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Cu^{2+}/Zeolite catalyzed synthesis and evaluation of antimicrobial activities of some chalcones

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ABSTRACT

Some aryl chalcones have been synthesized by Cu^{2+}/Zeolite catalyzed aldol condensation of aryl methyl ketones and substituted benzaldehydes under microwave irradiation conditions. The yields of the synthesized chalcones are more than 85%. These chalcones were characterized by their physical constants and spectroscopic data. The antimicrobial activities of synthesized chalcones were studied by Bauer-Kirby disc diffusion method.

Keywords: Aryl chalcones, Cu^{2+}/Zeolite, IR and NMR spectra, Antimicrobial activities

1. INTRODUCTION

The aryl α, β-unsaturated ketones are called as chalcones. They possess carbonyl group along with a vinyl moiety in linear combination in between the two aryl groups [1]. Many chalcones are possessing important multi-prolonged activities due to the presence of carbonyl, vinyl and polar groups present in the aryl rings [2]. They are good intermediates for carbon building blocks such as synthesis of pyrazolines [3], oxazines [4], pyrimidines [5], flavones and flavanones [6] etc. Numerous conventional and solvent-free methods are reported for the synthesis of chalcone derivatives. Extraction from natural plants [7] by organic chemists. For synthesizing chalcones various methods are available such as Aldol, Crossed-Aldol, Claisen-Schmidt, Knovenagal reactions, Greener methods-Grinding of reactants, solvent free and

oxides of nanoparticles with microwave irradiation. Solvent free Aldol condensation and Crossed-Aldol condensation [8-10] assisted by microwave were useful for synthesis of carbonyl compounds. Many catalyst were used for proceedings the chalcones synthesis reactions namely, Ethanol-NaOH [11], Methanol-KOH [12], EtOH-potassium hydroxide [13], Magnesium chloride [10], silica-H_2SO_4 [14], anhydrous $ZnCl_2$ [15], clay [16], Hydrotalcite [17], ground chemistry catalysts-grinding the reactants with NaOH [18], aqueous alkali in lower temperature [19], solid sulphonic acid from bamboo [20], $Ba(OH)_2$ [21], anhydrous Na_2CO_3 [22], microwave irradiation preparation [23], fly-ash: H_2O [24], fly-ash: H_2SO_4 [25], fly-ash: PTS [26], NaOH-CTABr [27], SiO_2-H_3PO_4 [28], $SOCl_2$ [29], sulfated titania [30], $FeCl_3$/Bentonite [31] and Fly-ash:H_3PO_4 nano catalyst [32]. These unsaturated ketones possess numerous biological activities such as antibacterial [33], antifungal [34], anti-oxidant [35], insect antifeedant [36], antidepressants [37], antiplosmodial [38], anti-aids [39] etc.

Through literature survey reveals that there is no report available for the Cu^{2+}/zeolite catalyst assisted synthesis of chalcones and evaluation of their antimicrobial activities. Therefore the authors have taken efforts to synthesize some chalcones and studied their antimicrobial activities by Bauer-Kirby [40] disc diffusion method.

2. EXPERIMENTAL

2. 1. General

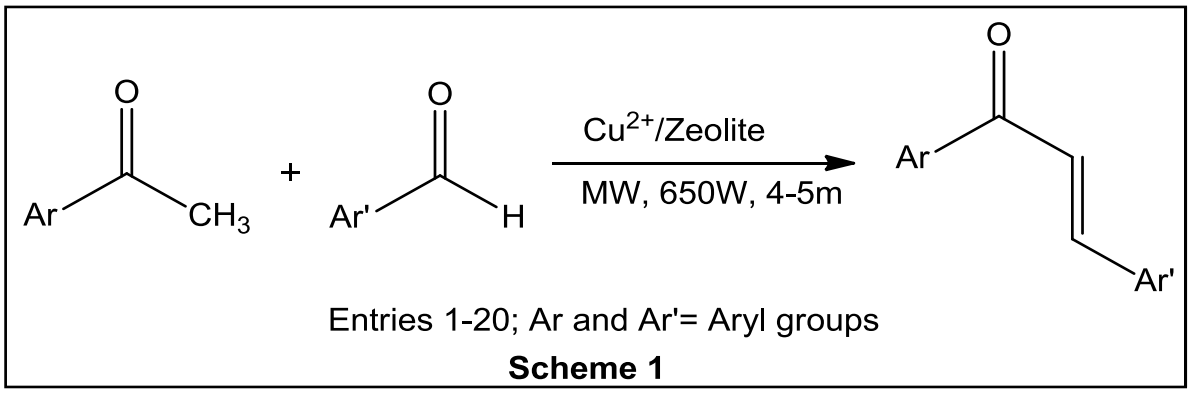
All used chemicals used in this investigation were purchased from Sigma-Aldrich and E-Merck chemical companies. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus. Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded Agilent cary 630 Model Fourier transform spectrophotometer. Bruker AV400 NMR spectrometer was used for recording NMR spectra operating at 500 MHz for ^1H spectra and 125.46 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard.

2. 2. Preparation of Cu^{2+}/zeolite clay catalyst

About 50 mL of 0.05 M $Cu(NO_3)_2$ in isopropanol solution was added to zeolite clay suspension drop wise using separating funnel, with constant stirring, using a magnetic stirrer. Zeolite suspension was prepared by about 1 gm of zeolite clay was dispersed in 50 mL of isopropanol in a 250 mL beaker. After completing the transformation of $Cu(NO_3)_2$ solution to the zeolite suspension, the mixture was sonicated to get a fine power. The resulting solution was stirred for 4 h at room temperature. The solution was slowly evaporated using rotary vacuum evaporator at room temperature. The obtained solid was dried at 110 °C for 5 h and grind with a pestle and mortar affords the Cu^{2+}/zeolite clay catalyst as fine powder. This catalyst was calcined at 250 °C [41].

2. 2. Synthesis of chalcones

Equimolar quantity of aryl methyl ketones (2 mmol) and substituted benzaldehydes (2 mmol), with 80 mg Cu^{2+}/zeolite catalysts were mixed thoroughly in a 25 mL Borosil tube and closed with lid. This mixture was subjected to microwave irradiation in microwave oven (Samsung, Grill GW73BD Model, 100-750 W, 2450 MHz, 230 A/c) at 650 W for 4-5 min (**Scheme 1**). The completion of reaction was checked by thin layer chromatography (TLC).



Scheme 1

The reaction mixture was extracted with 10 mL of ethyl acetate and filtered. After separating the organic layer with dichloromethane, the solid product was obtained on evaporation. Further this was purified by column chromatogram (Demetra), evaporation of solvent by rotary vacuum evaporator to afford glittering product. The catalyst was washed with ethanol and dried in an air oven at 110 °C, before it is used for further runs.

2. 3. Antimicrobial activities

The antimicrobial activities of these synthesized ketones have been measured by Bauer-Kirby [40] disc diffusion method. In this experiment there are two each gram positive/ negative and two fungal strains were used for measuring the antibacterial and antifungal activities of these ketones.

2. 3. 1. Measurement of antibacterial activities

The gram positive strains like *Staphylococcus aureus*, *Entrocccus faecalis* and some gram negative pathogenic strains like while *Escherichia coli* and *Klebsiella species* were used for measuring the activities. The disc diffusion technique was followed using the Kirby-Bauer method, at a concentration of 250 μg/mL with Streptomycin using as the standard drugs. The antibacterial activity of compounds were evaluated by measuring the mm of zone of inhibition of each compound against their bacterial strains.

The antibacterial sensitivity assay of synthesized chalcones (Entries 11-20) has been evaluated using Kirby-Bauer [40] disc diffusion technique. Every Petri plate, about 0.5 cm^3 the sterile glass spreader are used to spread the sample of test bacteria to over the medium uniformly at solidified Mueller-Hinton agar. The sterile forceps are used to impregnated by the discs of Whatman No.1 filter paper (5 mm diameter), the compound containing solution to place the medium. To avoid the water droplets collection on plates, then set the upside down over the medium, to incubated at 37 °C for 24 hours. The inhibition of zone of mm of inhibition values of diameter are visually surveyed after 24 hours at the plates. Same procedure was used for measured the antibacterial activities and taken the triplicate values.

2. 3. 2. Measurement of antifungal activity

Measurement of antifungal activities of all synthesized chalcones have been done using *Candida albicans* and *Aspergillus niger* as the fungal strains and the disc diffusion technique was adopted. *Griseofulvin* was taken as the standard drug. The antifungal activity of

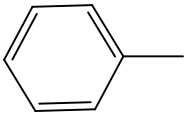
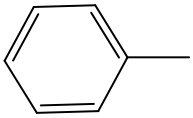
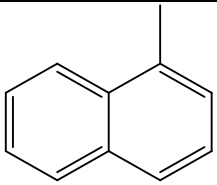
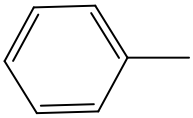
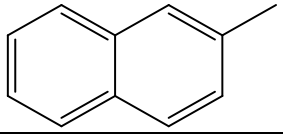
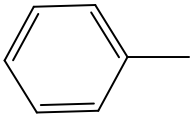
compounds were evaluated by measuring the mm of zone of inhibition of each compound against their bacterial strains.

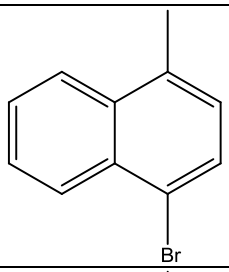
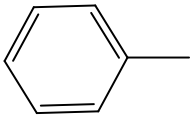
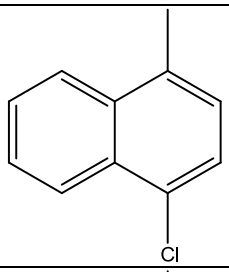
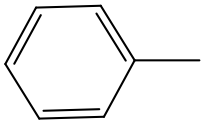
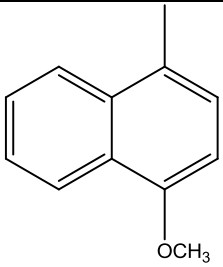
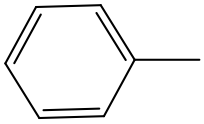
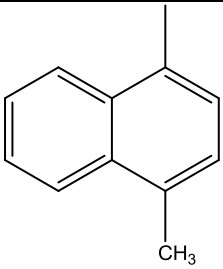
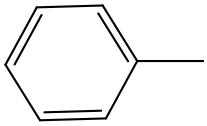
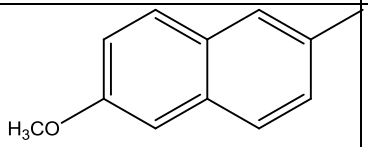
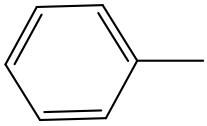
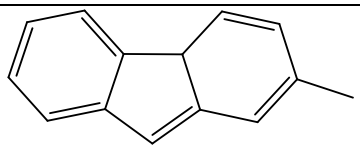
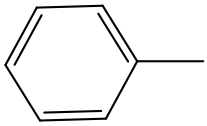
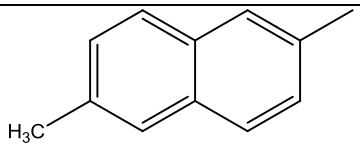
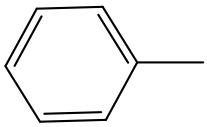
The antifungal sensitivity assay of synthesized chalcones (Entries 11-20) has been evaluated using Kirby-Bauer[40] disc diffusion technique. The sterilized PDA medium was prepared as stated earlier. The Petri-plate was filled with fungal species containing (1 mL) sample, then this was poured PDA medium in ear bearing heating condition. The antifungal action of the synthesized chalcones (Entries 11-20) compounds had been studied against three fungal species two fungal species *Candida albicans* and *Aspergillus niger*. The microbial species are spreading over the plates uniformly using clockwise and anti-clockwise rotations. The about 15 mg sample was used to prepare the test solution of prepared chalcones (Entries 11-20) in DMSO solvent (1 mL). The impregnation was applied and then followed by the disc in the test solution. The medium was permitted to solidified and kept for 24 hours. The mm of zone of inhibition values of the plates have been examined and measured in the diameters. The results were recorded by the repeating triplicate with the same procedure.

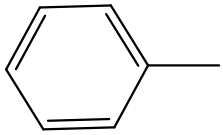
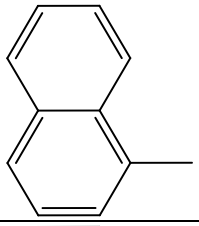
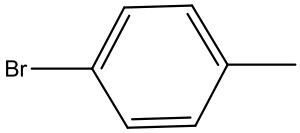
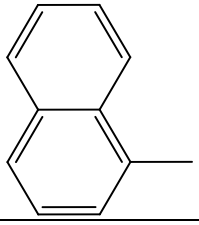
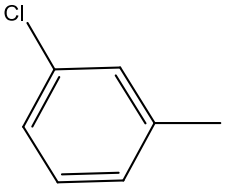
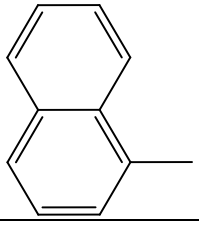
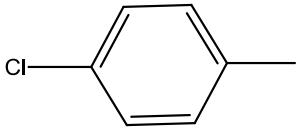
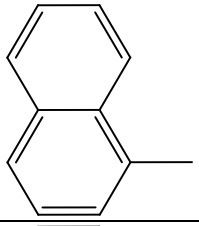
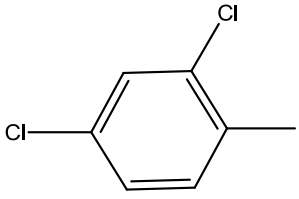
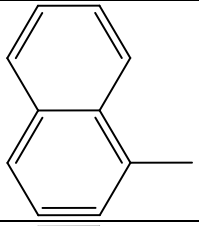
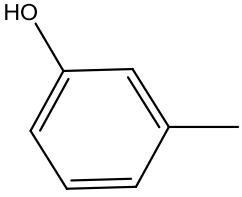
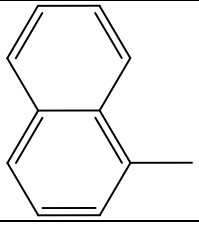
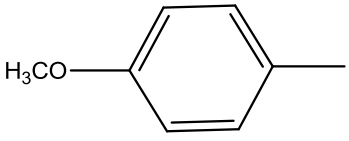
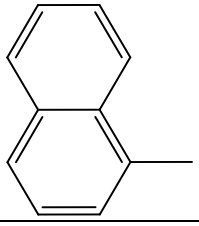
3. RESULTS AND DISCUSSION

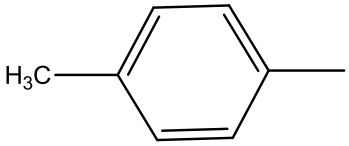
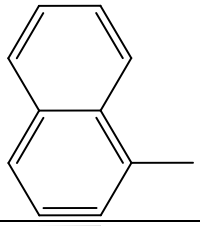
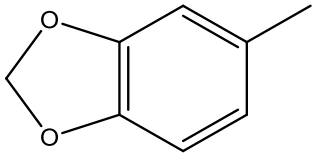
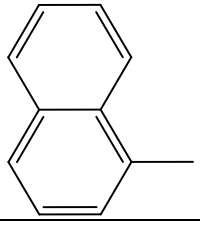
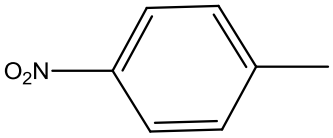
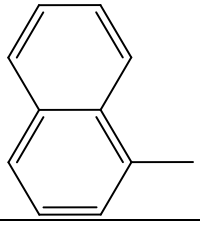
In our research laboratory, the authors have investigated the catalytic activity of Cu^{2+}/zeolite catalyst for the synthesis of aryl chalcones. As mentioned in the experimental section, the equimolar quantities of aryl methyl ketones are condensed with various electron-donating and electron-withdrawing substituted benzaldehydes in the presence of the catalytic amount of Cu^{2+}/zeolite catalyst under microwave irradiation conditions. All reactions gave more than 85% yields. These chalcones were characterized by their physical constants and are presented in **Table 1.** The infrared and nuclear magnetic resonance spectral data of the selective compounds are presented in **Table 2.**

Table 1. The physical constants and infrared and nuclear magnetic resonance spectral data of chalcones.

Entry	Ar	Ar′	Yiled (%)	m.p. (ºC)	Time (m)	MW
1			87	55-56 (55-58) [42]	4	208
2			86	100-102 (100-102) [42]	4	258
3			87	104-105 (104-105) [42]	4	258

4			85	103-104 (103-104) [42]	4.5	337
5			86	122-123 (122-123) [42]	5	292
6			85	113-114 (113-114) [42]	4	310
7			85	98-99 (98-99) [42]	4.5	292
8			85	67-68 (67-68) [42]	5	288
9			85	149-150 (149-150) [42]	5	296
10			85	122-123 (123-124) [42]	4	272

11			86	96-97 (95-97) [43]	4	258
12			85	118-119 (117-118) [43]	4.5	337
13			86	104-105	5	292
14			87	112-113 (110-113) [43]	5	292
15			85	118-119	5	327
16			85	127-128	4	274
17			87	131-132	4	288

18			85	132-133 (132-134) [43]	4.5	272
19			86	123-124	5	302
20			85	117-118 (117-119) [43]	5	303

From infrared spectra, the characteristic carbonyl stretches are obtained as a doublets viz., *s-cis* and *s-trans* conformers. These conformers are shown in Figure 1. The carbonyl *s-cis* conformers obtained between 1649.19-1687.59 cm^{-1}. The *s-trans* conformers obtained between 1560.07-1661.89 cm^{-1}.

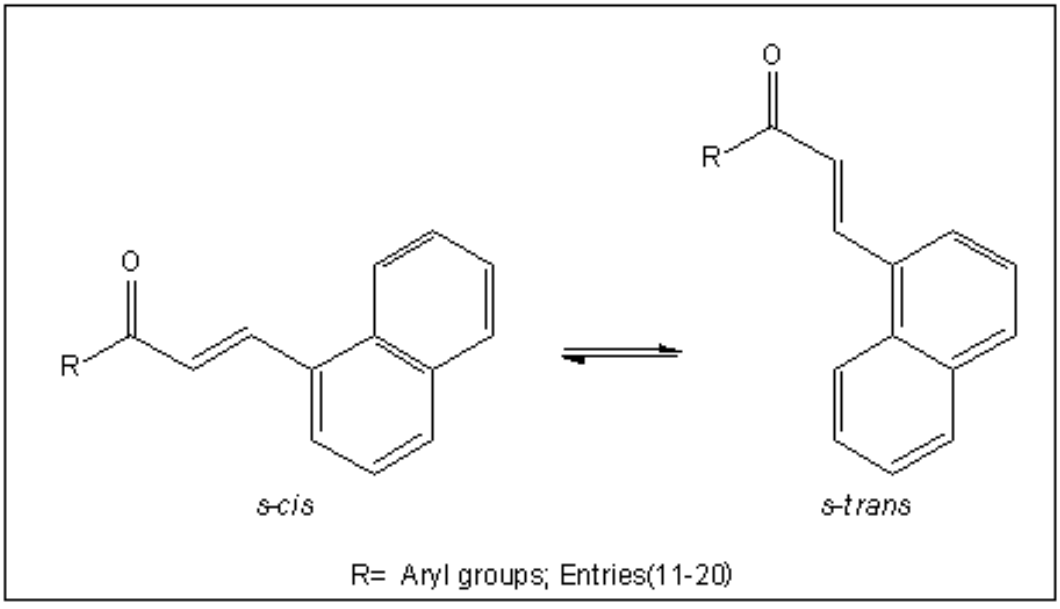


Figure 1. The *s-cis* and *s-trans* conformers of chalcones.

From the ^{1}H NMR spectra, the Hα and Hβ protons chemical shifts (δ, ppm) appeared as doublets with more than coupling constants of 15 Hz. It is evident for these protons are in *E* conformers. The Hα protons chemical shifts (δ, ppm) obtained as lower than Hβ. The Hα protons chemical shifts (δ, ppm) obtained between 7.241-8.226 ppm. The Hβ protons chemical shifts (δ, ppm) obtained between 7.824-8.689 ppm. The aromatic ring proton chemical shifts (δ, ppm) obtained in the range of 7.107-8.712 ppm.

From ^{13}H NMR spectra, the carbonyl carbon chemical shifts (δ, ppm) appeared in the range of 188.23-192.35 ppm. The Cα carbon chemical shifts (δ, ppm) obtained between 123.36-124.09 ppm. The Cα protons chemical shifts (δ, ppm) obtained between 139.25-143.19 ppm. The aromatic ring proton chemical shifts (δ, ppm) obtained in the range of 7.107-8.712 ppm. The aromatic ring carbon chemical shifts (δ, ppm) obtained in the range of 115.13-143.19 ppm. Bothe the infrared and NMR spectral data the electron donating group compound appeared as lower than the electron-withdrawing groups and are presented in Table 2.

Table 2. The infrared and nuclear magnetic resonance spectral data of chalcones (Entries 11-20).

Entry	IR (ν, cm^{-1})		^{1}H NMR (δ, ppm)			
	$CO_{s\text{-}cis}$	$CO_{s\text{-}trans}$	H_{α} (d)	H_{β} (d)	Ar-H (m)	Substituent
11	1661.55	1602.11	7.241	8.383	7.220-8.121	---
12	1659.60	1598.75	8.226	8.653	7.251-7.943	---
13	1649.19	1608.25	7.598	8.689	7.327-7.932	---
14	1658.16	1596.08	8.021	8.523	7.564-8.002	---
15	1663.13	1595.42	8.086	8.353	7.206-7.905	---
16	1637.03	1560.07	7.627	7.894	7.107-7.653	---
17	1664.76	1613.86	7.435	7.943	7.221-7.883	2.34 (OCH_3)
18	1686.40	1649.40	7.265	7.824	7.301-7.795	2.012 (CH_3)
19	1653.52	1597.57	7.523	8.215	7541-8.112	---
20	1687.59	1661.89	7.556	8.456	7.624-8.712	---

Entry	^{13}C NMR (δ, ppm)				
	CO	C_α	C_β	Ar-C	Substt.
11	192.35	125.52	143.19	123.26-143.19	---
12	189.17	124.03	142.33	123.44-136.92	---
13	189.01	124.09	142.31	122.45-141.56	---
14	188.23	124.09	139.58	124.25-136.25	---
15	192.29	123.14	143.15	125.15-135.57	---
16	190.16	120.31	142.10	115.13-136.27	---
17	188.64	123.65	139.80	121.34-139.34	63.81(OCH_3)
18	187.26	123.36	139.28	123.45-141.26	23.65(CH_3)
19	190.35	122.95	140.39	122.89-142.25	---
20	191.03	123.65	139.25	123.78-142.37	---

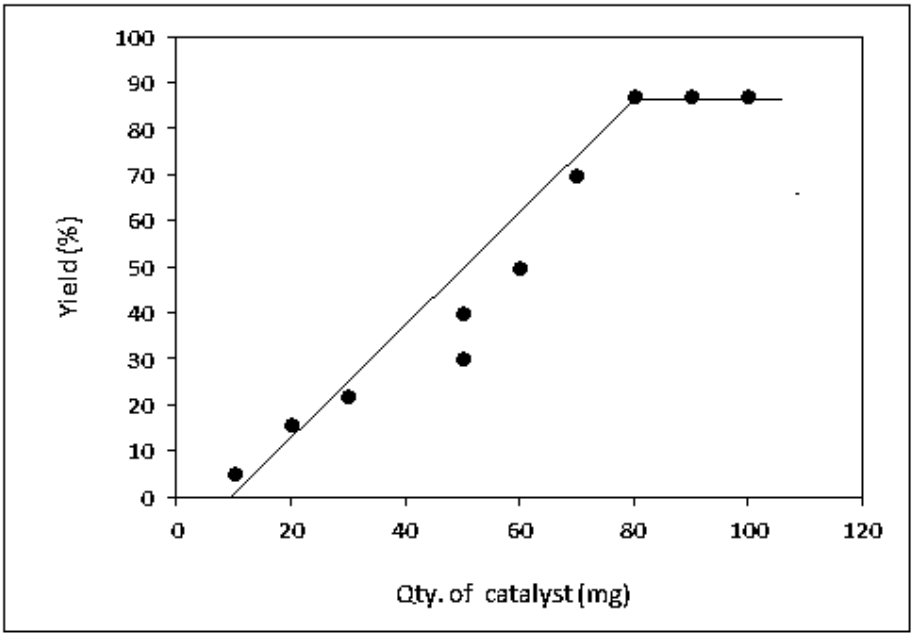


Figure 2. The quantity of catalyst versus yield (Entry 11).

The catalytic activity of this catalyst was studied by the same reaction with aryl methyl ketone and benzaldehyde in the same conditions (Entry 11). The catalyst quantity was increased from 10-100 mg, the percentage of yield increases from 5 to 87.

The 80 mg Cu^{2+}/zeolite catalyst assisted reaction gave 87% yield. The increment of this quantity of catalyst no appreciable increase of yield and remains constant. The optimum quantity of the catalyst was 80 mg. The statistical correlation diagram of this quantity of catalyst versus yield was presented in **Figure 2**.

Further the reusability of this catalyst was studied with the same reaction and the reaction conditions. The first run gave 87% yield. The second and third run gave 86% yield. The fourth and fifth runs gave 85% yield. The correlation diagram of yield versus runs was illustrated in **Figure 3.**

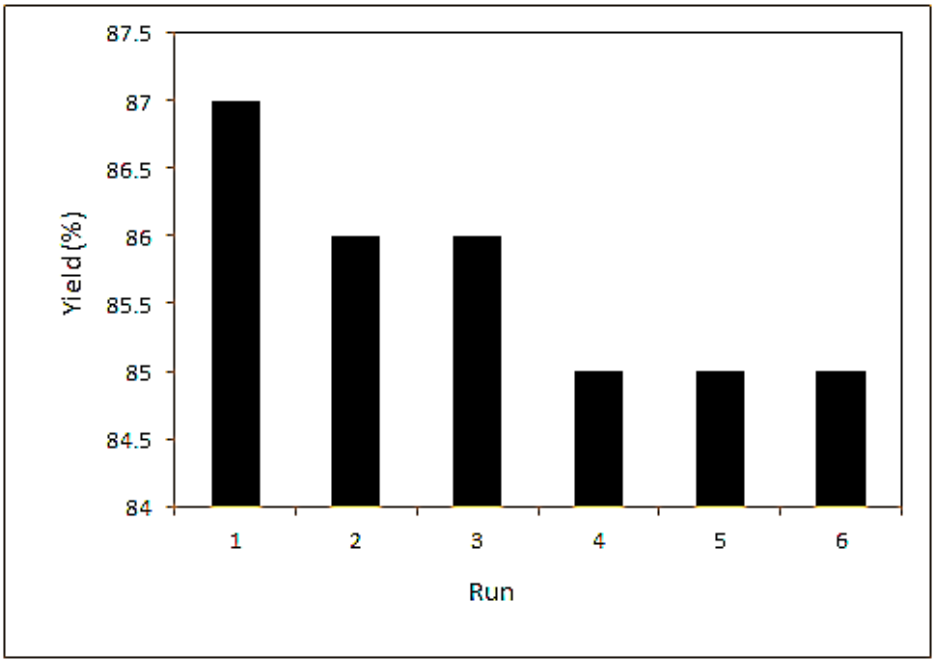


Figure 3. The reusability of catalyst with yield (Entry 11).

The effect of solvent on this reaction by means of conventional method and microwave method was studied. The solvent such as methanol, ethanol, dichloromethane, dioxane and tetrahydrofuran were employed and the obtained yields are less than 80% while compared to microwave methods gave 87% yield and are presented in **Table 3.**

Table 3. The effects of solvents on the yield (Entry 11).

Medium	**MeOH**	**EtOH**	**DCM**	**DO**	**THF**	**MW**
Yield (%)	77	82	83	80	84	87

MeOH: Methanol; EtOH: Ethanol; DCM: Dichloromethane; DO: Dioxane; THF: Tetrahydrofuran; MW: Microwave

Within these above observation, the authors concluded that the Cu^{2+}/zeolite catalyst under microwave irradiation conditions gave better yields of chalcones.

3. 1. Antibacterial activity assay

The measured antibacterial activities of the chalcones (Entries 11-20) by means of measurement of mm of zone of inhibition with respective bacterial microbes and compared with Streptomycin using as the standard drugs. The mm of zone of inhibition of antibacterial activities of these ketones are presented in **Table 4** and the statistical clustered column chart was shown in **Figure 4.** From the Table 4, the compound **15** shows excellent antibacterial activity against *S. aureus* strain. The chalcones **13** and **14** showed better antibacterial activity against *S. aureus* strain. The ketones **11, 12, 16-18** and **19** showed good antibacterial activity against *S. aureus* strain. The chalcones **20** had satisfactory antibacterial activity against *S. aureus* strain. The ketones **12-15** showed better antibacterial activity against *E. faecalis* strain. The chalcones **1, 16-19** showed good antibacterial activity against *E. faecalis* strain. The ketone **20** had least activity against *E. faecalis* strain.

Table 4. The antibacterial activity of chalcones (Entries 11-20) by means of mm of zone of inhibition in the disc.

Entry	**Mm of zone of inhibition**			
	Gram +ve bacteria		**Gram -ve bacteria**	
	S. aureus	***E. faecalis***	***E. coli***	***K. species***
11	10	9	11	10
12	11	10	12	12
13	12	11	12	13
14	12	12	13	11
15	13	12	12	10
16	10	9	10	12
17	9	9	8	9
18	9	8	9	8
19	10	9	10	9
20	7	6	9	7
Standard Streptomycin	12	14	10	13

The chalcones **11-15** shows excellent antibacterial activity against *E. coli* strain. Compounds **16** and **19** showed better antibacterial activity against *E. coli* strain. The ketones **17, 18** and **20** showed good antibacterial activity against *E. coli* strain. Compound **13** had better antibacterial activity against *K. species* strain. The ketones **11, 12, 13-16** shows better antibacterial activity against *K. species* strain. Compounds **17** and **19** showed good antibacterial activity against *K. species* strain. The ketones **18** and **20** had satisfactory antibacterial activity against *K. species* strain.

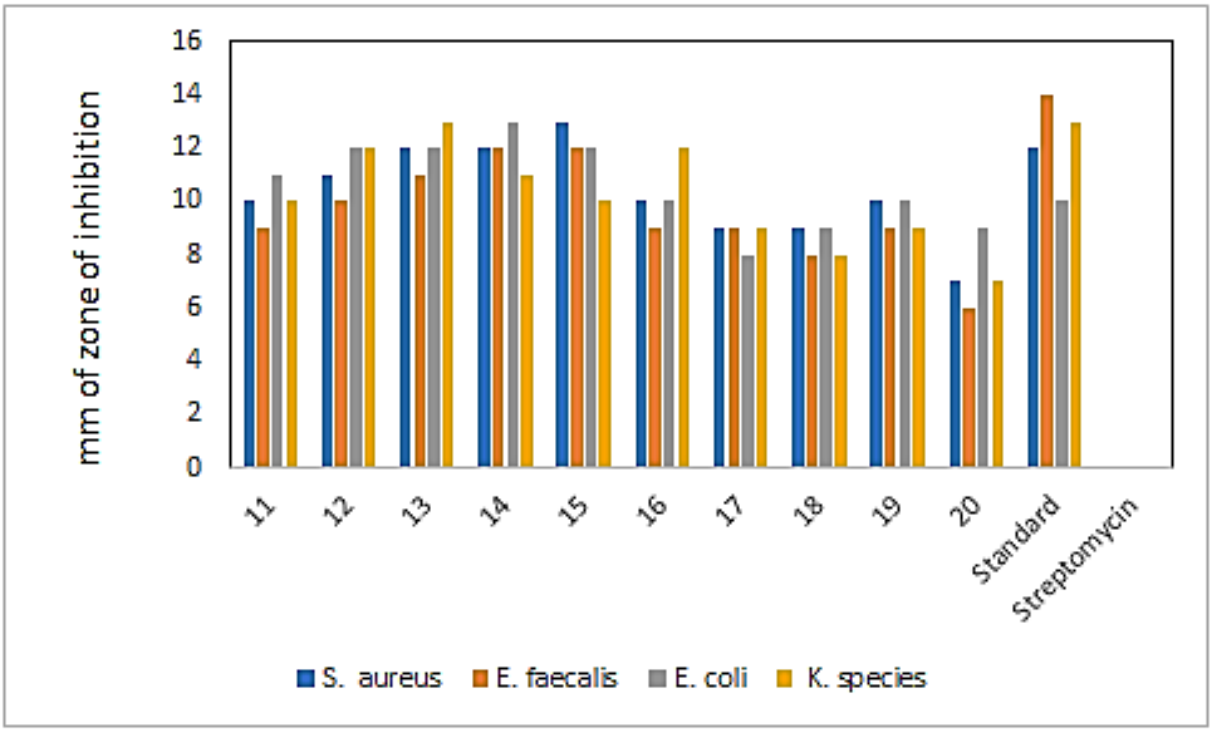


Figure 4. The clustered column chart of the antibacterial activity of chalcones (Entries 11-20).

3. 2. Antifungal activity assay

The measured antifungal activities of the chalcones (Entries 11-20) by means of measurement of mm of zone of inhibition with respective fungal microbes and compared with Griseofulvin using as the standard drug. The mm of zone of inhibition of antifungal activities of these ketones are presented in **Table 5** and the statistical clustered column chart was shown in **Figure 5.** From the Table 5, the chalcones **16-20** showed better antifungal activity against *C. albicans* strain. The ketones **11-15** showed good antifungal activity against *C. albicans* strain. The chalcones **18-20** had better antifungal activity against *A. niger* strain. The ketones **11, 13**, **14, 16** and **17** showed good antifungal activity against *A. niger* strain. The chalcones **12** and **18** least activity against *A. niger* strain.

Table 5. The antifungal activity of chalcones (Entries 11-20) by means of mm of zone of inhibition in the disc.

Entry	Mm of zone of inhibition	
	C. albicans	***A. niger***
11	8	10
12	9	9
13	8	11
14	9	10
15	9	8
16	10	12
17	12	13
18	14	15
19	13	14
20	14	16
Standard Griseofulvin	15	17

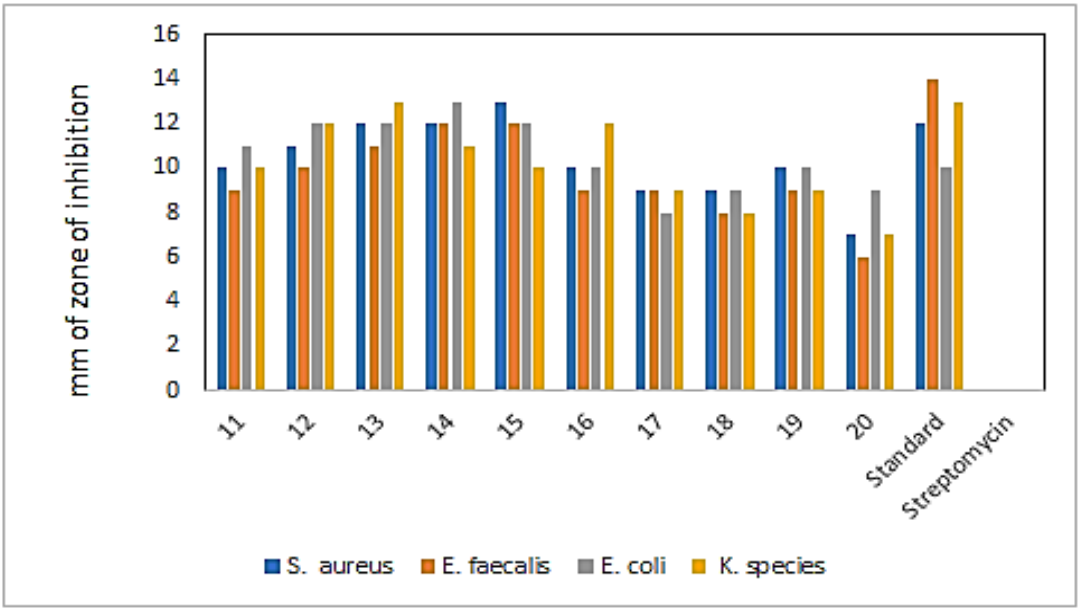


Figure 5. The clustered column chart of the antifungal activity of chalcones (Entries 11-20).

4. CONCLUSIONS

Good yields of more than twenty aryl chalcones have been synthesized by Cu^{2+}/Zeolite catalyzed Aldol condensation of aryl methyl ketones and substituted benzaldehydes under microwave irradiation conditions. These chalcones were characterized by their physical constants and spectroscopic data. The antimicrobial activities of synthesized chalcones were studied by Bauer-Kirby disc diffusion method. The compound **15** shows excellent antibacterial activity against *S. aureus* strain. The chalcones **13** and **14** showed better antibacterial activity against *S. aureus* strain. The ketones **11, 12, 16-18** and **19** showed good antibacterial activity against *S. aureus* strain. The chalcones **20** had satisfactory antibacterial activity against *S. aureus* strain. The ketones **12-15** showed better antibacterial activity against *E. faecalis* strain. The chalcones **1, 16-19** showed good antibacterial activity against *E. faecalis* strain. The ketone **20** had least activity against *E. faecalis* strain.

The chalcones **11-15** shows excellent antibacterial activity against *E. coli* strain. Compounds **16** and **19** showed better antibacterial activity against *E. coli* strain. The ketones **17, 18** and **20** showed good antibacterial activity against *E. coli* strain. Compound **13** had better antibacterial activity against *K. species* strain. The ketones **11, 12, 13-16** shows better antibacterial activity against *K. species* strain. Compounds **17** and **19** showed good antibacterial activity against *K. species* strain. The ketones **18** and **20** had satisfactory antibacterial activity against *K. species* strain. The chalcones **16-20** showed better antifungal activity against *C. albicans* strain. The ketones **11-15** showed good antifungal activity against *C. albicans* strain. The chalcones **18-20** had better antifungal activity against *A. niger* strain. The ketones **11, 13**, **14, 16** and **17** showed good antifungal activity against *A. niger* strain. The chalcones **12** and **18** least activity against *A niger* strain.

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