and Cation exchange capacity(CEC) of solid acid catalysts produced through modification of RHA-SiO ₂ surface by sulphonic acid species	26
3.2	Pechmanncondensation for production of coumarin derivatives over the catalytic activity of RHA-SiO ₂ /SO ₃ H using EAA and various phenols	27
3.3	Effect of solvent in catalytic Pechmann condensation reaction of resorcinol and EAA(1:2 molar ratios) over RHA-SiO ₂ /SO ₃ H(0.1 g)	28
3.4	The Reusability of RHA-SiO ₂ /SO ₃ Hcatalyst(0.1 g) in the Pechmann condensation reaction of Resorcinol and EAA for the production of HMC	33

List of Figures

Figure		Page
1.1	Structure of coumarin	4
3.1	The FT-IR spectrum of RHA Silica(RHA-SiO ₂)	23
3.2	The FT-IR spectrum of RHA-SO ₃ H(directly modified RHA silica)	24
3.3	The FT-IR spectrum of RHA-SiO ₂ /SO ₃ H(Post modified RHA silica)	24
3.4	The effect of Resorcinol:EAA reactants molar ratio inHMC yield for Pechmann condensation reaction(at 80°C and 1 h time) under solvent-free condition using 0.1 g of RHA-SiO ₂ /SO ₃ H catalyst	30
3.5	Effect of RHA-SiO ₂ /SO ₃ H on yield(wt%) of HMC from Resorcinol and EAA(1:2 molar ratio) at 80 °C for 30 min	31
36	Reaction profile of Pechmann condensation of resorcinol and EAA(1:2 molar ratio) at 80 °C,over the activity of RHA-SiO ₂ /SO ₃ Hcatalystfor30min in the presence of ethanol solvent	32

List of Scheme

Scheme		Page
1.1	Synthesis of 4-methylcoumarins	14
2.3	RHA-SiO ₂ /SO ₃ H catalyzed Pechmann condensation in a solvent-free condition	20

Chapter One

Introduction and Literature Review

1.1 General introduction

Recently, environmental and economic considerations have raised strong interest to redesign, commercially, important processes so that the use of harmful substances and the generation of toxic waste could be avoided (Rothenberg 2008). In this respect, there is no doubt that heterogeneous catalysis can play a key role in the development of environmentally benign processes in industrial chemistry (Atkins' et al. 2010). It is also the key factor in the production of useful compounds and fine chemicals, particularly, via the Pechmann condensation by replacing the most hazardous conventional Brønsted and Lewis acids (Sheldon and Downing 1999; Maheswara et al. 2006).

Solid acids heterogeneous catalysts can catalyze a much larger variety of reaction types, recovering and recycling catalysts from reaction environments than traditional acid catalysts. Many porous materials have been, intensively, studied for this purpose as solid acid catalysts, such as Zeolites, clays, super solid acids etc., (Weitkamp and Puppe 1999; Laufer et al 2003; Kaur and Kishore 2012) or as support for Lewis and/or Brønsted acids, such as Silica, Alumina, Zeolites, Mesoporous materials, Clays, Synthetic polymers, Resins, etc., (Corma 1997; Sheldon and Downing 1999; Laufer et al 2003; and Maheswara et al. 2006). Interestingly, Mesoporous silica based catalysts though suffer from the lack of acidity, but their larger pore diameters (Corma 1997) make them, highly active in Pechmann condensation reaction.

Silica is a weak Brønsted acidic oxides (surface hydroxyl groups) and therefore hardly, develops any catalytic activity. They are, however, amenable to hydrogen-

bonding and they are usually regarded as the most reactive native surface species, which are available for functionalization. The siloxane bridges are, at least after heating at elevated temperatures, essentially unreactive. For this reason, and because of the low acidity of silanol groups, silica is not used as active catalyst, but they plays an important role as oxide for the synthesis of functionalized oxide supports. The most commonly used type of silica in catalysis is amorphous silica (Zhuravlev 2000; Rothenberg 2008; Atkins' et al. 2010).

Tailored silica of good morphological and structural properties can be synthesized by controlling the preparation conditions. Therefore, important surface parameters such as, surface area, pore size and pore volume as well as mechanical stability can be varied by modifying synthesis conditions (Atkins' et al. 2010).

Nowadays, silica has been employed as porous support to immobilize a series of acid species towards the fabrication of novel solid acid catalysts. These materials have been employed in several organic reactions. Supported catalysts, which presents enhanced stability and increased selectivity, were, increasingly, used with success (Smith and Notheisz 2000). The majority of the novel heterogeneous catalysts are based on silica supports, primarily because silica displays some advantageous properties, such as excellent chemical and thermal stability, good accessibility and porosity (Polshettiwar et al. 2009).

1.2 Silica

Silica has been studied more than any other chemical compound except water. More than 22 phases have been described and, although, some of these phases may depend on the presence of impurities or defects, at least dozen polymorphs of pure SiO_2 are known. Various forms of crystalline SiO_2 occur naturally, but α -quartz is the most, commonly, occurring form of SiO_2 and is considered the major mineral constituent of many rocks. The less common, crystalline, modifications of SiO_2 are tridymite, cristobalite and extremely rare minerals coesite and stishovite. Earthy forms are, particularly, prevalent as kieselguhr and diatomaceous earth (Greenwood and Earnshaw 1984). Sands cover a large quantity of the Earth and are the source from which most silica is made. Different, ultrafine, particles of silica with different sizes are prepared, mainly, from the corresponding precursors.

The preparation of silica particles involves, several, precursors or intermediate reagents such as Tetraethoxysilane (TEOS), Sodium silicate (Na_2SiO_3), Methyltrichlorosilane (CH_3SiCl_3) and tetrachlorosilane (SiCl_4). Selecting a, proper, precursor depends mainly on the practical requirements of silica quality and function. The use of the gas phase method (drying method) or deposition method (wet method) depends on the application (Ke and Stroeve 2005). Amorphous form of silica with a very porous structure formed by acidification of aqueous solutions of sodium silicate, the gelatinous precipitate is washed free of electrolytes and then dehydrated. This material finds extensive use as selective absorbent, chromatographic support and catalyst substrate etc. Therefore, surface properties of amorphous silica, in many cases depend on the

presence of silanol groups and also existing surface siloxane(Si-O-Si) bridges (Greenwood and Earnshaw 1984; Zhuravlev 2000).

1.3 Coumarins

The IUPAC nomenclature of the coumarin ring system is *2H*-1-benzopyran-2-one. It occupies an important place in the realm of natural products and synthetic organic chemistry(Joule and Mills 2010). The structure of coumarin is illustrated in Fig. 1.1.

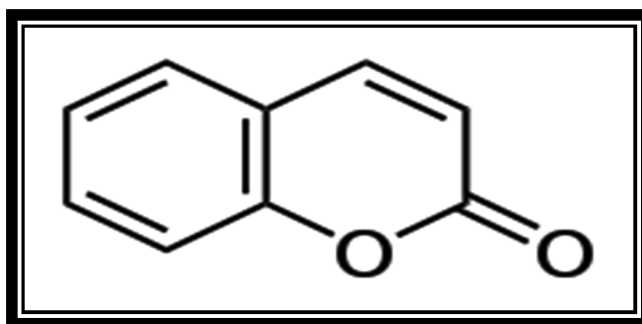


Fig.1.1: The structure of coumarin

Naturally occurring oxygen heterocyclic compounds having a distinct and important place in the realm of natural and synthetic organic chemistry as these compounds display useful ,and diverse, biological properties, viz. antibacterial, antiviral, anticancer and anti-HIV and also have been used as additives in food, cosmetics, and perfumes(Lacy and O’Kennedy 2004; Lunagariya and Bhavasar 2014). Optical brighteners, dispersed fluorescent, and laser dyes. Due to the importance of coumarins, efforts have been made to achieve simple and efficient procedures for the synthesis of these compounds(Li et al. 1998; Joule and Mills 2010; Vahabi and Hatamjafari 2014). Many synthetic methods, such as Pechmann condensation, Perkin, Reformatsky reaction,

Knoevenagel condensation and Claisen rearrangement, have been investigated for the synthesis of coumarins(Joule and Mills 2010).

1.3.1 Industrial Importance of Coumarins

Various coumarin derivatives, such as 7-hydroxy-4-methylcoumarin, are widely used in fine chemical industries. They are used as fluorescent brightener and as a standard for fluorometric determination of enzymatic activity(Joule and Mills 2010, Lunagariya and Bhavasar 2014). They act as a starting material in the preparation of insecticide hymecromon(Thimons et al. 1998). They also display physiological properties in humans and animals. Warfarin is the most famous coumarin, which is used in low doses in humans as a blood thinner. In high doses, it is a rat poison because it causes internal bleeding(Lacy and O’Kennedy 2004). The ultraviolet activity of 7-hydroxycoumarin(Umbelliferone) led to its use as a sunscreen agent, and an optical brightener for textiles(Joule and Mills 2010; Jain and Joshi 2012). It has also been used as a gain medium for dye lasers. Umbelliferone can be used as a fluorescence indicator for metal ions(Joule and Mills 2010).

1.3.2 Pechmann Condensation

The Pechmann condensation reaction is the most simple and widely used method, to synthesize coumarins(Benzo-2-Pyrones) from phenol and carboxylic acid or ester containing β -carbonyl group. The condensation is performed under acidic conditions. The mechanism involves an esterification/transesterification followed by attack of the activated carbonyl ortho to the oxygen to generate the new ring(Furniss et al. 1998). Also large number of condensing agents, such as strong acids(H_2SO_4) but this process has many drawbacks such as formation of by-products, requires long reaction time, and

causes corrosion problems. For these reasons, there have been some attempts to find alternative environmentally benign and heterogeneously catalyzed synthesis routes. On the other hand, heterogeneous solid systems are appropriate as they are easily recoverable, reusable and minimize the wastes. During the past few years, various solid acid catalysts such as Zeolites, Nafion-H, Amberlyst, Montmorillonite K 10(Weitkamp and Puppe 1999; Laufer et al. 2003; Kaur and Kishore 2012).

1.4 Catalysts

Many reactions proceed much faster in the presence of a substance that is not a product(or reactant) in the usual sense. These substance are called a catalysts, and the process whereby the rate is increased is catalysis(Missen et al. 1999). A catalyst is a substance that increases the rate of a chemical reaction without itself being changed in the process. During the reaction, it may become a different entity, but after the catalytic cycle is complete, the catalyst retains its initial form. A catalyst is not light or heat or any sort of electromagnetic radiation. These are not substances in the ordinary sense and therefore are not catalysts(Smith and Notheisz 2000). Depending on whether the catalyst and all the reaction components belong to a single phase or not, it can be classified to two categories, namely, homogeneous and heterogeneous catalysts. There are many types of catalysts used in Pechmann condensation reaction.

1.4.1 Homogeneous catalysts

Homogeneous catalysts operate in the same phase as the reactants, most often the liquid phase. Many homogeneous catalysts were employed in several reactions such as general acid and base catalysis(ester hydrolysis), Lewis acids as catalysts(Diels-Alder reactions) and organic catalysts(Van Leeuwen 2004) for the synthesis of coumarin and

their derivatives. Many other homogeneous catalysts like metal chlorides and sulfonic acid were reported as acid catalyst for the Pechmann condensation reaction. However, most of these acid catalysts are required in stoichiometric amount or more for high yields. They are corrosive, difficult to separate and create severe environmental problems due to difficulty of disposing post reaction wastes.

1.4.2 Heterogeneous catalysts

Heterogeneous catalysts have the desirable property that after reaction they are easily separated from the reactants and products. This is an important reason why heterogeneous catalysts are often preferred in industry, in particular for high-volume products, for instance, in the energy sector. For heterogeneous catalysts, the chemical reactions take place at the surface of the catalyst material. For that reason, heterogeneous catalysts are typically extremely porous materials so that the surface area is large. In some cases, the catalytic material itself can be made with high surface area (Nørskov et al. 2014). Heterogeneous catalysts exist in many forms such as pure metallic form, metal oxide, supported metals and supported metal oxides (Smith and Notheisz 2000). Amorphous silica from rice husk (RH) was used as alternative low cost source of silica support of many heterogeneous catalysts. RH based heterogeneous catalysts exhibit high catalytic performance for many reactions (Salehi et al. 2004; Adam and Ahmed 2008). The silica from RH and rice husk ash (RHA) is characterized with good textural and structural properties.

1.5 Rice husk

Rice husk (RH) is an agricultural residue obtained from rice mills; it can be burned at temperatures above 600 °C to form rice husk ash (RHA). RH composes of about 20%

ash and the rest are organic components. This ash contains more than 90% silica(Adam, F. 2007). Extraction of amorphous silica from RHA can be achieved by sol-gel technique(Ahmed and Adam 2007). Amorphous silica from RHA finds wide applications as filler, catalyst support, adsorbent and a source for synthesizing high performance silicon and its compounds(Della et al. 2002). Various metal ions and unburned carbon influence the purity and color of RHA. Controlled burning of the husk after removing these ions can produce white silica of high purity.

1.6 Literature Review

Pechmann reaction is an important reaction in organic synthesis and it can be catalyzed by brønsted or Lewis acids. Thimons et al.(1998) studied the Pechmann condensation in the presence Nafion 417 solid acid catalyst. The reaction was performed by condensing resorcinol with ethyl acetoacetate in the presence of toluene solvent while stirring at 110 °C for 90 min. It produced an off-white powder of 7-hydroxy-4-methylcoumarin with a15% yield.

Li et al.(1998) studied Montmorillonite K-10 and KSF clays catalysts for the synthesis of Coumarins via Pechmann condensation. Phenol and ethyl acetoacetate precursors were heated in the absence of solvent or in refluxing toluene. The optimum amount of the catalyst used was between 25 and 30% by weight of the total reactants. Many reaction parameters were investigated and the highest yields(~96%) were obtained using Montmorillonite K-10 in a solvent-free condition at 150 °C for 4 h reaction time.

High yields of ~90% coumarins were produced from the reaction over catalytic activity of KSF clays under toluene refluxing conditions for 10 h.

Potdar et al.(2001) studied the Pechmann condensation of phenols and ethyl acetoacetate in the presence of 1-butyl-3-methylimidazoliumchloroaluminate([bmim]Cl·2AlCl₃) ionic liquids acid catalysts for the formation of coumarin derivatives. The reaction time was reduced drastically even at ambient reaction conditions and the composition of ionic liquids is expressed as the apparent AlCl₃ mole fraction(N). This reaction was carried out in N = 0.33, 0.5 and 0.67 liquids. Amazing results were obtained only by applying an acidic ionic liquid with N value of 0.67 and a maximum yield of 95% was produced in a short time(10 min) at 30 °C.

Laufer et al.(2003) used Nafion resin/silica nano-composites as catalyst for the reaction of resorcinol with ethyl acetoacetate(Pechmann reaction) or with acrylic acid. Nafion resin/silica composite materials with 40 and 80 wt% of Nafion were tried for these reactions. The product 7-Hydroxy-4-methylcoumarin was obtained in high yields up to 81% over SAC 40(containing 40% Nafion on silica) after refluxing the mixture in toluene solvent for 2 h. Whereas, the highest yield of 96% was achieved over SAC 80 (80% of Nafion in composite) at similar refluxing condition.

Stoyanov and Mezger(2005) studied Pechmann reaction of substituted phenols with methyl acetoacetate over the catalytic activity of boron trifluoridedihydrate solid acid heterogeneous catalyst for the synthesis of 4-methylcoumarin derivatives. An optimum yield of 99% of 7-hydroxy-4-methylcoumarin was obtained under heated resorcinol and methyl acetoacetate to 20 minutes at 60 °C then put it to cooling to room temperature and poured into 50 g of crushed ice.

Valizadeh and Shockravi(2005) studied titanium(IV) chloride as a catalyst to promote the Pechmann condensation reaction with a range of phenols and β -keto esters. The reaction was carried out by addition of TiCl_4 to a mixture of phenol and β -keto ester with thorough stirring in the absence of a solvent and represented an improvement on the classical Pechmann conditions. TiCl_4 -catalysed this reaction in the presence of solid support under Microwave irradiation proved to be unsuccessful. The optimum reaction conditions which yielded 97% of 7-Hydroxy-4-methylcoumarin were stirring the reaction mixture for 50 seconds at room temperature under solvent-free conditions.

Maheswara et al.(2006) studied the Pechmann condensation in the presence of silica supported perchloric acid ($\text{HClO}_4 \cdot \text{SiO}_2$) as heterogeneous recyclable catalyst under solvent-free conditions. The reaction mixture was stirred at 130 °C in a preheated oil-bath to obtain coumarins derivatives. These reactions were carried out with series of monohydric and polyhydric phenols with ethyl or methyl acetoacetate. The optimum yield of 98% was reached after proceeding the reaction mixture of pyrogallol and ethyl acetoacetate for 75 min.

Joshi and Chudasama(2008) studied amorphous and crystalline M(IV) phosphates and tungstates solid acids as inorganic ion exchangers of the class of tetravalent metal acid(tma), to catalyze Pechmann condensation between phenols (resorcinol, pyrogallol and phloroglucinol) and methylacetoactate to give coumarins, under solvent free conditions. The optimum condition reaction in mixture of resorcinol and methylacetoactate at 130 °C, 10 h over ZrP catalyst give 61.1% as optimum yield, 54.9% over TiW in same reaction condition.

Sinhamahapatra et al.(2010) studied mesoporous zirconium phosphate (m-ZrP) as a solid acid catalyst for Pechmann condensation reaction to form coumarin derivatives from phenols and ethyl acetoacetate. The optimum reaction mixture was resorcinol and ethyl acetoacetate. This mixture yielded 97% of 7-hydroxy 4-methyl coumarin when microwave(with power of 600 w) heated to 160 °C for 15 min only in the presence of m-ZrP catalyst. The yield was found to decrease slightly to 94% when the mixture was heated to the same temperature in a conventional hotplate magnetic stirrer for 4 h.

Kuarm et al.(2010) studied cellulose sulfuric acid as a solid acid catalyst in the Pechmann condensation using different types of phenols and acetoacetates under solvent-free medium. The optimum mixture was investigated to be resorcinol and phenyl acetoacetate. Almost similar yields were obtained when the reaction was proceeded under stirring at room temperature for 20 min(96%) or under microwave (300-W power) irradiation for 2 min(97%).

Karami and Kiani(2011) studied $ZrOCl_2 \cdot 8H_2O/SiO_2$ as heterogeneous catalyst to catalyze the Pechmann condensation to synthesize coumarin derivatives using substituted phenols and β -ketoester. To produce an optimum yield of 94%, the reaction mixture (resorcinol and ethyl acetoacetate) was stirred in a preheated oil bath at 90 °C for 40 min in the presence of $ZrOCl_2 \cdot 8H_2O/SiO_2$ (10 mol %) under solvent-free conditions.

Sharma et al.(2011) studied Pechmann condensation for the synthesis of coumarins involving different phenols and β -ketoesters in the presence of p-toluene sulfonic acid(p-TSA).The reaction optimum conditions were a mixture of resorcinol and ethyl acetoacetate, room temperature and 20 min reaction time. At these conditions an optimum yield(95%) of 7-hydroxy 4-methyl coumarin was obtained.

J. Ċejka et al.(2012) studied metal–organic frameworks (MOFs) Cu-benzene-1,3,5-tricarboxylate(CuBTC) and Fe-benzene-1,3,5-tricarboxylate (FeBTC) heterogeneous catalysts to catalyze the Pechmann condensation of different phenols (resorcinol, pyrogallol, and naphthol) with ethyl acetoacetate. The conversions of phenolic substrates increased in the expected order, as a result of their reactivity : pyrogallol< resorcinol <naphthol .Naphthol gave the optimum conversion of 94% and 98 % after 1400 min at a temperature of 130 °C, over CuBTC and FeBTC, respectively in the presence of nitro-benzene solvent.

Yadav et al.(2012) studied super acidic sulfated zirconia catalyst with sulfur content(15% w/w) to catalyze Pechmann condensation reaction between resorcinol and ethyl acetoacetate to produce 7-hydroxy 4-methyl coumarin. The optimum conditions for this reaction were studied in a high-pressure autoclave of 100ml capacity. The optimum conditions were investigated for total reaction volume of 50 mL with makeup of toluene, temperature at 150 °C, 180 min and the speed of agitation at 1200 rpm with a catalyst loading of 0.03 g/cm³ to produce 7-hydroxy 4-methyl coumarin.

Khodabakhshi(2012) studied Barium dichloride-catalyzed Pechmann condensation reaction of various phenols and β -keto esters under solvent-free conditions for the synthesis various coumarin derivatives. The optimum yield(90%) of 5,7-dihydroxy-4-methylcoumarin was obtained on heating the reaction mixture of phloroglucinol and ethyl acetoacetate at 100 °C under solvent-free conditions for 25 min in the presence 10 mol%(BaCl₂).

Ghodke and Chudasama(2013) studied solid acid catalysts, ZrPW (Zirconium (IV) Phosphotungstate) and 12-TPA/ZrO₂ [12-Tungstophosphoric acid(12-TPA) supported onto ZrO₂] to catalyze Pechmann condensation of phenols(resorcinol as optimum) and methyl acetoacetate to give 7-hydroxy 4-methyl coumarin. The reaction was conducted under solvent-free conditions at **130 °C** for 8h.Almost similar yields (~58%) were obtained when the reaction was conducted over either ZrPW or 12-TPA/ZrO₂ catalysts. The yield was observed to slightly increase(~61%) when microwave (MW) heating conditions (MW power of 250 W) was applied at **130 °C** for 30 min over the two prescribed catalysts.

Datta and Pasha(2013) studied the Pechmann condensation in the presence of Silica-ZnCl₂ catalyst for the synthesis of 4-methylcoumarins from ethyl acetoacetate and substituted phenols. The reaction mixture of resorcinol & ethyl acetoacetate was heated in an oil bath at **80 °C** for 15 min to get an optimum yield of 95% in solvent-free conditions.

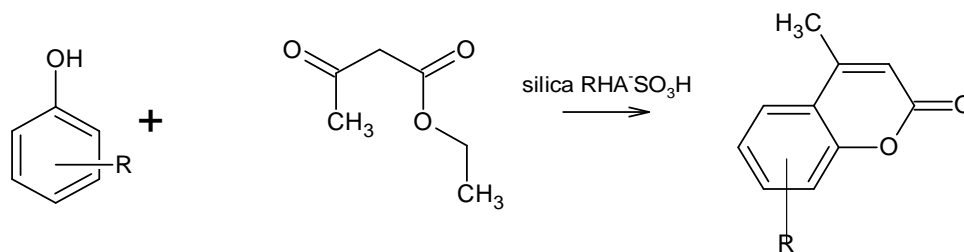
Niknam et al.(2014) investigated the catalytic activity of Silica-bonded *n*-propyl di ethylene tri amine sulfamic acid (SBPDSA) heterogeneous catalyst for the synthesis of coumarin derivatives adopting Pechmann condensation reaction. Various phenols and β-keto-esters (methyl, ethyl, allyl, and benzyl acetoacetate) were used as reactants. The reaction of Floroglucinol and ethyl acetoacetate which was, magnetically, stirred at **80 °C** under solvent-free conditions for 5 min gave an optimum yield of 92% coumarins.

Jafari et al.(2014) tried the Zinc oxide nano-rods ZnONRs catalysts for the synthesis of substituted coumarins(4-hydroxycoumarins) from the reaction of aryl

glyoxal and benzamide in solvent free conditions. The reaction, which was conducted at **80 °C** for 180 min using small quantity(5 mol%) of ZnO NRs heterogeneous catalyst, gave an optimum yield of 80% coumarin derivative.

1.7 Objectives

Supported solid acids are environmental friendly catalysts. They can replace liquid acids to minimize the pollution and harmfulness to the environment. Many solid acids are expensive and also synthesized from hazardous fine chemicals in difficult conditions. Rice husk is an agricultural residue and is highly, abundant in many countries including Sudan. Moreover, it is not recommended as cattle feed and hence it is either disposed off without treatment or burned openly. Any of these disposing methods causes many environmental problems. Therefore, many researchers have tried to utilize its silica constituent for useful applications. Interestingly, no any application of catalysts derived from RH of RHA was reported in literature for the synthesis of coumarin derivatives. It is the aims of this project to fabricate useful material to be used as a heterogeneous catalyst for the synthesis of coumarin derivatives using ethyl acetoacetate and various phenols derived precursors. In this study, sulfuric acid modified amorphous silica from rice husk has been used as solid acid catalyst for Pechmann condensation reaction. As will be discussed later, the catalyst showed good catalytic performance for the production of 4-methyl coumarin compound and its derivatives(Scheme1.1).



Scheme 1.1: Synthesis of 4-methylcoumarins

In general, the major objectives of this study are:

- To prepare various sulphonic acid modified rice ash silica solid acid catalysts (RHA-SiO₂-SO₃H) by adopting the established methods reported by Zolfigol (2000) and Hello et al. (2014).
- To characterize the as-synthesized (RHA-SiO₂-SO₃H) heterogeneous catalysts.
- To study the catalytic activity of the for the Pechmann condensation of phenol derivatives with ethyl acetoacetate (EAA) for the selective production of substituted 4-methylcoumarins.

Chapter Two Materials and Methods

2.1 Materials

- Chlorosulfonic acid(Assay 99.9%), England.
- Phenols(Resorcinol, β -naphthol, α -naphthol, *o*-Cresol, *o*-amino phenol),(Assay 98–99.5%),ALPHA CHEMIKA, INDIA.
- Ethyl acetoacetate(Assay>98%), ALPHA CHEMIKA, INDIA.
- Ethanol absolute anhydrous, CARLO ERBA Reagents.
- Toluene(Assay >98), ALPHA CHEMIKA, INDIA.
- Potassium hydrogen phthalate (Assay 100%), ANALAR.
- Potassium hydroxide(Assay 98.5%), ALPHA CHEMIKA, INDIA.
- Sodium hydroxide(Assay 98.9%), ALPHA CHEMIKA.
- Nitric acid(Assay 69-72%), ALPHA CHEMIKA.

All chemicals were of analytical grade and were used directly without further purification. Rice husk(RH) was collected from a rice mill in Algazera state –Sudan.

2.2 Methods

2.2.1 Pre- treatment of RH

The rice husk(RH) was washed with water and rinsed with distilled water then dried at room temperature for 24 h. The clean rice husk was stirred with suitable volume of 1.0 M nitric acid at room temperature for about 24 h(to reduce all metallic impurities to negligible levels). It was, thoroughly, washed with distilled water until the pH of the rinse became constant. The wet RH was subsequently dried in an oven at 100 °C for 24 h. The acid-leached RH was burned in a furnace at 800 °C for 5 h for complete combustion. The rice husk ash(RHA) obtained was used as a source of silica and catalysts(Ahmed and Adam 2007).

2.2.2 Preparation of silica

An amount of 5.0 g of RHA white powder was added to 250 mL of 1.0 M NaOH in a plastic container and stirred for about 18 h at room temperature to extract the silica as sodium silicate. The solution was filtered using filter paper and the extracted sodium silicate was titrated with 3.0 M HNO₃. The acid solution was added at a slow rate of ca. 1.0 mL/ min with constant stirring. Silica gel started to precipitate when the pH decreased to less than 10. The titration was continued until the pH of the solution reached 5(Ahmed and Adam 2007). The silica gel/precipitate was aged for 24 h. The silica gel/precipitate was filtered washed thoroughly with distilled water and dried at 100 °C for 18 h. The silica xerogel was ground to powder and washed again with distilled water several times then filtered and dried at 100 °C for 6-8 hours and labeled as RHA-SiO₂.The extra washing enabled to wash-off the residual nitrate ions completely.

2.2.3 Preparation of the catalysts

2.2.3.1 Direct modification

The silica RHA-SO₃H catalyst materials were synthesized according to the established procedures reported by (Ahmed and Adam 2007; Zolfigol 2001; Hello et al. 2014). 3.0 g of RHA were added to 100 mL of 1.0 M NaOH in a plastic container and stirred for 30 min at room temperature to convert silica to sodium silicate. The sodium silicate formed was filtered to remove undissolved particles. The solution was then titrated slowly with 3.0 M nitric acid and 3.0 mL (51.0 mmol) of chlorosulphonic acid with constant stirring. The change in pH was monitored by using a pH meter. A white gel started to form when the pH reached 10.0. The titration was continued until the pH of the solution reached 3.0. The gel was aged for 24 h at room temperature and it was later separated (Hello et al. 2014). The separation process of white gel was repeated 6 times with copious amount of distilled water, and the final washing was done with acetone. The sample was then dried at 110 °C for 24 h and finally ground to a fine powder and labeled as RHA-SO₃H.

2.2.3.2 Post modification

A volume of 3 mL Chlorosulfonic acid were added drop-wise to a quantity of 10.0 g of as-produced RHA silica (RHA-SiO₂) in a round bottom flask (250 mL) over a period of 40 min at room temperature (Zolfigol 2001). The whole experiment was implemented in the fume-hood to avoid the intensive exposure to HCl gas released during the silica-sulphonic acid reaction. After the addition was complete the mixture was shaken for 30 min, a white solid silica (RHA-SiO₂) sulphonic acid (-SO₃H) was obtained and labeled as RHA-SiO₂/SO₃H.

2.2.4 Catalyst characterization

The prepared catalysts were characterized by FT-IR Spectrometric analysis, acidity measurement and Cation exchange capacity(CEC).

2.2.4.1 FT-IR Spectroscopic Analysis

The Fourier Transform Infra-Red(FT-IR) spectroscopic analysis was conducted over an FT-IR 300 Spectrometer(Model Thermo Nicolet).

2.2.4.2 Acidity Measurement

Many procedures can be used to indicate the presence of the Bronsted acid sites and to quantify them .In this work, Acid–base titration technique was used to determine the absolute number of sulphonic acid groups per gram of RHA-SiO₂/SO₃H acid catalyst. In this test, 0.1229 g of the catalyst was carefully suspended in an aqueous solution of NaCl(2.54 mM, 250 mL) for 20 min then separated by filtration. A volume of 10 mL of the filtrate solution was taken and 3 drops of thymol blue/EtOH indicator were added. The solution was titrated against standard titration solution of 3.5mM KOH(standardized with potassium hydrogen phthalate) to the end point of the indicator(Dijs et al. 2002). The Cationic Exchange Capacity(CEC) was calculated according to Eq. 2.1.

$$\text{CEC} = (\text{Normality of KOH} \times \text{Volume of KOH}) / \text{g of solid acid} \quad (2.1)$$

2.2.5 Catalytic Reactions

2.2.5.1 Pechmann condensation Reactions

A mixture of ethyl acetoacetate(4mmol), phenols(Resorcinol, β -naphthol, α -naphthol, *o*-Cresol, *o*-amino phenol)(2mmol), and 100 mg of the catalyst(RHA-SO₃H or RHA-SiO₂/SO₃H)were transferred to a 35mL round-bottomed flask fitted with a condenser in solvent or solvent-free conditions. The solution was mixed well and heated

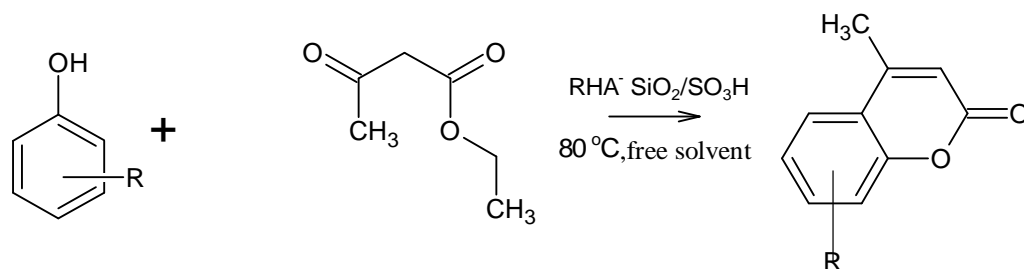
in an oil bath at 80 °C for 1-6 h. After completion of the reaction, the contents were cooled to 25 °C and 5 mL of ethyl acetate (EtOAc) were added to the reaction mixture. The solid catalyst was removed by filtration and washed by acetone several times; whereas, the EtOAc was removed by evaporation at room temperature. The crude products were purified by recrystallization using ethanol as a solvent. The product (7-hydroxy 4-methyl coumarin) was dried and kept for analysis. Some physical parameters were measured such as yield percentage and melting point. The yield (wt %) of coumarins compounds was obtained according to Eq. 2.2.

$$\text{Yield (wt \%)} = \frac{\text{Obtained weight of product}}{\text{Theoretical weight of product}} \times 100\% \quad (2.2)$$

To monitor the extent of the reaction, very small portion of the reaction mixture was periodically withdrawn and analyzed by a GC (Shimadzu GC 2010). The conversion of phenols and selectivity of coumarins were calculated. To attain the maximum conversion and selectivity, the reaction of resorcinol and ethyl acetoacetate (EAA) was optimized by varying the reaction time, temperature, molar ratio of resorcinol to EAA and the amount of catalyst with respect to resorcinol.

2.2.5.2 The Reusability of the catalyst

The extent of reusability of catalyst was tested by running the Pechmann condensation, successively, with the same catalyst under the same reaction conditions. The reaction was first run with the fresh catalyst to complete conversion and then the catalyst was filtered and washed with acetone several times and dried. The recovered catalyst was reused in the subsequent reactions. The procedures were repeated three times.



Scheme 2.3: RHA-SiO₂/SO₃H catalyzed Pechmann condensation in a solvent-free condition.

2.2.5.3 Gas Chromatography(GC)

Gas Chromatographic analysis was performed using GC chromatograph equipped with FID detector and capillary column.

Brand: GC-2010

Column type: BD-210 capillary column high polarity.

GC Conditions

Injector temperature: 250 °C.

Column temperature: Initial temperature: 100 °C, Final temperature: 220°C(20°C/min, hold for 15min).

Detector temperature: 250 °C.

Carrier gas: Nitrogen.

Injection volume: 1.0 micro liter.

Split ratio: 50:1

Chapter Three

Results and Discussion

3.1 Catalyst characterization

3.1.1 FT-IR spectroscopy

FT-IR spectra of synthesized RHA silica(RHA-SiO₂) and sulphonic acid modified RHA silica(RHA-SO₃H and RHA-SiO₂/SO₃H) are shown in Fig.(3.1,3.2,3.3). The stretching frequency of free surface silanol(SiO—H) groups at above 3000 cm⁻¹ difficult to detect due to the high intensity of the O—H stretching vibrations of absorbed water. Therefore, the peak at 3746 cm⁻¹ wave length, is assigned to stretching vibration of H—OH groups of adsorbed water(Hello et al. 2014, Ahmed and Adam 2007). The band at 1638cm⁻¹ is due to bending vibration of HO—H of adsorbed water .The strong peak at 1101cm⁻¹ is due to asymmetric stretching vibrations of structural siloxane(Si—O—Si) bonds. This peak shifted to 1117.81 cm⁻¹ for RHA-SO₃H and1120 cm⁻¹ RHA-SiO₂/SO₃Hcatalysts maybe due to modification by chlorosulphonic acid. The band at 964cm⁻¹ is attributed to Si—O asymmetric stretching vibration(WeitkamandPuppe1999; Ahmed and Adam 2007).It reserves its intensity and slightly shifted to lower frequency of

959 cm^{-1} for RHA-SO₃H. However, its intensity drastically decreased for RHA-SiO₂/SO₃H indicating major displacement of silanols by sulphonyl groups predominantly occurred for post-modified material (Hello et al. 2014). Interestingly, new peak at around 877 cm^{-1} appeared for sulphonic acid modified material, which could be related to vibrations of S-O. The band at about 800 cm^{-1} is assigned to Si-O-Si symmetric stretching vibration (Ahmed and Adam 2007). This peak slightly shifted to lower frequency for RHA-SO₃H (789 cm^{-1}) and RHA-SiO₂/SO₃H (795 cm^{-1}) materials (Rothenberg 2008). The band at 466 cm^{-1} is due to Si-O-Si bending vibration (Weitkamp and Puppe 1999). It did not show an obvious shift for the modified RHA-SiO₂ materials i.e. RHA-SO₃H and RHA-SiO₂/SO₃H catalysts. It is interesting to note that new peaks are also observed at 619 cm^{-1} and 575 cm^{-1} for RHA-SO₃H and RHA-SiO₂/SO₃H catalysts, respectively. These peaks were not detected for unmodified silica (RHA-SiO₂), and hence perhaps are due to chemical transformation by chlorosulphonic acid.

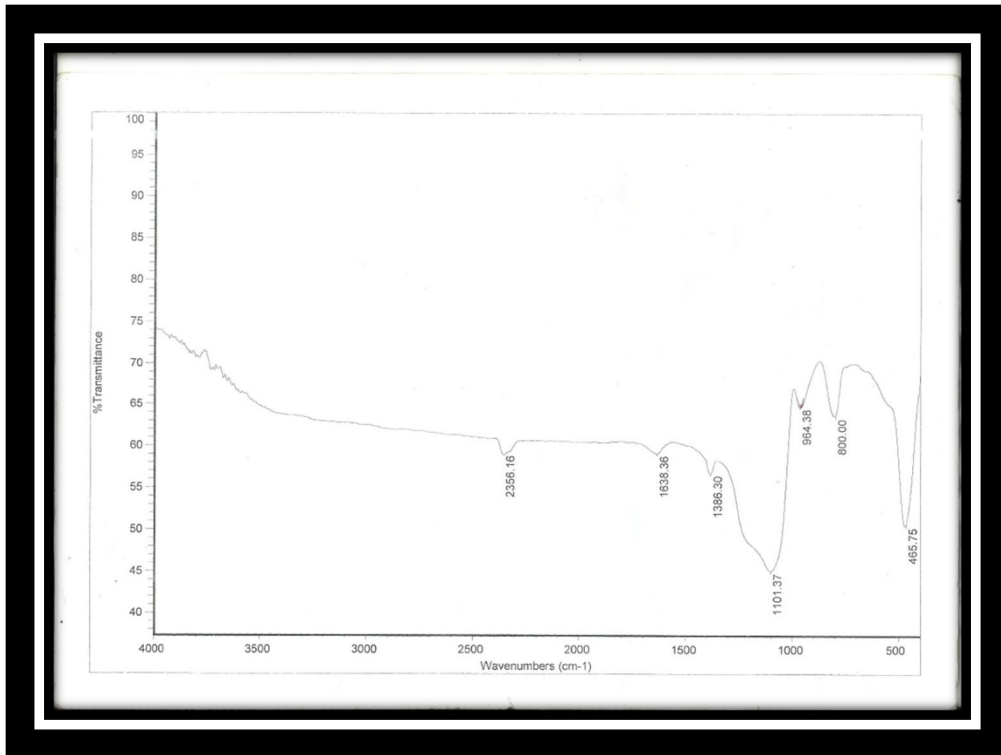


Fig.3.1: The FT-IR spectrum of RHA Silica (RHA-SiO₂).

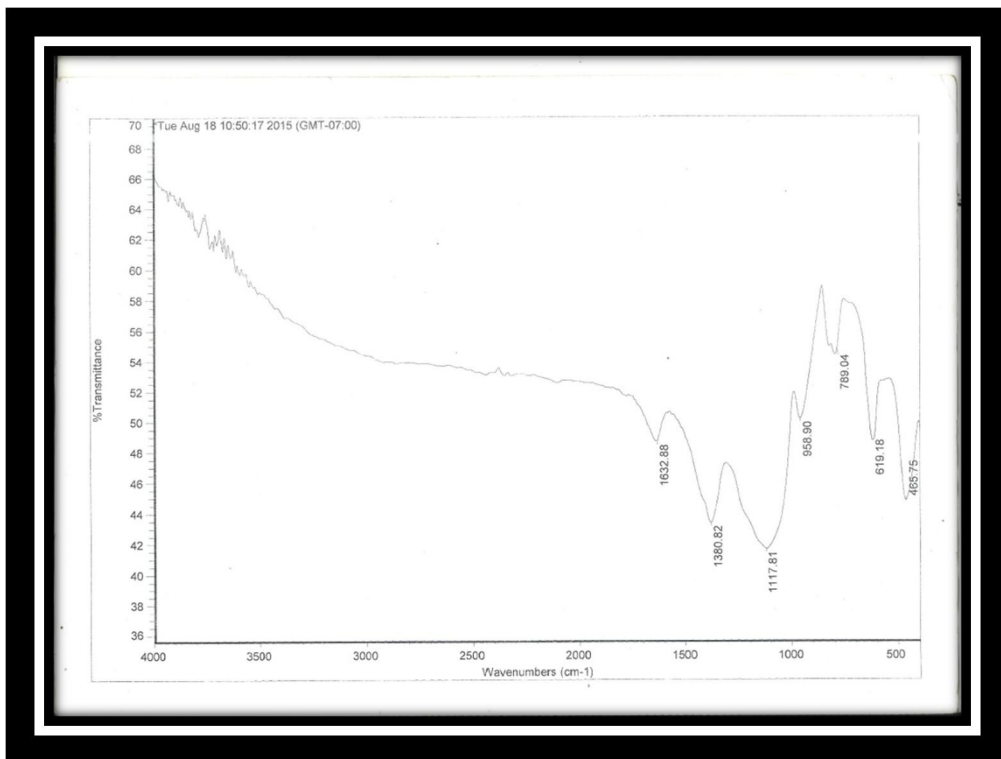


Fig.3.2: The FT-IR spectrum of RHA-SO₃H(directly modified RHA silica).

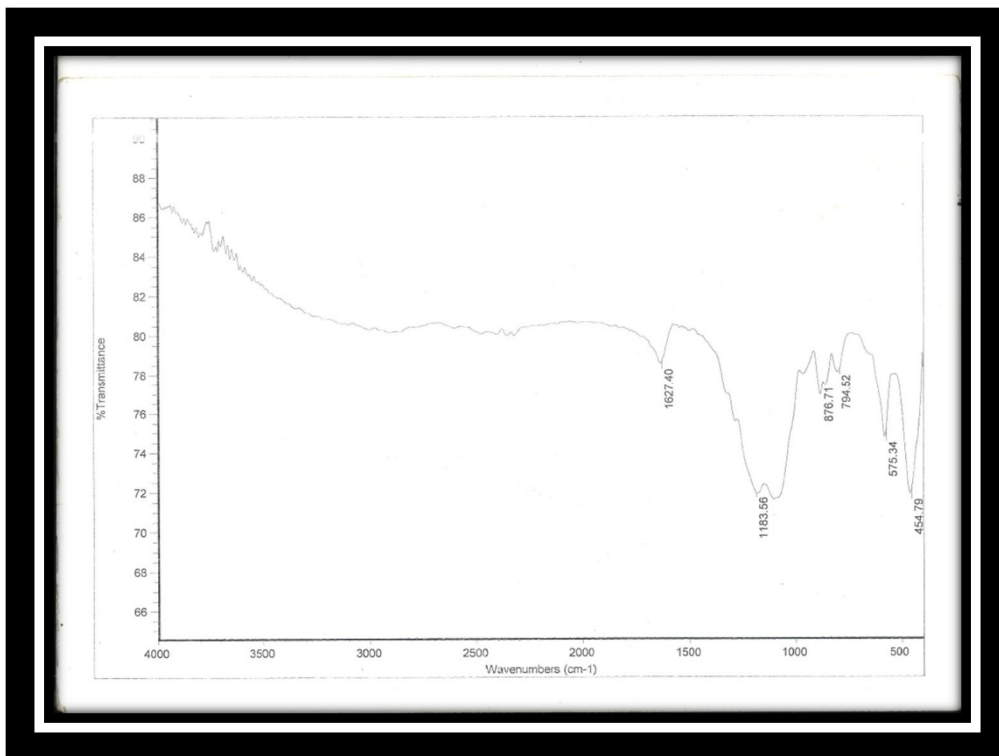


Fig.3.3: The FT-IR spectrum of RHA-SiO₂/SO₃H(Post modified RHA silica).

3.1.2 Acidity measurement

Acid–base titrations were used to determine the absolute number of sulphonic acid groups per gram of sulphonic acid surface-functionalized silica(Rothenberg 2008). In this test, Potassium hydroxide(KOH) was used as the basic probe compound to determine the Bronsted acidity of the catalyst material in mmol per gram of solid acid. The CEC is the number of positively charged hydrogen cations (H⁺) necessary to fill the catalysts acid holding sites per grams of catalysts and used to describe the holding capacity of the acid sites of catalyst for positively-charged elements (cations). The values of CEC as well as absolute numbers of sulphonic acid groups per gram of solid acid materials were calculated and presented in Table 3.1. The low CEC value of the directly-modified solid acid catalyst could be attributed to the poor accessibility of the sulphonic

acid group by the titrating base. The low CEC value associated with the same material could also give evidence that sulphonic acid groups were, deeply, within the silica framework (Adam et al. 2012). Another possible explanation is the crowdedness of sulphonic groups in the pore walls of the catalyst thereby limiting the exchange capacity between NaCl and the sulphonic acid group before the titration (Li et al. 2009). Studies on the structure of this material (RHA-SO₃H) as well as a proper quantitative measurement of sulphur are needed to clear all doubts concerning the low acidity. It is important to note that none of such studies were so far reported in literature. According to fundamental chemistry, the acidity associated with RHA-SO₃H is not sufficient to catalyze the Pechmann condensation reaction and hence the catalytic study will be carried out only in the presence of RHA-SiO₂/SO₃H solid acid catalyst.

Table 3.1: Acidity and Cation exchange capacity (CEC) of solid acid catalysts produced through modification of RHA-SiO₂ surface by sulphonic acid species.

Type of Expression	Post-modified material RHA-SiO ₂ /SO ₃ H	Directly-modified material (RHA-SO ₃ H and)
Molarity mol L ⁻¹	0.003	0.001
Acidity mmolH ⁺ g ⁻¹	0.75	0.239
CEC mequivg ⁻¹	0.22	0.07

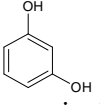
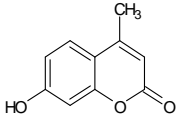
3.2 Pechmann catalytic condensation of phenolic compounds

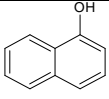
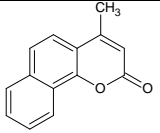
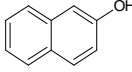
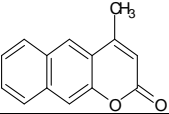
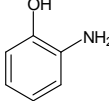

Various coumarin derivatives were synthesized from the Pechmann reaction of phenols and ethyl acetoacetate over the catalytic activity of post-modified solid acid i.e. RHA-SiO₂/SO₃H. Many reaction parameters were tried for the production of high yields of coumarin derivatives. These parameters included type of phenol, type of solvent, reactants molar ratios, catalyst loading, reaction time and re-usability of the catalyst.

3.2.1 Effect of type of phenolic compound

The effect of phenol type was investigated using resorcinol, α -naphthol, β -naphthol, *o*-aminophenol and cresol. As shown in Table 3.2, resorcinol afforded the best yield (98.9%) at 80 °C for one hour reaction time. Other reaction conditions were fixed, i.e. resorcinol /EAA molar ratio of 1:2, solvent-free condition and 0.1g RHA-SiO₂/SO₃H catalyst. Reactions of α - and β -naphthols gave moderate percentages of yield, i.e. 66% and 58%, respectively, at different reaction conditions. Only the reaction time was increased to 3h for α -naphthol and 4h for β -naphthol reaction. The temperature was also raised to 100 °C for the reaction of α -naphthol. The reaction of *o*-cresol and *o*-aminophenol registered no yields of coumarin derivatives. From the experimental results, it can be indicated that the presence of electron-donating substituents at *meta* position to the phenol hydroxy group promotes the condensation process. However, the +E effects polarized carbonation at *ortho* position (Li *et al.* 1998; Joule and Mills 2010). An alkyl group is not strong enough to furnish the activation needed and thus given no yield after reaction time of 5h at 120 °C adopting a solvent-free condition. Whereas, amino group in *o*-aminophenol could be strongly bonded to catalyst surface and poisoning the catalyst active sites (Li *et al.* 1998).

Table 3.2: Pechmann condensation for production of coumarin derivatives over the catalytic activity of RHA-SiO₂/SO₃H using EAA and various phenols.

Entry	Substrate	product	Temperature (°C)	Time (h)	Yield(%)
1	 Resorcinol		80	1	98.9

2	 α -Naphthol		100	3	66
3	 β -Naphthol		80	4	58
4	 <i>o</i> -aminophenol	no reaction	80	6	–
5	 Cresol	no reaction	120	5	–

* Phenols: EAA molar ratio of 1:2, solvent-free condition and 0.1 g of catalyst.

3.2.2 Effect of solvent

Intermolecular Pechmann condensation was performed in the presence of polar and non-polar solvents and in the absence of solvent. Ethanol was used to represent the polar solvents, whereas, toluene was applied as an example of weakly polar solvents. Optimum reaction conditions were adopted, i.e. resorcinol and EAA reactants at a molar ratio of 1:2, reaction temperature 80 °C and over the catalytic activity of 0.1g of RHA-SiO₂/SO₃H. The reaction mixture was allowed to react for 30 min only in order to be able to observe the variation in reaction performance in the presence of different solvent systems. The progress of reaction was followed through the conversion of EAA using GC chromatography. The results were listed in Table 3.3.

Table 3.3: Effect of solvent in catalytic Pechmann condensation reaction of resorcinol and EAA(1:2 molar ratios) over RHA-SiO₂/SO₃H(0.1 g)

Solvent	Time (min)	Temp (°C)	Conversion (%)
Ethanol	30	80	87.5
Toluene	20	80	9.5
Solvent-free	30	80	89.4

Percentage of conversion was found to 87.47% at 80 °C after 30 min when using ethanol as solvent. The same reaction when performed in weakly polar solvent (toluene) registered 9.5% conversion only after 20 min. Maximum conversion of 89.4% was obtained when conducting the reaction in a solvent-free condition for 30 min. Low conversion in the presence of toluene solvent may be attributed to a competitive adsorption of reactants and solvent on the catalyst active sites (Tyagi et al. 2007, Maheswara et al. 2006). Further studies are needed using wide spectra of solvent polarity to come-up with a clear evidence for the effects of solvent polarity for the synthesis of coumarins. Due to the fact that conducting reaction in the absence of foreign solvent reduces the hazardous effects of chemicals and also because reaction in solvent-free condition exhibited optimum results of performance it is considered as optimal to study the subsequent parameters.

3.2.3 Effect of reactants molar ratio

The effect of reactants molar ratios in the yield percentage (wt%) of 7-hydroxy-4-methylcoumarins (HMC) was studied for the Pechmann condensation of resorcinol and EAA at 80°C for 1h using 100 mg of RHA-SiO₂/SO₃H solid acid catalyst. Various resorcinol/EAA molar ratios were tested, ca. 1:1, 1:2 and 1:3, in a solvent-free condition. It is quite obvious in Fig. 3.4 that the yield percentage of HMC is proportional to the amount of EAA added and hence the increment in Resorcinol/EAA beyond 1:1 drastically increased the yield of HMC from 50% to about 98%. It was also observed that further increase in the ratio of substrates from 1:2 to 1:3 did not alter the yield percentage of HMC, but it rather slightly reduced it to lower value. The depression in yield

percentage when using 1:1 molar ratio could be attributed to the competitive adsorption of reactants in the surface of catalyst(Sinhamahapatra et al. 2010). Further increment of molar ratio beyond 1:2 could also affect the catalyst activity due to the crowding of EAA molecules.

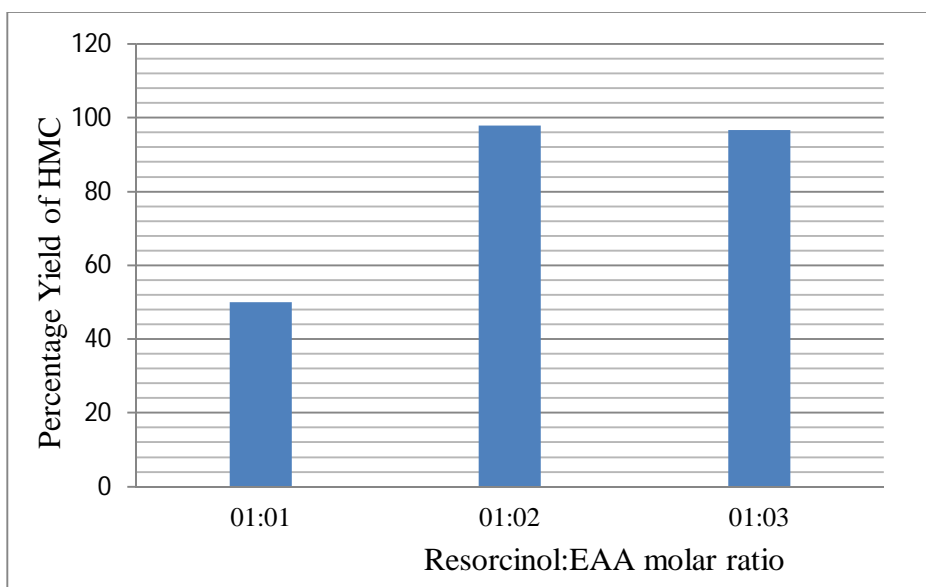


Fig. 3.4:The effect of Resorcinol: EAA reactants molar ratio in HMC yield for Pechmann condensation reaction(at 80°C and 1 h time) under solvent-free condition using 0.1 g of RHA-SiO₂/SO₃H catalyst.

3.2.4 Effect of catalyst loading

The amount of catalyst used to catalyze the Pechmann condensation reaction was varied to investigate its influence. Various weights of RHA-SiO₂/SO₃H catalyst were applied to catalyze the reaction between Resorcinol and EAA at 80 °C for 3 hours to produce HMC in a solvent-free condition. The yields obtained by these reactions are presented in Fig. 3.5. It could be observed that the product yield is ,strongly, affected by

the amount of catalyst used. The best result was obtained when the reaction was proceeded in the presence of 0.1g RHA-SiO₂/SO₃H.

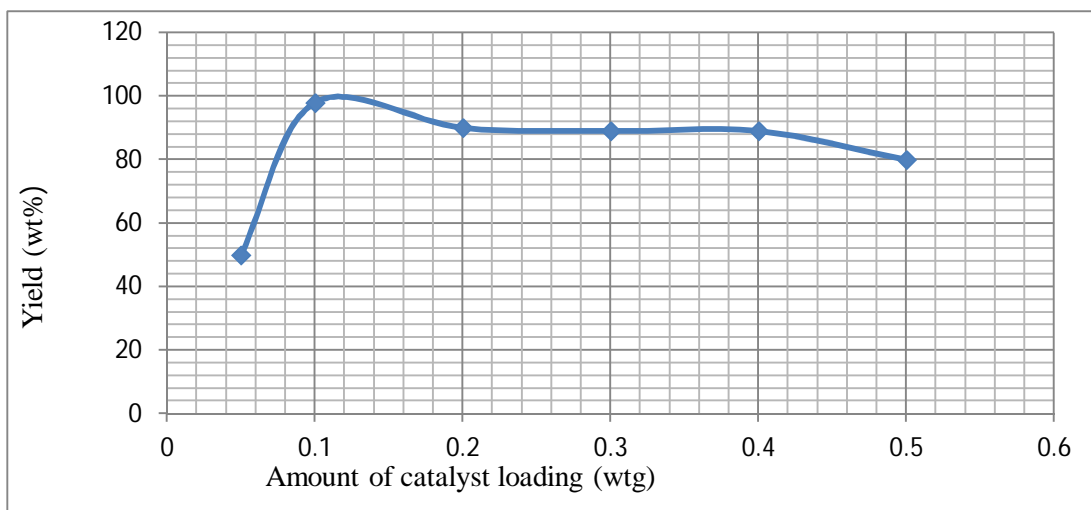


Fig. 3.5: Effect of RHA-SiO₂/SO₃H on yield(wt%) of HMC from Resorcinol and EAA(1:2 molar ratio) at 80 °C for 30 min

3.2.5 Effect of reaction time

The effect of reaction time of Pechmann condensation reaction of Resorcinol and EAA(1:2 molar ratio) in the presence of ethanol was investigated. The results, depicted in Fig. 3.6, showed that the conversion of EAA increased rapidly with increasing reaction time until 25 min(88.2%). Interestingly, the obtained results were found better than those reported earlier in the literature for the same reaction on catalytic activity of other solid acids such as hetero poly acid & resins(Romanelli et al.2004; Sabouet et al.2005; Wang et al.2014).

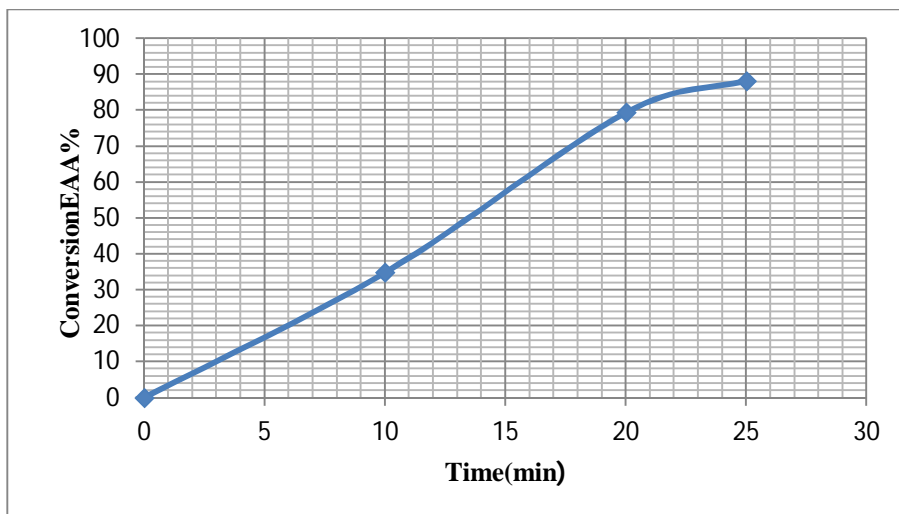


Fig. 3.6: Reaction profile of Pechmann condensation of resorcinol and EAA(1:2 molar ratio) at 80 °C, over the activity of RHA-SiO₂/SO₃H catalyst for 30 min in the presence of ethanol solvent.

3.2.6 Reusability of the catalyst

In order to check the recyclability of the catalyst, after each cycle, the catalyst was filtered, washed with acetone successively, and then dried. The dried catalyst was reused for the Pechmann condensation reaction using fresh reactants mixture. These steps were repeated three times. As illustrated in Table 3.4, it is very interesting to note that the activity of regenerated RHA-SiO₂/SO₃H catalyst was almost similar to fresh catalyst on subsequent runs. The catalyst was recycled successfully three times without significant change in its activity or selectivity.

Table 3.4: The reusability of RHA-SiO₂/SO₃H catalyst (0.1 g) in the Pechmann condensation reaction of Resorcinol and EAA for the production of HMC

Run	Recycle	Yield of HMC (%)
1	0	99.8
2	1	98,5

3	2	94
4	3	89.7

*Resorcinol: EAA molar ratio 1:2; reaction temperature 80°C; Reaction time 1h.

3.3 Characterization of 7-hydroxy 4-methyl coumarin

The appearance of synthesized 7-hydroxy 4-methyl coumarin was off white powder. Its m.p. was 178°C. Its UV-Vis spectrum in methanol has given λ_{\max} of 221-325nm, while, its FT- IR spectrum(KBr) showed the absorption bands of the functional groups of targeted coumarin derivative 3298.63 cm^{-1} (-OH), 1704.11 cm^{-1} (lactone carbonyl) and 1572.6 cm^{-1} (-C=C-).

Chapter Four Conclusion and Recommendations

4.1 Conclusion

The catalytic activity of RHA-SiO₂/SO₃H was tested in the synthesis of 4-methyl coumarins via Pechmann condensation using different phenols and ethyl acetoacetate(EAA). Many reaction parameters were studied including molar ratios of the reactants, temperature, catalyst loading and catalyst re-usability .In general, the catalyst showed high catalytic performance in this reaction when resorcinol was used as phenolic precursor for the production 7-hydroxy4-methyl coumarin(HMC). The optimum molar ratio of this reaction was found to be 1:2, whereas, the optimum medium of the reaction was found to be solvent-free medium. Furthermore, the catalyst was found reusable for Pechmann condensation reaction several times without significant changes in its activity and selectivity. Other advantages of the RHA-SiO₂/SO₃H catalyst over previously catalyst include its ease of preparation at ambient conditions from RH which is an agricultural waste and does not require hazardous chemicals or surfactant template molecules.

4.2 Recommendations

In this study, the Pechmann condensation reaction of phenols and ethyl acetoacetate were observed to be directly dependent on the acidic properties of the solid acids, temperatures

and solvent type. However, the following points need deep considerations for better understanding of the reaction:

- Catalysts of various strength of Bronsted acidity should be tried to investigate the lower and maximum acidity limit required for the production of high yields of coumarins.
- The effect of moisture on the catalytic performance of catalyst also needs to be considered.
- Studies on other Benzopyran derivatives compounds should be handled as further and complementary studies.
- The use of alternative reagents and/or catalysts should also be investigated.
- Effect of solvents needs deep investigations to assign for the actual relationship between catalyst activity and solvent polarity.

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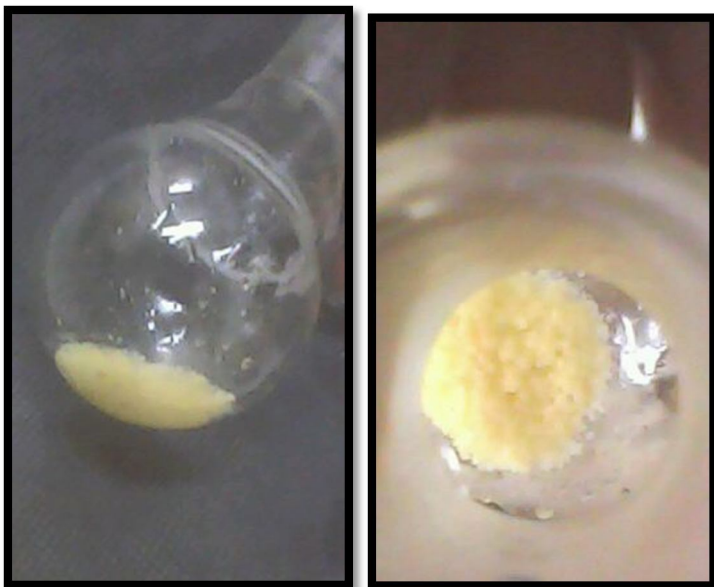
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Appendices



(a)

(b)

Fig.1A: Photographs of 4 – methyl-7-hydroxycoumarin product.



(2a)

(2b)

Fig.2A: Photographs of RH before (a) and after (b) washing by Nitric acid.



Fig. 3A:A photograph of RHA.



Fig. 4A:A photograph of RHA-SiO₂ hydrogel.



Fig. 5A: A photograph of RHA silica powder.

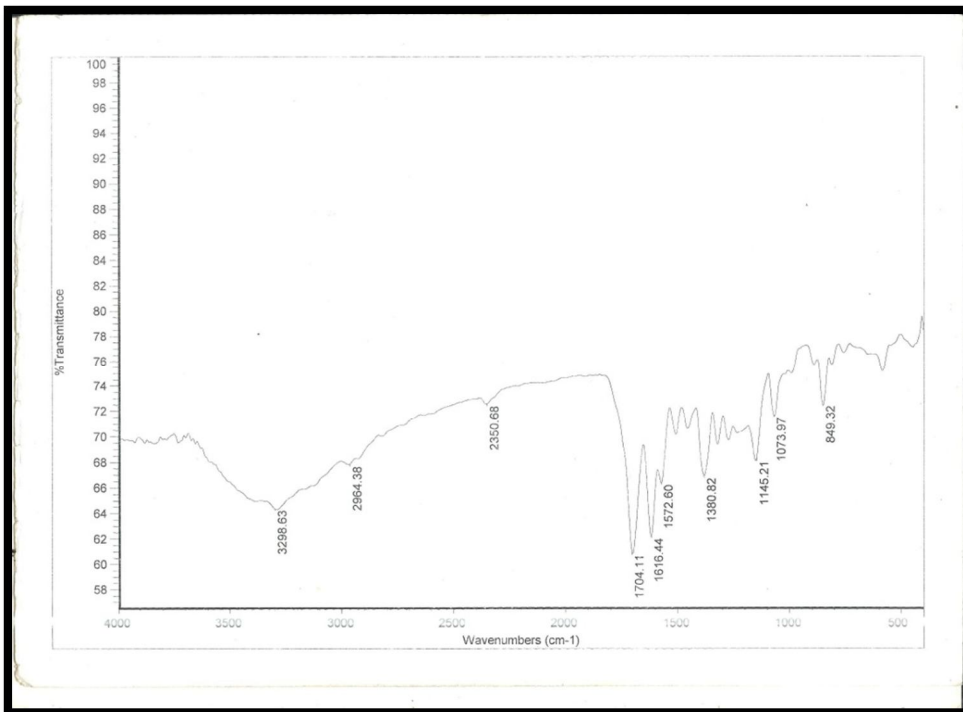


Fig. 6A: FT-IR spectrum of 7-hydroxy 4-methyl coumarin

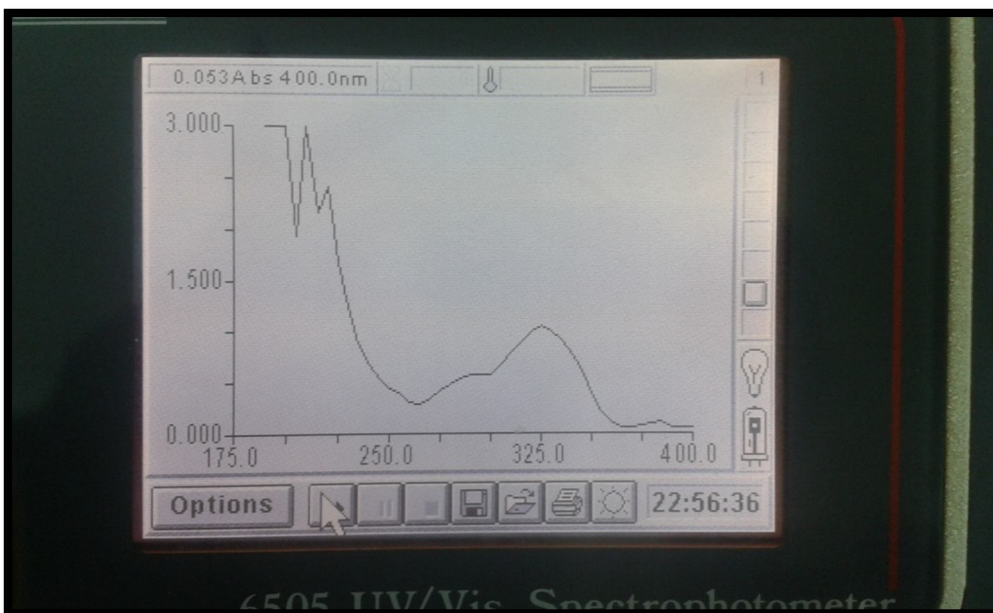


Fig. 7A: UV/Vis spectrum of 7-hydroxy 4-methyl coumarin

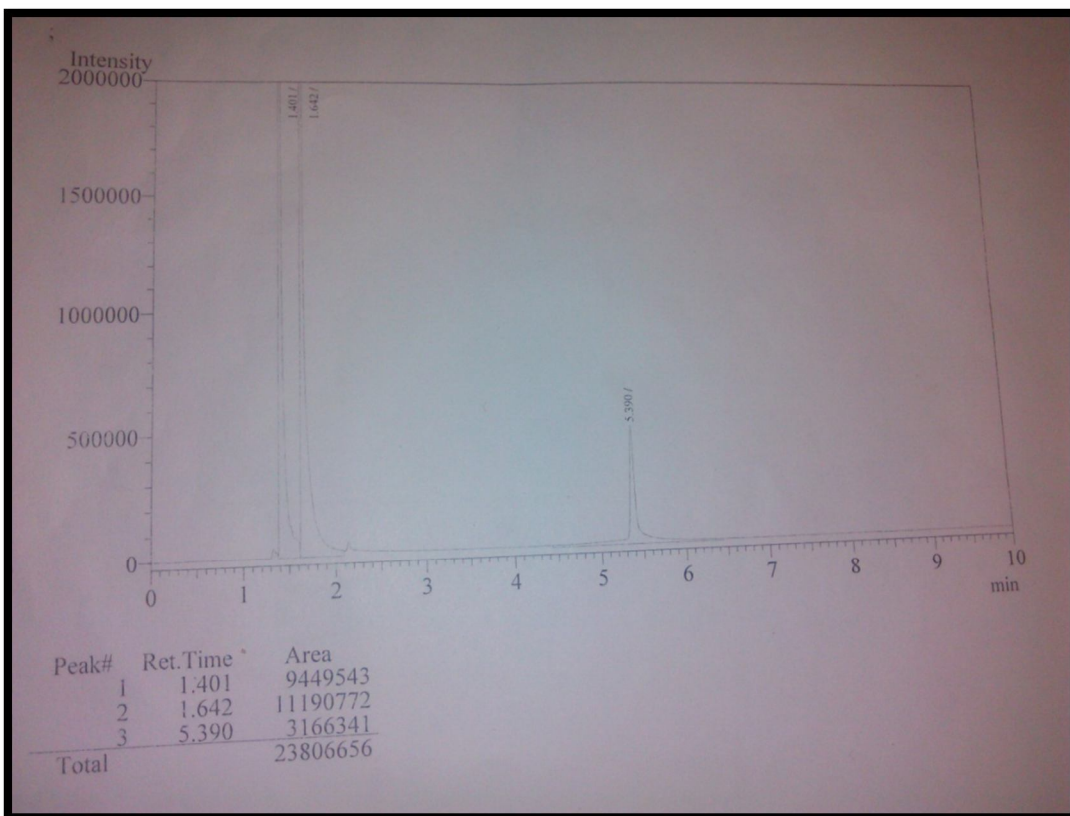


Fig.8A:GC chromatogram for the catalytic reaction of production 7-hydroxy 4-methyl coumarin at 80°C after 0 min using resorcinol/ EAA molar ratio of 1:2.

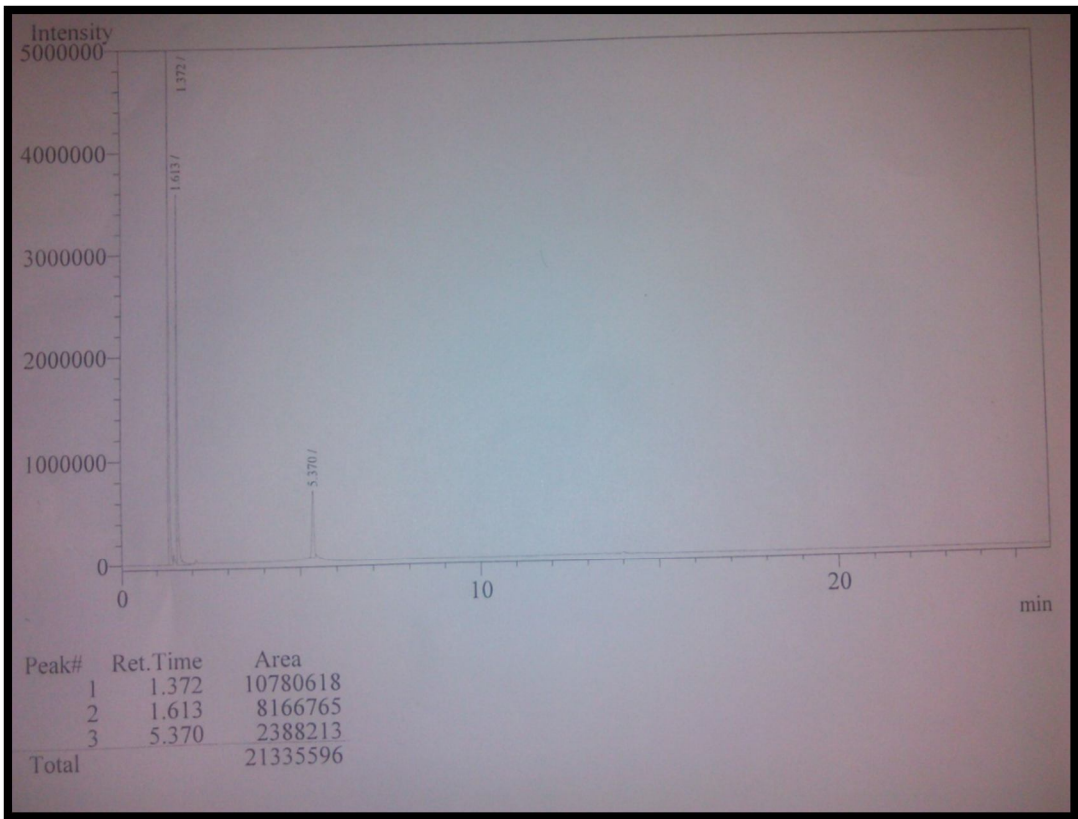


Fig.9A:GC chromatogram for the catalytic reaction of production 7-hydroxy 4-methyl coumarin at 80°C after 10min using resorcinol/EAA molar ratio of 1:2.

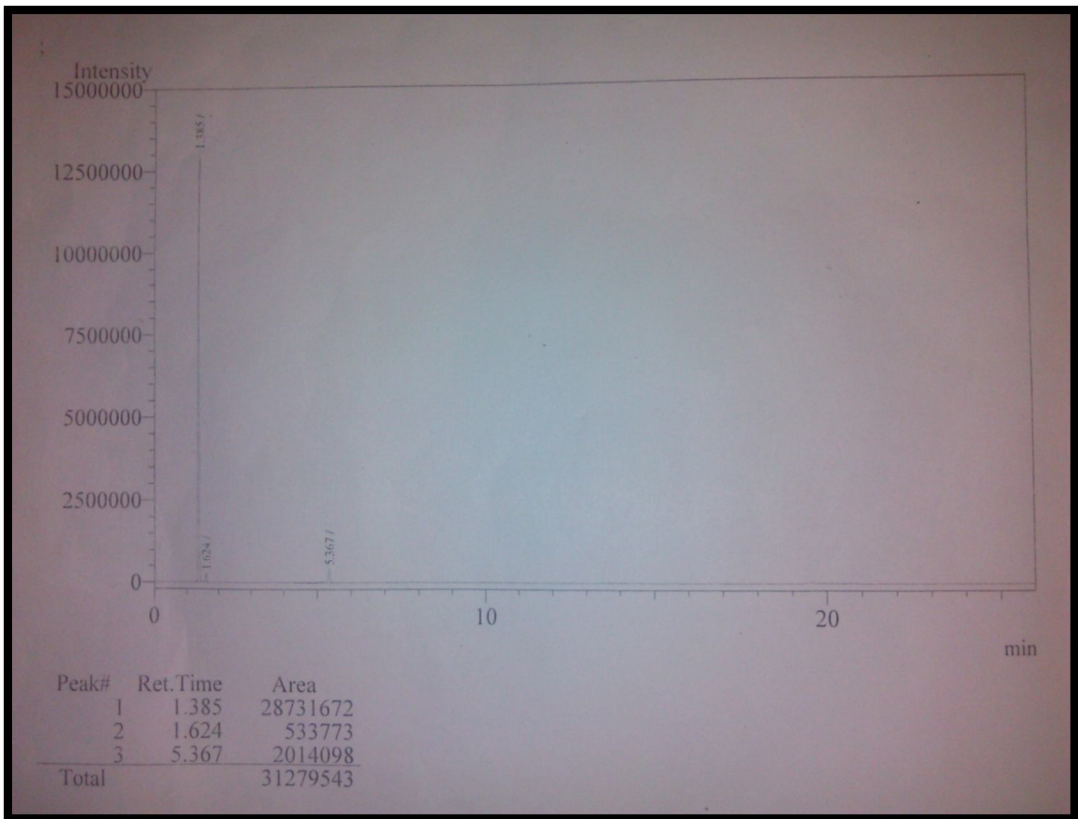


Fig.10A:GC chromatogram for the catalytic reaction of production 7-hydroxy 4-methyl coumarin at 80°C after 20 min using resorcinol/EAA molar ratio of 1:2.

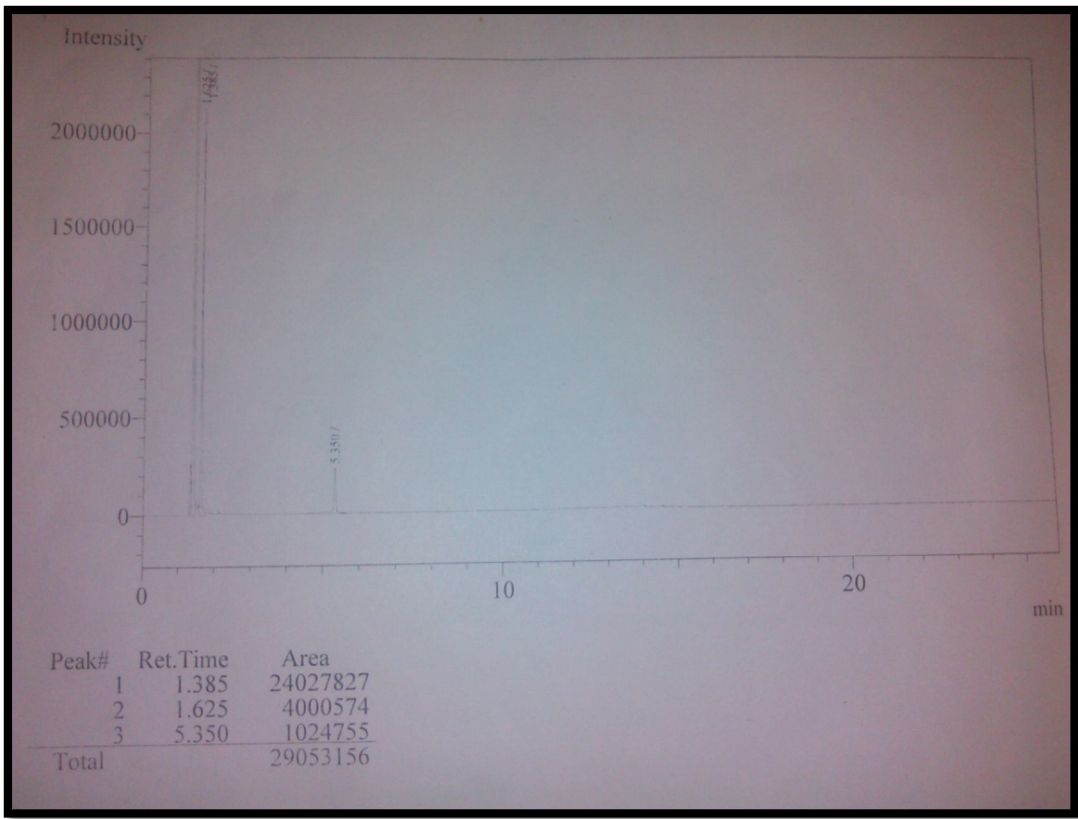


Fig. 11A:GC Chromatogram for the catalytic reaction of production 7-hydroxy 4-methyl coumarin at 80°C after 25 min using resorcinol/EAA molar ratio of 1:2.